THE CONSTANTS OF NATURE

PART V

A RECALCULATION

OF

THE ATOMIC WEIGHTS

THIRD EDITION, REVISED AND ENLARGED

BY

FRANK WIGGLESWORTH CLARKE, LL. D., D. Sc.

Chief Chemist U. S. Geological Survey

TABLE OF CONTENTS.

A RECALCULATION OF THE ATOMIC WEIGHTS.

(Third Edition, Revised and Enlarged.)

By FRANK WIGGLESWORTH CLARKE.

INTRODUCTION.

In the autumn of 1877 the writer began collecting data relative to determinations of atomic weight, with the purpose of preparing a complete résumé 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 since been issued [1] 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."

In due time my work was completed, and early in 1882 it was published.[2] About a year later Meyer and Seubert's recalculation appeared, to be followed later still by the less elaborate discussions of Sebelien and of Ostwald. All of these works differed from one another in various essential particulars, presenting the subject from different points of view, and with different methods of calculation. Each one, therefore, has its own special points of merit, and, in a sense, reinforces the others. At the same time, the scientific activity which they represent shows how widespread was the interest in the subject of atomic weights, and how fundamentally important these constants undoubtedly are.

The immediate effect of all these publications was to render manifest the imperfections of many of the data, and to point out most emphatically in what directions new work needed to be done. This led to an extraordinary activity in the determination of atomic weights, and so much

---

[1] Smithsonian Miscellaneous Collections, Vol. 27, Serial No. 358, pp. 152.
[2] Smithsonian Miscellaneous Collections, Vol. 27, Serial No. 441, pp. 279.

new material accumulated that in 1897 [1] a new edition of this work, revised to date, became necessary. Since then, much more has been done, with great improvements in technique, especially by Richards and his colleagues at Harvard University, by Edgar F. Smith in Philadelphia, and by Guye at Geneva, not to mention many other workers of high merit. The assimilation of this new material, and its combination with the older data, is the object of the present volume.

At the very beginning of my work, a fundamental question 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, in a special, limited form, was chosen as the best method of dealing with the problem.

The mode of discussion and combination of results was briefly as follows. The formulæ employed are given in another place. Beginning with the ratio between oxygen and hydrogen, each series of experiments was taken by itself, its arithmetical mean was determined, and the probable error of that mean was computed. Then the several means were combined according to the appropriate formula, each one receiving a weight dependent upon its probable error. The general mean thus established was taken as the most probable value for the ratio, and at the same time its probable error was mathematically assigned. In the former editions of this work it was used to give the atomic weight of oxygen referred to hydrogen as unity. In the present edition the oxygen standard is assumed, and the atomic weight of hydrogen is determined. This is in accordance with the decisions of the International Committee on Atomic Weights; although my personal preference, on theoretical grounds, is for the hydrogen standard. The subsequent computations, however, are rendered simpler by assuming that $O = 16$, and that is a principal reason for my change of policy.

Next in order came a number of elements which were best considered together; namely, silver, chlorine, bromine, iodine, potassium, sodium, nitrogen, sulphur and carbon. Their atomic weights, with those of hydrogen and oxygen, form a fundamental group, by means of which

<hr>

[1] Smithsonian Miscellaneous Collections, Vol. 38, Serial No. 1075, pp. vi, 370.

other atomic weights are determined. Direct comparisons with oxygen or hydrogen are relatively few; indirect determinations with the aid of silver and the halogens are many. For the elements in question there were data from many experimenters. All similar figures, that is, the figures for each ratio, were first reduced to a common standard, and then the individual means were combined into general means. Thus all the data were condensed into fifty-five ratios, from which a number of values for each atomic weight could be computed. The ratios represent the actual experimental work; the atomic weights are inferential. Finally, the several values for each atomic weight are treated as if they were means of the usual type, and combined by the method of least squares into a general mean, which is supposed to represent the most probable value for each constant. The fundamental values having been determined, they are next applied to the calculation of what may be called the secondary atomic weights, and in this work the probable error of each term in each ratio is taken into account. This will appear more clearly evident in the subsequent actual calculations.

But although the discussion of atomic weights is ostensibly mathematical, it cannot be purely so. Chemical considerations are necessarily involved at every turn. In assigning 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 worthless 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. Probably many chemists would differ with me upon such points of judgment. In fact, it is doubtful whether any two chemists, 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 conclusions. 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 other cases chemists have neglected this correction 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.[1]

---

[1] For a discussion of these vacuum corrections see Guye and Zachariades, Compt. Rend., 149, 593. The errors in reductions to a vacuum are larger than has been commonly supposed.

Necessarily, this work omits many details relative to experimental methods, and particulars as to the arrangement 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 standards, and for each series of figures the probable error has been determined. Thus far, however much my methods of combination may be criticised, I feel that my labors will have been useful. The ground is 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.

On the mathematical side my method of recalculation has obvious deficiencies. It is special, rather than general, and at some future time, when a sufficiently large mass of evidence has accumulated, it must give way to a more thorough mode of treatment. For example, the ratio $Ag_2 : BaBr_2$ has been used for computing the atomic weight of barium, the atomic weights of silver and bromine being supposed to be known. But these atomic weights are subject to small errors, and they are superimposed upon that of the ratio itself in the process of calculation. Obviously, the ratio should contribute to our knowledge of all three of the atomic weights involved in it, its error being distributed into three parts instead of appearing in one only. The errors may be in part compensatory; but that is not certainly known.

Suppose now that for every element we had a goodly number of atomic weight ratios, connecting it with at least a dozen other elements, and all measured with reasonable accuracy. These hundreds of ratios could then be treated as equations of observation, reduced to linear form, and combined by the general method of least squares into normal equations. All errors would thus be distributed, never becoming cumulative; and the normal equations, solved once for all, would give the atomic weights of all the elements simultaneously. The process would be laborious but the result would be the closest possible approach to accuracy. The data as yet are inadequate, although some small groups of ratios may be handled in that way; but in time the method is sure to be applied, and indeed to be the only general method applicable. Even if every ratio was subject to some small constant error, this, balanced against the similar errors of other ratios, would become accidental or unsystematic

with reference to the entire mass of material, and would practically vanish from the final means.

Concerning this subject of constant and accidental errors, a word may be said here. My own method of discussion eliminates the latter, which are, in great part at least, removable by ordinary averaging; but the constant errors, vicious and untractable, remain, at least partially. Still, where many ratios are considered, even the systematic errors may in part compensate each other, and do less harm than might be expected. They have, moreover, a peculiarity which deserves some attention.

In the discussion of instrumental observations, the systematic errors are commonly constant, both as to direction and as to magnitude. They are therefore independent of the accidental errors, and computation of means leaves them untouched. But in the measurement of chemical ratios the constant errors are most frequently due to an impurity in one of the materials investigated. If different samples of a substance are studied, although all may contain the same impurity, they are not likely to contain it in the same amount; and so the values found for the ratio will vary. In other words, such errors may be constant in direction but variable in magnitude. That variation appears in the probable error computed for the series of observations, diminishes its weight when combined with other series, and so, in part, corrects itself. It is not removed from the result, but it is self-mitigated. The constant errors familiar to the physicist and astronomer are obviously of a different order.

That all methods of averaging are open to objections, I am of course perfectly aware. I also know the doubts which attach to all questions of probable error, and to all combinations of data which depend upon them. I have, however, preferred to face these objections and to recognize these doubts rather than to adopt any arbitrary scheme which permits of a loose selection of data. After all, the use of probable error as a means of weighting is only a means of weighting, and perhaps more justifiable than any other method of attaining the same result. When observations are weighted empirically—that is, by individual judgment —far greater dangers arise. Almost unconsciously, the work of a famous man is given greater weight than that of some obscure chemist, although the latter may ultimately prove to be the best. But the probable error of a series of measurements is not affected by the glamor of great names; and the weight which it assigns to the observations is at least as good as any other. In the long run, I believe it assigns weight more accurately, and therefore I have trusted to its indications, not as if it were a mathematical fetish, but regarding it as a safe guide, even though sometimes fallible.

One possibly weak point in the method adopted, deserves to be men-

tioned. Its fairness depends in part upon the fairness of the experimenter. One chemist, making a series of measurements, gives all of his determinations. Another chemist selects those which are most concordant, and suppresses others which seem to him less trustworthy. The latter series, therefore, is likely to receive higher weight than belongs to it; while the former series will be underweighted. The rejection of data, even by the man who is most familiar with them, is always a dangerous proceeding, and one which should be discouraged.

The other and more usual method of adjusting the atomic weights, that of selecting determinations in accordance with their apparent chemical merit, has recently been followed by Brauner. In his excellent and critical discussion of the subject, now appearing in Abegg's Handbuch der anorganischen Chemie, he gives all the determinations for each element, and then assigns preference to those which most appeal to his judgment. In most instances his findings agree with mine, and therefore our conclusions reinforce each other. Sometimes we differ, and in such cases it would seem that new determinations are desirable. When values derived from different sources, and computed by different methods are concordant, they may be regarded as probably well established; but even then certainty is not attained. The history of atomic weight determinations bears abundant witness to this assertion.

For example: Until within very recent years the work of Stas, emphasized by that of Marignac, was regarded as almost final. Now, however, some of the ratios measured by these chemists are found to be out of harmony with the best modern investigations, and there is a tendency towards rejecting the older work altogether. But the researches of Stas give a homogeneous and concordant group of atomic weights, which cannot be entirely thrown aside without much more evidence against them than as yet exists. It is probable that the silver used by Stas contained occluded oxygen, as was pointed out by Dumas[1]; and this would account for some, but not all of the variations from recent revisions of the ratios. It is also probable, as Richards has shown, that Stas underrated the solubility of silver chloride. How large these errors may be in Stas' work, assuming them to exist, is uncertain; and to assign zero weight to his determinations would be too extreme a procedure. His data and Marignac's are therefore retained in the present recalculation, with the proper mathematical weight; and the final results seem to be satisfactory. Indeed, the Stas values for silver, chlorine and bromine, applied to the determinations of other atomic weights, sometimes give more concordant results than the modern figures. This is especially true in the cases of cæsium, barium and magnesium, although the discrepancies are not large.

---

[1] Ann. Chim. Phys. (5), 14, 289. See also the Appendix to the first edition of this Recalculation, in which the influence of a correction for occluded oxygen is considered.

The data of Richards and his collaborators for the chlorides of these metals give a ratio between silver and chlorine in agreement with the measurements by Stas, and lower than that which Richards and Wells have established. If, therefore, the work of Stas is in error, the same error inheres in the atomic weights of the three metals above mentioned, and the latter, even if the uncertainty is small, ought to be revised. The sharp concordance found when the atomic weights were computed with Stas' figures is either illusive, or else the modern data for silver and chlorine are wrong. The first of these alternatives is the more probable. In spite of the discordance now evident, the determinations for cæsium, barium and magnesium are by far the best we have, and their uncertainties need not be regarded as serious.

In Meyer and Seubert's recalculation, weights are assigned in quite a novel manner. In each series of experiments the maximum and minimum results are given, but instead of the mean there is a value deduced from the sum of the weighings—that is, each experiment is weighted proportionally to the mass of the material handled in it. For this method I am unable to find any complete justification. Of course, the errors due to the operations of weighing become proportionally smaller as the quantity of material increases, but these errors, with modern apparatus, are relatively unimportant. The real errors in atomic weight determinations are much larger than these, and due to different causes. Hence an experiment upon ten grammes of material may be a little better than one made upon five grammes, but it is by no means necessarily twice as good. The ordinary mean of a series of observations, with its measure of concordance, the probable error, is a better value than one obtained in the manner just described. If only errors of weighing were to be considered, Meyer and Seubert's summation method would be valid, but in the presence of other and greater errors it seems to have but little real pertinency to the problem at hand.

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.

BECKER, G. F.   Atomic Weight Determinations: a Digest of the Investigations Published since 1814.   Smithsonian Miscellaneous Collections, Vol. 27, No. 358.   Washington, 1880.

STAS, J. S.   Untersuchungen über die Gesetze der Chemischen Proportionen über die Atomgewichte und ihre gegenseitigen Verhältnisse.   Uebersetzt von Dr. L. Aronstein.   Leipzig, 1867.
    See also his " Oeuvres Complètes," 3 vols., published at Bruxelles in 1894.[1]

MEYER, L., and SEUBERT, K.   Die Atomgewichte der Elemente, aus den Originalzahlen neu berechnet.   Leipzig, 1883.

SEBELIEN, J.   Beiträge zur Geschichte der Atomgewichte.   Braunschweig, 1884.

OSTWALD, W.   Lehrbuch der allgemeinen Chemie.   Zweite Aufl.   I Band. SS. 18-138.   Leipzig, 1891.

MARIGNAC, J. C. G. DE.   Oeuvres Complètes.   2 vols.   Geneva, 1902.

RICHARDS, T. W.   Experimentelle Untersuchungen ueber Atomgewichte. Hamburg and Leipzig, 1909.

Abegg's Handbuch, containing Brauner's recalculation, has already been mentioned.   Its value is very great.   The four Dutch monographs above cited are also especially valuable.   They represent a revision of all atomic weight data down to 1853, as divided between four writers.

---

[1] The citations used in the present Recalculation are all from the Oeuvres Complètes.

FORMULÆ FOR THE CALCULATION OF PROBABLE ERROR.

The formula for the probable error of an arithmetical mean, familiar to all physicists, is as follows:

(1.)
$$e = 0.6745 \sqrt{\frac{S}{n(n-1)}}$$

Here n represents the number of observations or experiments in the series, and S the sum of the squares 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 inversely proportional to the square of its probable error. Let A, B, C, etc., be such means, and a, b, c their probable errors respectively. Then the general mean is determined by the formula:

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

For the probable error of this general mean we have:

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

In the calculation of atomic and molecular weights the following formulæ are used: Taking, as before, capital letters to represent known quantities, and small letters for their probable errors respectively, we have for the probable error of 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.)
$$e = \frac{\sqrt{\left(\dfrac{Ba}{A}\right)^2 + b^2}}{A}$$

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

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

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 commonly large:

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

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 or weighted mean of all trustworthy determinations. This method of combination is not theoretically perfect, but it seems to be the one most available in practice.

THE FUNDAMENTAL RATIOS.

In the determination of atomic weights, a small number of values are to be regarded as fundamental. They are the standards of reference; and by comparison with them all the other atomic weights are established. Two of these values, the atomic weights of hydrogen and oxygen, are primary; that is, one or the other of them is the basis of the entire system; hydrogen as unity in the older arrangements; oxygen equal to sixteen in the more modern scheme. Over the relative merits of these two ultimate standards there has been much controversy; but with discussions of that sort the present work has nothing to do. The oxygen standard is now recognized by international agreement, and will therefore be accepted here.

Comparatively few of the atomic weights, however, are fixed by direct comparison with either oxygen or hydrogen. In most cases other values intervene, and especially the atomic weights of silver, chlorine, bromine, iodine, nitrogen, carbon, sulphur, potassium and sodium. These constants are first to be determined, and their establishment may be compared to a primary triangulation, of which the hydrogen-oxygen ratio is the base line. The ratios connecting these eleven elements with one another are to be discussed in the following pages.

THE OXYGEN-HYDROGEN RATIO.

Leaving out of account the earliest researches, which now have only historical interest, the first determinations of this ratio worth considering are those by Dulong and Berzelius,[1] who, like some of their successors, effected the synthesis of water over heated oxide of copper. The essential features of the method are in all cases the same. Hydrogen gas is passed over the hot oxide, and the water thus formed is collected and weighed. From this weight and the loss of weight which the oxide undergoes, the composition of water is readily calculated. Dulong and Berzelius made but three experiments, which gave the following percentages of oxygen and hydrogen in water:

O.	H.
88.942	11.058
88.809	11.191
88.954	11.046

---

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

From these figures the ratio H : O becomes—

16.124
15.863
16.106
———— ——
Mean, 16.031, ± .057

As the weighings were not reduced to a vacuum, this correction was afterwards applied by Clark,[1] who showed that these syntheses really make O = 15.894; or, in Berzelian terms, if O = 100, H = 12.583. The value 15.894, ± .057 we may therefore take as the true result of Dulong and Berzelius' experiments, a figure curiously close to that reached in the latest and best researches.

In 1842 Dumas[2] 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.

A.	B.	C.	D.	E.	F.	G.	H.	I.
H_2SO_4	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
P_2O_5	625.829	568.825	884.190	948.323	57.004	64.044	1250.6	1249.0
H_2SO_4	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
"	661.915	627.104	839.304	878.482	34.811	39.178	1254.6	1253.3

[1] Phil. Mag. (3), 20, 341.
[2] Compt. Rend., 14, 537.

P₂O₅	612.625	566.738	824.624	876.244	45.887	51.623	1250.0	1249.0
"	904.643	844.612	822.660	890.246	60.031	67.586	1258.3	1255.1
H₂SO₄	642.325	590.487	741.095	799.417	51.838	58.320	1250.4	1248.9
P₂O₅	587.645	535.137	874.832	933.910	52.508	59.078	1251.2	1249.0
"	673.280	613.492	931.487	998.700	59.789	67.282	1253.3	1250.8
H₂SO₄	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
"	937.845	881.362	1064.762	1128.319	56.483	63.577	1255.8	1252.2
P₂O₅	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 ratio H : O, calculated in mass, is 1 : 15.9608. In the following column the values are deduced from the individual data given under the headings F and G:

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

Mean, 15.9607, ± .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.

2

The investigation of Erdmann and Marchand [1] followed closely after
that of Dumas. The method of procedure was essentially that of the
latter chemist, differing from it only in points of detail. The hydrogen
used was prepared from zinc and sulphuric acid, and the zinc, which
contained traces of carbon, was proved to be free from arsenic and sul-
phur. The copper oxide was made partly from copper turnings and
partly by the ignition of the nitrate. The results obtained are given in
two series, in one of which the weighings were not actually made in
vacuo, but were, nevertheless, reduced to a vacuum standard. In the
second series the copper oxide and copper were weighed in vacuo. The
following table contains the corrected weights of water obtained and of
the oxygen in it, with the value found for the ratio in a third column.
The weights are given in grammes.

First Series.

Wt. Water.	Wt. O.	Ratio.
62.980	55.950	15.917
95.612	84.924	15.891
94.523	84.607	15.977
35.401	31.461	15.970

Mean, 15.939, $\pm$ .014

Second Series.

Wt. Water.	Wt. O.	Ratio.
41.664	37.034	15.996
44.089	39.195	16.018
53.232	47.321	16.011
55.636	49.460	16.017

Mean, 16.010, $\pm$ .0036

The effect of discussing these two series separately is somewhat start-
ling. 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 Erdmann and Marchand's experiments as one series,
giving all equal weight, the mean now becoming $O = 15.975, \pm .0113$.
If we take the sum of the eight experiments, 483.137 grammes water
and 429.352 grammes oxygen, and compute from these figures, then
$O = 15.966$.

---

[1] Journ. prakt. Chem., 26, 461. 1842.

It would be easy to point out the sources of error in the foregoing sets of determinations, but it is hardly worth while to do so in detail. A few leading suggestions are enough for present purposes. First, there is an insignificant error due to the occlusion of hydrogen by metallic copper, rendering the apparent weight of the latter a trifle too high. Secondly, as shown by Dittmar and Henderson, hydrogen dried by passage through sulphuric acid becomes perceptibly contaminated with sulphur dioxide. In the third place, Morley [1] has found that hydrogen prepared from zinc always contains carbon compounds not removable by absorption and washing. Erdmann and Marchand themselves note that their zinc contained traces of carbon. Finally, copper oxide, especially when prepared by the ignition of the nitrate, is very apt to contain gaseous impurities, and particularly occluded nitrogen.[2] Any or all of these sources of error may have vitiated the three investigations so far considered, but it would be useless to speculate as to the extent of their influence. They amply account, however, for the differences between the older and the later determinations of the constant under discussion.

Leaving out of account all measurements of the relative densities of hydrogen and oxygen, to be considered separately later, the next determination to be noted is that published by J. Thomsen in 1870.[3] Unfortunately this chemist has not published the details of his work, but only the end results. 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 is therefore subject to the corrections recently applied by Crafts and others to the latter. These corrections, which will be discussed further on, reduce the value of O from 15.9605 to 15.91. In order to combine this value with others, it is necessary to assign it weight arbitrarily, and as Thomsen made eight experiments, which are said to be concordant, it may be fair to rank his determination with that of Erdmann and Marchand, and to assume for it the same probable error. The value 15.91, ± .0113 will therefore be taken as the outcome of Thomsen's research.

In 1887 Cooke and Richards published the results of their elaborate investigation.[4] These chemists weighed hydrogen, burned it over copper

[1] Amer. Chem. Journ., 12, 469. 1890.
[2] See Richards' work cited in the chapter on copper.
[3] Ber. Deutsch. chem. Ges., 3, 928. 1870.
[4] Proc. Amer. Acad., 23, 149. Amer. Chem. Journ., 10, 81.

oxide, and weighed the water produced. The copper oxide was prepared from absolutely pure electrolytic copper, and the hydrogen was obtained from three distinct sources, as follows: First, from pure zinc and hydrochloric acid; second, by electrolysis, in a generator containing dilute hydrochloric acid and zinc-mercury amalgam; third, by the action of caustic potash solution upon sheet aluminum. The gas was dried and purified by passage through a system of tubes and towers containing potash, calcium chloride, glass beads drenched with sulphuric acid, and phosphorus pentoxide. No impurity could be discovered in it, and even nitrogen was sought for spectroscopically without being found.

The hydrogen was weighed in a glass globe holding nearly five litres and weighing 570.5 grammes, which was counterpoised by a second globe of exactly the same external volume. Before filling, the globe was exhausted to within 1 mm. of mercury and weighed. It was then filled with hydrogen and weighed again. The difference between the two weights gives the weight of hydrogen taken.

In burning, the hydrogen was swept from the globe into the combustion furnace by means of a stream of air which had previously been passed over hot reduced copper and hot cupric oxide, then through potash bulbs, and finally through a system of driers containing successively calcium chloride, sulphuric acid, and phosphorus pentoxide. The water formed by the combustion was collected in a condensing tube connected with a U tube containing phosphorus pentoxide. The latter was followed by a safety tube containing either calcium chloride or phosphorus pentoxide, added to the apparatus to prevent reflex diffusion. Full details as to the arrangement and construction of the apparatus are given. The final results appear in three series, representing the three sources from which the hydrogen was obtained. All weights are corrected to a vacuum.

First Series.—*Hydrogen from Zinc and Acid.*

Wt. of H.	Wt. H_2O.	Ratio H:O.
.4233	3.8048	15.977
.4136	3.7094	15.937
.4213	3.7834	15.960
.4163	3.7345	15.941
.4131	3.7085	15.954

Mean, 15.954, $\pm$ .0048

Second Series.—*Electrolytic Hydrogen.*

.4112	3.6930	15.962
.4089	3.6709	15.955
.4261	3.8253	15.955
.4197	3.7651	15.942
.4144	3.7197	15.953

Mean, 15.953, $\pm$ .0022

Third Series.—Hydrogen from Caustic Potash.

.42205	3.7865	15.943
.4284	3.8436	15.944
.4205	3.7776	15.967
.43205	3.8748	15.937
.4153	3.7281	15.954
.4167	3.7435	15.967

Mean, 15.952, $\pm$ .0035

Mean of all as one series, 15.953, $\pm$ .0020

Shortly after the appearance of this paper by Cooke and Richards Lord Rayleigh pointed out the fact, already noted by Agamennone, that a glass globe when exhausted is sensibly condensed by the pressure of the surrounding atmosphere. This fact involves a correction to the foregoing data, due to a change in the tare of the globe used, and this correction was promptly determined and applied by the authors.[1] By a careful series of measurements they found that the correction amounted to an average increase of 1.98 milligrammes to the weight of hydrogen taken in each experiment. Hence O equals not 15.953, but 15.869, the probable error remaining unchanged. The final result of Cooke and Richards' investigation, therefore, is

$$O = 15.869, \pm .0020$$

Keiser's determinations of the ratio were published almost simultaneously with those of Cooke and Richards. He burned hydrogen occluded by palladium, and weighed the water so formed. In a preliminary paper[2] the following results are given:

Wt. of H.	Wt. of H_2O.	Ratio H:O.
.65100	5.81777	15.873
.60517	5.41540	15.897
.33733	3.06655	15.822

Mean, 15.864, $\pm$ .015

Not long after the publication of the foregoing data Keiser's full paper appeared.[3] Palladium foil, warmed to a temperature of 250°, was saturated with hydrogen prepared from dilute sulphuric acid and zinc free from arsenic. From 100 to 140 grammes of palladium were taken, and it was first proved that the metal did not absorb other gases which might contaminate the hydrogen. Before charging, the foil was heated to bright redness in vacuo. After charging, the tube containing the palladium

---

[1] Proc. Amer. Acad., 23, 182. Am. Chem. Journ., 10, 191.

[2] Berichte, 20, 2323. 1887.

[3] Amer. Chem. Journ., 10, 249. 1888.

hydride was exhausted by means of a Geissler pump to remove any nitrogen which might have been present. In the preliminary investigation cited above, the latter precaution was neglected, which may account for the low results.

Between the palladium tube and the combustion tube a U tube was interposed, containing phosphorus pentoxide. This was to determine the amount of moisture in the hydrogen. The combustion tube was filled with granular copper oxide, prepared by reducing the commercial oxide in hydrogen, heating the metal so obtained to bright redness in a vacuum, and then reoxidizing with pure oxygen.

Upon warming the palladium tube, which was first carefully weighed, hydrogen was given off and allowed to pass into the combustion tube. When the greater part of it had been burned, the tube was cut off by means of a stopcock and allowed to cool. Meanwhile a stream of nitrogen was passed through the combustion tube, sweeping hydrogen before it. This was followed by a current of oxygen, reoxidizing the reduced copper; and the copper oxide was finally cooled in a stream of dry air. The water produced by the combustion was collected in a weighed bulb tube, followed by a weighed U tube containing phosphorus pentoxide.

A second phosphorus pentoxide tube served to prevent the sucking back of moisture from the external air. The loss in weight of the palladium tube, corrected by the gain in weight of the first phosphorus pentoxide, gave the weight of hydrogen taken. The gain in weight of the two collecting tubes gave the weight of water formed. All weights in the following table of results are reduced to a vacuum:

Wt. of H.	Wt. H_2O.	Ratio H:O.
.34145	3.06338	15.943
.68394	6.14000	15.955
.65529	5.88200	15.952
.65295	5.86206	15.954
.66664	5.98116	15.944
.66647	5.98341	15.955
.57967	5.20493	15.958
.66254	5.94758	15.952
.87770	7.86775	15.950
.77215	6.93036	15.951

Mean, 15.9514, ± .0011

In sum, 6.55880 grammes of hydrogen gave 52.30383 of water, whence O = 15.9492.

In March, 1889, Lord Rayleigh [1] published a few determinations of the ratio obtained by still a new method. Pure hydrogen and pure oxygen

---

[1] Proc. Roy. Soc., 45, 425.

were both weighed in glass globes. From these they passed into a mixing chamber, and thence into a eudiometer, where they were gradually exploded by a series of electric sparks. After explosion the residual gas remaining in the eudiometer was determined and measured. The results, given without weighings or explicit details, are as follows:

<div align="center">

15.93
15.98
15.98
15.93
15.92

</div>

<div align="center">

Mean, 15.948, ± .009

</div>

Correcting this result for shrinkage of the globes and consequent change of tare, it becomes $O = 15.89, \pm .009$.

In the same month that Lord Rayleigh's paper appeared, W. A. Noyes [1] published his first series of determinations. His plan was to pass hydrogen into an apparatus containing hot copper oxide, condensing the water formed in the same apparatus, and from the gain in weight of the latter getting the weight of the hydrogen absorbed. The apparatus devised for this purpose consisted essentially of a glass bulb of 30 to 50 cc. capacity, with a stopcock tube on one side and a sealed condensing tube on the other. In weighing, it was counterpoised by another apparatus of nearly the same volume but somewhat less weight, in order to obviate reductions to a vacuum. After filling the bulb with commercial copper oxide (90 to 150 grammes), the apparatus was heated in an airbath, exhausted by means of a Sprengel pump, cooled, and weighed. It was next replaced in the airbath, again heated, and connected with an apparatus delivering purified hydrogen. When a suitable amount of the latter had been admitted, the stopcock was closed, and the heating continued long enough to convert all gaseous hydrogen within it into water. The apparatus was then cooled and weighed, after which it was connected with a Sprengel pump, in order to extract the small quantity of nitrogen which was always present. The latter was pumped out into a eudiometer, where it was measured and examined. The gain in weight of the apparatus, less the weight of this very slight impurity, gave the weight of hydrogen oxidized.

The next step in the process consisted in heating the apparatus to expel water, and weighing again. After this, pure oxygen was admitted and the heating was resumed, so as to oxidize the traces of hydrogen which had been retained by the copper. Again the apparatus was cooled and weighed, and then reheated, when the water formed was received in a

[1] Amer. Chem. Journ., 11, 155. 1889.

bulb filled with phosphorus pentoxide, and the gaseous contents were collected in a eudiometer. On cooling and weighing the apparatus, the loss of weight, less the weight of gases pumped out, gave .the amount of water produced by the traces of residual hydrogen under consideration. This weight, added to the loss of weight when the original water was expelled, gives the weight of oxygen taken away from the copper oxide. Having thus the weight of hydrogen and the weight of oxygen, the ratio sought for follows. Six results are given, but as they are repeated, with corrections, in Noyes' second paper, they need not be considered now.

Noyes' methods were almost immediately criticised by Johnson,[1] who suggested several sources of error. This chemist had already shown in an earlier paper[2] that copper reduced in hydrogen persistently retains traces of the 'latter, and also that when the reduction is effected below 700°, water is retained too. The possible presence of sulphur in the copper oxide was furthermore mentioned. Errors from these sources would tend to make the apparent atomic weight of oxygen (referred to hydrogen as unity) too low.

In his second paper[3] Noyes replies to the foregoing criticisms, and shows that they carry no weight, at least so far as his work is concerned. He also describes a number of experiments in which oxides other than copper oxide were tried, but without distinct success, and he gives fuller details as to manipulations and materials. His final results are in four series, as follows:

First Series.—Hydrogen from Zinc and Hydrochloric Acid.

Wt. of H.	Wt. of O.	Ratio H:O.
.9443	7.5000	15.885
.6744	5.3555	15.882
.7866	6.2569	15.909
.5521	4.3903	15.904
.4274	3.3997	15.909
.8265	6.5686	15.895

Mean, 15.8973, ± .0032

This series appeared in the earlier paper, but with an error which is here corrected.

---

[1] Chem. News, 59, 272.
[2] Journ. Chem. Soc., May, 1879.
[3] Amer. Chem. Journ., 12, 441. 1890.

Second Series.—Electrolytic Hydrogen, Dried by Phosphorus Pentoxide.

Wt. of H.	Wt. of O.	Ratio H:O.
.5044	4.0095	15.898
.6325	5.0385	15.932
.6349	5.0517	15.913
.5564	4.4175	15.879
.7335	5.8224	15.876
.6696	5.3181	15.885

Mean, 15.8971, ± .0064

Third Series.—Electrolytic Hydrogen, Dried by Passage Through a Tube Packed with Sodium Wire.

Wt. of H.	Wt. of O.	Ratio H:O.
.9323	7.4077	15.891
.9952	7.9045	15.885
.3268	2.5977	15.898
.7907	6.2798	15.884
.7762	6.1671	15.891
1.1221	8.9131	15.887

Mean, 15.8893, ± .0014

At the end of this series it was found that the hydrogen contained a trace of water, estimated to be equivalent to an excess of three milligrammes in the total hydrogen of the six experiments. Correcting for this, the mean becomes O = 15.899.

Fourth Series.—Electrolytic Hydrogen, Dried over Freshly Sublimed Phosphorus Pentoxide.

Wt. of H.	Wt. of O.	Ratio H:O.
1.0444	8.3017	15.898
.7704	6.1233	15.896
.8231	6.5421	15.896
.8872	7.0490	15.890
.9993	7.9403	15.892
1.1910	9.4595	15.885

Mean, 15.8929, ± .0013

The mean of all the twenty-four determinations, taken as one series, with the correction to the third series included, is O = 15.8966, ± .0017. In sum, there were consumed 18.5983 grammes of hydrogen and 147.8145 of oxygen; whence O = 15.8955.

Dittmar and Henderson,[1] who effected the synthesis of water over copper oxide by what was essentially the old method, begin their memoir

---

[1] Proc. Roy. Soc. Glasgow, 22, 33. Communicated Dec. 17, 1890.

with an exhaustive criticism of the work done by Dumas and by Erd-
mann and Marchand. They show, as I have already mentioned, that
hydrogen dried by sulphuric acid becomes contaminated with sulphur
dioxide, and also that a gas passed over calcium chloride may still retain
as much as one milligramme of water per litre. Fused caustic potash
they found to dry a gas quite completely.

In their first series of syntheses, Dittmar and Henderson generated
their hydrogen from zinc and acid, sometimes hydrochloric and some-
times sulphuric, and dried it by passage, first through cotton wool, then
through vitrioled pumice, then over red-hot metallic copper to remove
oxygen. In later experiments it first traversed a column of fragments
of caustic soda to remove antimony derived from the zinc. The oxide
of copper used was prepared by heating chemically pure copper clip-
pings in a muffle, and was practically free from sulphur. In weighing
the several portions of apparatus it was tared with somewhat lighter
similar pieces of as nearly as possible the same displacement. The re-
sults of this series of experiments, which are vitiated by the presence,
unsuspected at first, of sulphur dioxide in the hydrogen, are stated in
values of H when $O = 16$, but in the following table have been recalcu-
lated to conformity with the earlier determinations:

Wt. of Water.	Wt. of O.	Ratio H : O.
4.7980	4.26195	15.901
7.55025	6.71315	16.039
6.2372	5.53935	15.875
11.29325	10.03585	15.963
11.6728	10.3715	15.940
11.8433	10.5256	15.976
11.7317	10.4243	15.947
19.2404	17.0926	15.916
20.83435	18.5234	16.031
17.40235	15.4598	15.917
19.2631	17.11485	15.934

Mean, 15.949, $\pm$ .0103

Reducing to a vacuum, this becomes 15.843, while a correction for the
sulphur dioxide estimated to be present in the hydrogen brings the value
up again to 15.865. Still another correction is suggested, namely, that
as the reduced copper in the combustion tube, before weighing, was ex-
posed to a long-continued current of dry air, it may have taken up traces
of oxygen chemically, thereby increasing its weight. As this correction,
however, is quantitatively uncertain, it may be neglected here, and the
result of this series will be taken as $O = 15.865, \pm .0103$. Its weight,
relatively to some other series of experiments, is evidently small.

In their second and final series Dittmar and Henderson dried their hydrogen, after deoxidation by red-hot copper, over caustic potash and subsequently phosphorus pentoxide. The copper oxide and copper of the combustion tube were both weighed in vacuo. The results were as follows, vacuum weights being given:

Wt. of Water.	Wt. of O.	Ratio H:O.
19.2057	17.0530	15.843
19.5211	17.3342	[15.853]
19.4672	17.2882	15.868
22.9272	20.3540	15.820
23.0080	20.4421	[15.934]
23.4951	20.8639	15.859
23.5612	20.9226	[15.859]
23.7542	21.0957	15.870
23.6568	21.8994	15.884
23.6179	21.8593	15.848
24.6021	21.8499	15.878
24.3047	21.5788	15.832
23.6172	20.9709	15.849

Mean, 15.861, ± .0052

The authors reject the three bracketed determinations, because of irregularities in the course of the experiments. The mean of the ten remaining determinations is 15.855, ±.0044. Both means, however, have to be corrected for the minute trace of hydrogen occluded by the reduced copper. This correction, experimentally measured, amounts to +.006. Hence the mean of all the experiments in the series becomes 15.867, ±.0052, and of the ten accepted experiments, 15.861, ±.0044. The authors themselves select out seven experiments, giving a corrected mean of 15.866, which they regard as the best value. Taking all their evidence, their two series combine thus:

First series .... 15.865, ± .0103
Second series .... 15.867, ± .0052

General mean .... 15.8667, ± .0046

Leduc,[1] who also effected the synthesis of water over copper oxide, following Dumas' method with slight modifications, gives the results of two experiments, as follows:

---

[1] Compt. Rend., 115, 41. 1892. See also the complete memoir in Ann. Chim. Phys. (7), 15, 48. 1898. In the latter Leduc gave a preliminary determination which made O = 15.860.

Wt. Water.	Wt. O.	Ratio H:O.
22.1632	19.6844	15.882
19.7403	17.5323	15.880

Mean, 15.881

These experiments we may arbitrarily assign equal weight with two in Dittmar and Henderson's later series, when the result becomes 15.881, ±.0132, the value to be accepted. Leduc states that his copper oxide, which was reduced at as low a temperature as possible, was prepared by heating clippings of electrolytic copper in a stream of oxygen.

To E. W. Morley [1] we owe the first complete quantitative syntheses of water, in which both gases were weighed separately, and afterwards in combination. The hydrogen was weighed in palladium, as was done by Keiser, and the oxygen was weighed in compensated globes, after the manner of Regnault. The globes were contained in an artificial " cave," to protect them from moisture and from changes of temperature; being so arranged that they could be weighed by the method of reversals without opening either the " cave " or the balance case. For each weighing of hydrogen about 600 grammes of palladium were employed. After weighing, the gases were burned by means of electric sparks in a suitable apparatus, from which the unburned residue could be withdrawn for examination. Finally, the apparatus containing the water produced was closed by fusion and also weighed. Rubber joints were avoided in the construction of the apparatus, and the connections were continuous throughout. The weights and derived ratios are as follows:

H taken.	O taken.	H₂O formed.	H:O.	H:H₂O.
3.2645	25.9176	29.1788	15.878	17.877
3.2559	25.8531	29.1052	15.881	17.878
3.8193	30.3210	34.1389	15.878	17.873
3.8450	30.5294	lost	15.880	. . . . .
3.8382	30.4700	34.3151	15.877	17.881
3.8523	30.5818	34.4327	15.877	17.876
3.8298	30.4013	34.2284	15.877	17.875
3.8286	30.3966	34.2261	15.878	17.879
3.8225	30.3497	34.1742	15.879	17.881
3.8220	30.3479	34.1743	15.881	17.883
3.7637	29.8865	33.6540	15.881	17.883
3.8211	30.3429	34.1559	15.882	17.878

Mean, 15.8792, 17.8785,
± .00032 ± .00066

[1] " On the Density of Oxygen and Hydrogen, and on the Ratio of their Atomic Weights," by Edward W. Morley. Smithsonian Contributions to Knowledge, 29, 1895, 4to, xi + 117 pp., 40 cuts. Abstract in Am. Chem. Journ., 17, 267 (gravimetric), and Ztschr. phys. Chem., 17, 87 (gaseous densities); also note in Am. Chem. Journ., 17, 396. Preliminary notice in Proc. Amer. Association, 1891, p. 185. See also a discussion by Morley of all the earlier determinations, in the Western Reserve University Bulletin, for April, 1895.

Combined, these data give:

> From ratio H:O............ 15.8792, ± .00032
> From ratio H:H₂O.......... 15.8785, ± .00066
>
> General mean .... 15.8790, ± .00028

For details Morley's original memoir must be consulted. No abstract can do full justice to it.

Two other series of determinations, by Julius Thomsen, are radically different in method from all the previous work. In the first series [1] he determined the ratio between HCl and NH₃; and thence, using Stas' values for Cl and N, fixed by reference to O=16, computed the ratio H : O. This method was so indirect as to be of little importance, and gave for the atomic weight of oxygen approximately the round number 16. I shall use the data farther on for another purpose. The paper has been sufficiently criticised by Meyer and Seubert,[2] who have discussed its sources of error.

In Thomsen's later memoir [3] a method of determination is described which is, like the preceding, quite novel, but more direct. First, aluminum, in weighed quantities, was dissolved in caustic potash solution. In one set of experiments the apparatus was so constructed that the hydrogen evolved was dried and then expelled. The loss of weight of the apparatus gave the weight of the hydrogen so liberated. In the second set of experiments the hydrogen passed into a combustion chamber in which it was burned with oxygen, the water being retained. The increase in weight of this apparatus gave the weight of oxygen so taken up. The two series, reduced to the standard of a unit weight of aluminum, gave the ratio between oxygen and hydrogen.

The results of the two series, reduced to a vacuum and stated as ratios, are as follows:

First.	*Second.*
Weight of H	Weight of O
Weight of Al	Weight of Al
0.11180	0.88788
0.11175	0.88799
0.11194	0.88774
0.11205	0.88779
0.11189	0.88785
0.11200	0.88789
0.11194	0.88798
0.11175	0.88787
0.11190	0.88773

[1] Zeitsch. physikal Chem., 13, 398. 1894.
[2] Ber. Deutsch. chem. Ges., 27, 2770.
[3] Zeitsch. anorg. Chem., 11, 14. 1895.

0.11182	0.88798
0.11204	0.88785
0.11202	———
0.11204	0.88787, ± 0.000018
0.11179	
0.11178	
0.11202	
0.11188	
0.11186	
0.11185	
0.11190	
0.11187	

0.11190, ± 0.000015

Dividing the mean of the second column by the mean of the first, we have for the equivalent of oxygen:

$$\frac{0.88787, \pm 0.000018}{0.11190, \pm 0.000015} = 7.9345, \pm 0.0011$$

Hence $O = 15.8690, \pm 0.0022$.

The details of the investigation are somewhat complicated, and involve various corrections which need not be considered here. The result as finally stated includes all corrections and is evidently good.

The syntheses of water reported by Keiser[1] in 1898, involved the direct oxidation of hydrogen occluded in palladium, with subsequent weighing of the water so produced in the vessel in which it was generated. That vessel was tubular in form, and divided into two compartments; one containing phosphorus pentoxide, to absorb the water, the other holding the palladium hydride. Each determination required five weighings, as follows: First, of the vessel, containing only the drying agent, and exhausted of air. Second, the same as the first, plus the palladium. Third, the gain in weight was measured after saturating the palladium with hydrogen. Fourth, the entire apparatus after complete oxidation of the hydrogen to water. The gain in weight gave the oxygen absorbed. Fifth, like the fourth, but with the palladium removed. The difference between the first and fifth weighings gave the amount of water formed. All the operations were thus performed in a single piece of apparatus, and troublesome corrections were avoided. The data obtained were as follows, with weights not reduced to a vacuum standard:

H taken.	O taken.	H_2O formed.	$H:O$.	$H:H_2O$.
.27549	2.18249	2.45975	15.8444	17.8573
.27936	2.21896	2.49923	15.8860	17.8925
.27091	2.15077	2.42355	15.8781	17.8919
.26845	2.13270	2.40269	15.8890	17.9005
			———	———
		Mean,	15.8744	15.8855

[1] Amer. Chem. Journ., 20, 733.   1898.

Taken as one series, the two sets of values, eight determinations in all, give for the ratio H : O the number 15.8799, ±.0046. This figure is slightly higher than Morley's average, but below his maximum.

Late in 1907, an elaborate investigation by Noyes[1] was published, covering five series of syntheses. The first series of twenty experiments, however, was found to be affected by a small constant error, and it was therefore rejected. The other series gave the subjoined results, with all corrections, including the reduction to a vacuum, applied.

Second Series. Electrolytic hydrogen, from sulphuric acid, was weighed in palladium, and again in the copper oxide tube in which it was oxidized to water. The apparatus was similar to that used in his former research, and so, too, but with differences in detail, was the procedure.

H taken.	O taken.	H₂O formed.	H : O.	H : H₂O.
3.72565	29.57891	33.30408	15.8785	17.8783
3.80318	30.18400	33.98748	15.8730	17.8732
3.75873	29.83358	33.59127	15.8743	17.8737
2.96328	23.5197	26.48379	15.8742	17.8746
2.11395	lost	18.89214	......	17.8734
3.53136	28.02910	31.56024	15.8744	17.8743
3.53959	28.09619	31.63554	15.8754	17.8753
			Mean, 15.8750,	17.8747,
			± .00052	± .00045

Third Series. Hydrogen from sulphuric acid was passed directly into the copper oxide bulb and there converted into water.

H taken.	O taken.	H₂O formed.	H : O.	H : H₂O.
2.44279	19.39757	21.84042	15.8813	17.8815
2.18739	17.36305	19.55117	15.8756	17.8763
2.75129	21.84345	24.59389	15.8787	17.8781
4.00062	....	35.75082	......	17.8726
4.04057	32.07689	36.11762	15.8774	17.8775
			Mean, 15.8782,	17.8772,
			± .00091	± .00097

Fourth Series. Hydrogen and oxygen, both obtained by electrolysis of sulphuric acid, were directly combined by means of palladium, somewhat as in Keiser's determinations. The use of copper oxide was thus avoided.

---

[1] Amer. Chem. Journ., 29, 1718. 1907. In Vol. 30, p. 4, 1908, Noyes discusses all determinations of the atomic weight of hydrogen, and proposes criteria for the rejection of doubtful data.

H taken.	O taken.	H_2O formed.	$H:O.$	$H:H_2O.$
2.27916	18.08455	20.36128	15.8695	17.8674
4.12734	32.76527	36.89043	15.8772	17.8761
4.17556	33.13449	37.30787	15.8707	17.8696
4.19346	33.27384	37.46453	15.8694	17.8681
2.30746	18.30863	20.61357	15.8691	17.8669
4.59692	36.48543	41.08162	15.8739	17.8735
4.63625	36.79354	41.42905	15.8721	17.8718
4.57274	36.28696	40.85834	15.8710	17.8704
			Mean, 15.8716,	17.8705,
			$\pm$ .00066	$\pm$ .00074

Fifth Series. Essentially like series four, except that the two gases were prepared by electrolysis of barium hydroxide.

H taken.	O taken.	H_2O formed.	$H:O.$	$H:H_2O.$
4.61180	36.60909	41.22105	15.8763	17.8763
4.62358	36.69575	41.31647	15.8733	17.8721
4.59853	36.50484	41.10212	15.8768	17.8762
4.55832	36.17887	40.73904	15.8738	17.8746
4.20399	33.37000	37.57336	15.8754	17.8751
			Mean, 15.8751.	17.8749,
			$\pm$ .00046	$\pm$ .00051

Since these series of measurements represent different methods, and are evidently of unequal value, it is best to combine them mathematically, giving each mean a weight inversely proportional to the square of its probable error. Noyes computed all of the experiments on the basis of the oxygen standard, giving for each one its expression as the atomic weight of hydrogen. I have chosen the present form for simplicity of calculation, and for greater ease of combination with previous determinations. In the following table I give Noyes' deductions in an additional column [1]:

		Ratio $H:O.$	*Atomic weight $H.$*
Series 2.	$H:O$	15.8750, $\pm$ .00052	1.00787
	$H:H_2O$	15.8747, $\pm$ .00045	1.00789
Series 3.	$H:O$	15.8782, $\pm$ .00091	1.00767
	$H:H_2O$	15.8772, $\pm$ .00097	1.00774
Series 4.	$H:O$	15.8716, $\pm$ .00066	1.00809
	$H:H_2O$	15.8705, $\pm$ .00074	1.00815
Series 5.	$H:O$	15.8751, $\pm$ .00046	1.00786
	$H:H_2O$	15.8749, $\pm$ .00051	1.00788
	General mean..	15.8745, $\pm$ .00021	1.00783, $\pm$ .000013

[1] See Noyes' memoir for the results of combining his data in different ways. The 48 experiments, taken as one series, give H = 1.00793, $\pm$ .00002.

Referring to his determinations published in 1890, Noyes points out a constant error in them, the elimination of which reduces the value of the ratio to 15.879, in agreement with the measurements by Morley.

The details of Noyes' investigation are too voluminous for repetition here. It goes almost without saying that every precaution was taken which his own previous experience and the experience of others could suggest, and that his materials were of the highest degree of purity. The true value of the ratio must lie somewhere within the range of variation shown by his individual determinations, which it may be observed, overlap those of Morley.

We have now before us, for combination, fifteen sets of determinations of the hydrogen-oxygen ratio. I have arranged them in the order of descending magnitude, and computed their general mean as follows:

	Ratio.	*Atomic weight H.*
1. Erdmann and Marchand..	15.975, ± .0113	1.00156
2. Dumas	15.9607, ± .0070	1.00246
3. Keiser, 1888	15.9514, ± .0011	1.00305
4. Thomsen, 1870	15.91, ± .0113	1.00565
5. Noyes, 1890, uncorrected..	15.8966, ± .0017	1.00650
6. Dulong and Berzelius....	15.894, ± .0570	1.00667
7. Rayleigh	15.89, ± .0090	1.00692
8. Leduc	15.881, ± .0132	1.00750
9. Keiser, 1898	15.8799, ± .0046	1.00756
10. Morley	15.8790, ± .00028	1.00762
11. Noyes, 1907	15.8745, ± .00021	1.00783
12. Cooke and Richards......	15.8690, ± .0020	1.00825
13. Thomsen, 1895	15.8690, ± .0022	1.00825
14. Dittmar and Henderson..	15.8677, ± .0046	1.00834
15. Keiser, 1887	15.864, ± .0150	1.00857
General mean	15.8779, ± .00016	1.00769, ± .00001

In this combination, which includes all the syntheses, good or bad, the general mean lies between the values found by Noyes and Morley. It is, therefore, not far from the truth. If we reject the high values, Nos. 1 to 7, the general mean becomes 15.8760, ±.00017, and H = 1.00781, ±.00001. Values 10 and 11, combined, give 15.8761, ±.00017, and H = 1.00780, ±.00001. That is, the Morley and Noyes determinations control all the others, and practically eliminate them. The high and low figures tend to balance one another, and so to disappear from the final combination.

In discussing the relative densities of oxygen and hydrogen gases we need consider only the more modern determinations, beginning with those of Dumas and Boussingault. As the older work has some historical value, I may in passing just cite its results. For the density of

3

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.[1]

In 1841 Dumas and Boussingault[2] 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, ± .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, ±.00013. This mean hydrogen value, combined with the mean for oxygen, gives for the latter, when H=1, the density ratio 15.9538, ±.031.

Regnault's researches, published four years later,[3] were much more elaborately executed. Indeed, they long stood among the classics of physical science, and it is only recently that they have been supplanted by other measurements.

For hydrogen three determinations of density gave the following results:

$$.06923$$
$$.06932$$
$$.06924$$

Mean, .069263, ± .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, ± .000008

---

[1] 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.

[2] Compt. Rend., 12, 1005. Compare also with Dumas, Compt. Rend., 14, 537.

[3] Compt. Rend., 20, 975.

Now, combining the hydrogen and oxygen series, we have the ratio H : O :: 1 : 15.9628, ±.0044. According to Le Conte,[1] Regnault's reductions contain slight numerical errors, which, corrected, give for the density of oxygen, 1.105612, and for hydrogen, .069269. Ratio, 1 : 15.9611.

A much weightier correction to Regnault's data has already been indictated in the discussion of Cooke and Richards' work. He assumed that the globes in which the gases were weighed underwent no changes of volume, but Agamennone,[2] and after him, but independently,[3] Lord Rayleigh showed that an exhausted vessel was perceptibly compressed by atmospheric pressure. Hence its volume when empty was less than its volume when filled with gas. Crafts, having access to Regnault's original apparatus, has determined the magnitude of the correction indicated.[4] Unfortunately, the globe actually used by Regnault had been destroyed, but another globe of the same lot was available. With this the amount of shrinkage during exhaustion was measured, and Regnault's densities were thereby changed to 1.10562 for oxygen, and .06949 for hydrogen. Corrected ratio, 1 : 15.9105. Doubtless Dumas and Boussingault's data are subject to a similar correction, and if we assume that it is proportionally the same in amount, the ratio derived from their experiments becomes 1 : 15.9015.

In the same paper, that which contained the discovery of this correction, Lord Rayleigh gives a short series of measurements of his own. His hydrogen was prepared from zinc and sulphuric acid, and was purified by passage over liquid potash, then through powdered mercuric chloride, and pulverized solid potash successively. It was dried by means of phosphorus pentoxide. His oxygen was derived partly from potassium chlorate, and partly from the mixed chlorates of sodium and potassium. Equal volumes of the two gases weighed as follows:

H.	O.
.15811	2.5186, ± .00061 [5]
.15807	
.15798	
.15792	

Mean, .15802, ± .000029

Corrected for shrinkage of the exhausted globe these become—H, 0.15860; O, 2.5192. Hence the ratio 1 : 15.884, ±.0048.

[1] Private communication. See also Phil. Mag. (4), 27, 29, 1864, and Smithsonian Report, 1878, p. 428.

[2] Atti Rendiconti Acad. Lincei, 1885.

[3] Proc. Roy. Soc., 43, 356. Feb., 1888.

[4] Compt. Rend., 106, 1662.

[5] Arbitrarily assigned the probable error of a single experiment in Rayleigh's paper of 1892.

In 1892 Rayleigh published a much more elaborate determination of this ratio.[1] The gases were prepared electrolytically from caustic potash, and dried by means of solid potash and phosphorus pentoxide. The hydrogen was previously passed over hot copper. The experiments, stated like the previous series, are in five groups; two for oxygen and three for hydrogen; but for present purposes the similar sets may be regarded as equal in weight, and so discussable together. The weights of equal volumes are as follows:

	$H.$		$O.$	
	.15807		2.5182	
	.15816		2.5173	
First set	.15811		2.5172	First set
Mean, .15808	.15803		2.5193	Mean, 2.51785
	.15801		2.5174	
	.15809		2.5177	
	.15800		2.5183	
	.15820		2.5168	
Second set	.15792		2.5172	Second set
Mean, .15797	.15788		2.5181	Mean, 2.5172
	.15783		2.5156	
	.15807			
	.15801		Mean, 2.5176, $\pm$ .00019	
	.15817			
Third set	.15790			
Mean, .15804	.15810			
	.15798			
	.15802			
	.15807			

Mean, .15804, $\pm$ .000019

These weights with various corrections relative to temperatures and pressures, and also for the compression of the exhausted globe, ultimately become for H, .158531; and for O, 2.51777. Hence the ratio 1 : 15.882, $\pm$ .0023. For details relative to corrections the original memoir should be consulted.

In his paper " On a new method of determining gas densities," [2] Cooke gives three measurements for hydrogen, referred to air as unity. They are:

.06957
.06951
.06966

Mean, .06958, $\pm$ .000029

[1] Proc. Roy. Soc., 50, 448, Feb. 18, 1892.
[2] Proc. Amer. Acad., 24, 202. 1889. Also Am. Chem. Journ., 11, 509.

Combining this with Regnault's density for oxygen, as corrected by Crafts, $1.10562, \pm.000008$, we get the ratio $H : O :: 1 : 15.890, \pm.0067$.

Leduc, working by Regnault's method, somewhat modified, and correcting for shrinkage of exhausted globes, gives the following densities [1]:

H.	O.
.06947	1.10501
.06949	1.10516
.06947	

Mean, .06948, $\pm$ .00006745

The two oxygen measurements are the extremes of three, the mean being $1.10506, \pm.0000337$. Hence the ratio $1 : 15.905, \pm.0154$.

In a later memoir Leduc [2] gives two more measurements of the density of oxygen. They are 1.10527 and 1.10521. If we include these in series with the other values the mean becomes $1.10514, \pm.0000321$. The use of this figure in subsequent combinations of data has an insignificant effect upon the computations. It raises O from 15.905 to 15.906.

The first two hydrogen determinations were made with gas produced by the electrolysis of caustic potash, while the third sample was derived from zinc and sulphuric acid. The oxygen was electrolytic. Both gases were passed over red-hot platinum sponge, and dried by phosphorus pentoxide.

Much more elaborate determinations of the two gaseous densities are those made by Morley.[3] For oxygen he gives three series of data: two with oxygen from potassium chlorate, and one with gas partly from the same source and partly electrolytic. In the first series, temperature and pressure were measured with a mercurial thermometer and a mano-barometer. In the second series they were not determined for each experiment, but were fixed by comparison with a standard volume of hydrogen by means of a differential manometer. In the third series the gas was kept at the temperature of melting ice, and the mano-barometer alone was read. The results for the weight in grammes, at latitude 45°, of one litre of oxygen are as follows:

First Series.	Second Series.	Third Series.
1.42864	1.42952	1.42920
1.42849	1.42900	1.42860
1.42838	1.42863	1.42906
1.42900	1.42853	1.42957
1.42907	1.42858	1.42910

[1] Compt. Rend., 113, 186. 1891.
[2] Ann. Chim. Phys. (7), 15, 29. 1898. In C. R., 148, 42, Leduc claims that the probable error of his H is only $\pm$ .00001.
[3] Paper already cited, in the gravimetric portion of this chapter.

1.42887	1.42873	1.42930
1.42871	1.42913	1.42945
1.42872	1.42905	1.42932
1.42883	1.42896	1.42908
———	1.42880	1.42910
Mean, 1.42875, ± .000051	1.42874	1.42951
Corrected,[1] 1.42879, ± .000051	1.42878	1.42933
	1.42872	1.42905
	1.42859	1.42914
	1.42851	1.42849
	———	1.42894
	Mean, 1.42882, ± .000048	1.42886
	Corrected, 1.42887, ± .000048	———

Mean, 1.42912, ± .000048

Corrected, 1.42917, ± .000048

General mean of all three series, 1.42896, ±.000028.

Morley himself, for experimental reasons, prefers the last series, and gives it double weight, getting a mean density of 1.42900. The difference between this mean and that given above is insignificant with reference to the atomic weight problem.

In the case of hydrogen, Morley's determinations fall into two groups, but in both the gas was prepared by the electrolysis of pure dilute sulphuric acid, and was most elaborately purified. In the first group there are two series of measurements. Of these, the first involved the reading of temperature and pressure by means of a mercurial thermometer and mano-barometer. In the second series, the gas was delivered into the weighing globes after occlusion in palladium; it was then kept at the temperature of melting ice, and only the syphon barometer was read. In this group the hydrogen was possibly contaminated with mercurial vapor, and the results are discarded by Morley in his final summing up. For present purposes, however, it is unnecessary to reject them, for they have confirmatory value, and do not appreciably affect the final mean. The weight of one litre of hydrogen at 45° latitude, as found in these two sets of determinations, is as follows:

First Series.	Second Series.
.089904	.089977
.089936	.089894
.089945	.089987
.089993	.089948
.089974	.089951
.089941	.089960
.089979	.090018

[1] Correction applied by Morley to all his series, for a slight error, $\frac{1}{30000}$, in the length of his standard metre bar.

.089936	.089909
.089904	.089953
.089863	.089974
.089878	.089922
.089920	.090093
.089990	.090007
.089926	.089899
.089928	.089974
	.089900
Mean, .089934, ± .000007	.089869
Corrected, .089938, ± .000007	.090144
	.089984

Mean, .089967, ± .000011
Corrected, .089970, ± .000011

In the second group of experiments, the hydrogen was weighed in palladium before transfer to the calibrated globe; and in weighing, the palladium tube was tared by a similar apparatus of nearly equal volume and weight. After transfer, which was affected without the intervention of stopcocks, the volume and pressure of the gas were taken at the temperature of melting ice. A preliminary set of measurements was made, followed by three regular series; of these, the first and second were with the same apparatus, and are different only in point of time, a vacation falling between them. The last series was with a different apparatus. The data are as follows, with the means as usual:

Preliminary.	*Third Series.*	*Fourth Series.*	*Fifth Series.*
.089946	.089874	.089972	.089861
.089915	.089891	.089877	.089877
.089881	.089886	.089867	.089870
.089901	.089866	.089916	.089867
.089945	.089911	.089770	.089839
	.089856	.089846	.089874
Mean, .089918,	.089912		.089864
± .0000271	.089872	Mean, .089875,	.089883
Corrected, .089921		± .0000187	.089830
	Mean, .089883,	Corrected, .089880	.089877
	± .0000049		.089851
	Corrected, .089886		
			Mean, .089863,
			± .0000034
			Corrected, .089866

Now, rejecting nothing, we may combine all the series into a general mean, giving the weight of one litre of hydrogen as follows:

First series .... .089938, ± .000007
Second series .... .089970, ± .000011
Preliminary series, second method.... .089921, ± .0000271
Third series .... .089886, ± .0000049
Fourth series .... .089880, ± .0000187
Fifth series .... .089866, ± .0000034

General mean .... .089897, ± .0000025
Rejecting the first three.............. .089872, ± .0000028

This last mean value for hydrogen will be used in succeeding chapters of this work for reducing volumes of the gas to weights. Combining the general mean of all with the value found for the weight of a litre of oxygen, 1.42896, ±.000028, we get for the ratio H : O,

$$O = 15.8955, \pm .0005$$

If we take only the second mean for H, excluding the first three series, we have—

$$O = 15.9001, \pm .0005$$

This value is undoubtedly nearest the truth, and is preferable to all other determinations of the density ratio. Its probable error, however, is given too low; for some of the oxygen weighings involved reductions for temperature and pressure. These reductions involve, again, the co-efficient of expansion of the gas, and its probable error should be included. Since, however, that factor has been disregarded elsewhere, it would be an over-refinement of calculation to include it here. Other corrections, of a mathematical character, have been recently applied to Morley's data by Guye and Mallet.[1] They find, for the normal weight of one litre of each gas, $O = 1.42886$, and $H = 0.089875$. The difference between these figures and those given by Morley is so small as to be negligible.

Still more recently, by a novel method, J. Thomsen has measured the two densities in question.[2] In his gravimetric research, already cited, he ascertained the weights of hydrogen and of oxygen equivalent to a unit weight of aluminum. In his later paper he describes a method of measuring the corresponding volumes of both gases during the same reactions. Then, having already the weights of the gases, the volume-weight ratio, or density, is in each case easily computable. From 1.0171 to 2.3932 grammes of aluminum were used in each experiment. Omitting details, the volume of hydrogen in litres, equivalent to one gramme of the metal, is as follows:

---

[1] Compt. Rend., 138, 1034. 1904.
[2] Zeitsch. anorg. Chem., 12, 4. 1896.

1.24297
1.24303
1.24286
1.24271
1.24283
1.24260
1.24314
1.24294

Mean, 1.24289, $\pm$ .00004

The weight of hydrogen evolved from one gramme of aluminum was found in Thomsen's gravimetric research to be 0.11190, $\pm$.000015. Hence the weight of one litre at 0°, 760 mm., and 10.6 meters above sea level at Copenhagen is:

.090032, $\pm$ .000012

or at sea level in latitude 45°,

.089947, $\pm$ .000012 gramme

The data for oxygen are given in somewhat different form, namely, for the volume of one gramme of the gas at 0°, 760, and at Copenhagen. The values are, in litres:

.69902
.69923
.69912
.69917
.69903
.69900
.69901
.69921
.69901
.69922

Mean, .69910, $\pm$ .00002
At sea level in latitude 45°, .69976, $\pm$ .00002

Hence one litre weighs 1.42906, $\pm$.00004 grammes.

Dividing this by the weight found for hydrogen, 0.089947, $\pm$.000012 we have for the ratio H : O,

15.8878, $\pm$ .0022

The determinations, by Jaquerod and Pintza,[1] of the weight of a litre of oxygen, can hardly be utilized here. They give, as the mean of five observations, the value 1.4292 grammes, but without the individual figures, and with no corresponding data for hydrogen. The ratio now under consideration, therefore, is not directly given by their work.

---

[1] Compt. Rend., 139, 129. 1904. Compare also Jaquerod and Scheuer, *ibid.*, 140, 1384. 1905.

The density ratios, $H:O$, now combine as follows:

Dumas and Boussingault, corrected....	15.9015, ± .031
Regnault, corrected	15.9105, ± .0044
Rayleigh, 1888	15.884, ± .0048
Rayleigh, 1892	15.882, ± .0023
Cooke	15.890, ± .0067
Leduc	15.906, ± .0154
Morley, including all the data........	15.8955, ± .0005
Thomsen	15.8878, ± .0022
General mean	15.8948, ± .00048

If we reject all of Morley's data for the density of hydrogen except his third, fourth and fifth series, the mean becomes

$$15.8991, \pm .00048$$

In either case Morley's data vastly outweigh all others.

If oxygen and hydrogen were perfect gases, uniting by volume exactly in the ratio of one to two, then their relative densities would also indicate their relative molecular weights. But, in fact, the two gases vary from Boyle's law in opposite directions, and the true composition of water by volume diverges from the theoretical ratio to a measurable extent. Hence, in order to deduce the atomic weight of hydrogen from its density, or that of oxygen, if the hydrogen scale is preferred, a small correction must be applied which depends upon the amount of the divergence. Until modern times our knowledge of the volumetric composition of water rested entirely upon the determinations made by Humboldt and Gay Lussac [1] early in the last century, which gave a ratio between H and O of a little less than $2:1$, but their data need no farther consideration here.

In 1887 Scott [2] published his first series of experiments, 21 in number, finding as the most probable result a value for the ratio of $1.994:1$. In March, 1888,[3] he gave four more determinations, ranging from 1.9962 to $1.998:1$; and later in the same year [4] another four, with values from 1.995 to 2.001. In 1893,[5] however, by the use of improved apparatus, he was able to show that his previous work was vitiated by errors, and to give a series of measurements of far greater value. Of these, twelve were especially good, being made with hydrogen from palladium hydride, and with oxygen from silver oxide. In mean the value found is 2.00245, ±.00007, with a range from 2.0017 to 2.0030.

[1] Journ. de Phys., 60, 129.
[2] Proc. Roy. Soc., 42, 396.
[3] Nature, 37, 439.
[4] British Assoc. Report, 1888, 631.
[5] Proc. Roy. Soc., 53, 130. In full in Philosophical Transactions, 184, 543. 1893.

In 1891 an elaborate paper by Morley[1] appeared, in which twenty concordant determinations of the volumetric ratio gave a mean value of 2.00023, ±.000015. These measurements were made in eudiometer tubes, and were afterwards practically discarded by the author. In his later and larger paper,[2] however, he redetermined the ratio from the density of the mixed electrolytic gases, and found it to be, after applying all corrections, 2.00274. The probable error, roughly estimated, is .00005. Morley also reduces Scott's determinations, which were made at the temperature of the laboratory, to 0°, when the value becomes 2.00285. The mean value of both series may therefore be put at 2.0028, ±.00004, with sufficient accuracy for present purposes. Leduc's[3] single determination, based upon the density of the mixed gases obtained by the electrolysis of water, gave 2.0037; but Morley shows that some corrections were neglected. This determination, therefore, may be left out of account.

There is also a corroborative measurement by Rayleigh,[4] who assigns to the ratio the value 2.0026. This agrees well with the figures given by Scott and Morley. Rayleigh also gives measurements of gaseous densities at very low pressures, and obtains molecular ratios differing considerably from those ordinarily found. At atmospheric pressure, for example, $H = 1.0075$; and at very low pressures its atomic weight becomes 1.0088.

Now, including all available data, we have as a mean value for the density ratio:

(A.) $\qquad$ H:O::1:15.8948, ± .00048

or, omittting Morley's rejected series,

(B.) $\qquad$ H:O::1:15.8991, ± .00048

Correcting these by the volume ratio, 2.0028, ±.00004, the final result for the atomic weight of oxygen, in terms of the hydrogen unit, and as computed from the gaseous densities becomes—

$$\text{From A} \ldots\ldots\ldots\ldots O = 15.8726, \pm .00058$$
$$\text{From B} \ldots\ldots\ldots\ldots O = 15.8769, \pm .00058$$

Combining these figures with the values deduced from the syntheses of water, rejecting nothing, we have—

$$\text{By syntheses of water} \ldots\ldots\ldots O = 15.8779, \pm .00016$$
$$\text{By gaseous densities} \ldots\ldots\ldots\ldots O = 15.8726, \pm .00058$$

$$\text{General mean} \ldots\ldots\ldots\ldots\ldots O = 15.8775, \pm .00015$$

[1] Amer. Journ. Sci. (3), 46, 220 and 276.

[2] Already cited with reference to syntheses of water.

[3] Compt. Rend., 175, 311. 1892. In a later, more complete memoir, Ann. Chim. Phys. (7), 15, 49, Leduc gives the figure 2.0034. He also criticizes Morley's deductions.

[4] Proc. Roy. Soc., 73, 153. 1904.

Hence, on the oxygen scale, $H = 1.00772 \pm .00001$.

If we reject the seven highest values under the first heading, and omit Morley's defective hydrogen series under the second, we get—

By syntheses of water........ $O = 15.8760, \pm .00017$, or $H = 1.00781, \pm .00001$
By gaseous densities.......... $O = 15.8769, \pm .00058$, or $H = 1.00775, \pm .000035$

General mean .... $O = 15.8762, \pm .00016$, or $H = 1.00779, \pm .00001$

The two component values of the last mean are remarkably concordant, differing by only one part in 17640. For practical purposes the last decimal of the hydrogen value may be rounded off, giving

$$H = 1.0078, \pm .00001$$

as the atomic weight under consideration. The actual uncertainty of this value, however, is greater than the so-called " probable error." The latter, it must be borne in mind, is a mathematical expression which should not be used in a colloquial sense. For computations of this kind the probable error is essentially a *coefficient of concordance*, which merely indicates the relative value or weight assignable to a given series of observations in comparison or combination with others.

THE NITROGEN-OXYGEN RATIO.

The direct ratio between nitrogen and oxygen has been determined by analyses of nitrous and nitric oxides, and by measurements of gaseous densities. The different methods may be considered in regular order.

The exact analysis of nitrous oxide, with reference to the atomic weight of nitrogen, was effected by Guye and Bogdan.[1] The gas itself was condensed in carefully purified charcoal, and so weighed; it was then passed slowly through a tube containing a spiral of iron wire, which was heated to redness by an electric current. The iron was oxidized, and its gain in weight gave the amount of oxygen in the N_2O. The results obtained were as follows:

Weight N_2O	Weight O.	At. Wt. O.
1.1670	.4242	14.0085
.9498	.3453	14.0052
.8652	.3145	14.0083
1.2247	.4455	13.9924
1.4202	.5159	14.0229

Mean, $14.0075, \pm .0033$

For the complete gravimetric analysis of nitric oxide we have the elaborate data furnished by R. W. Gray.[2] The gas was weighed, and

---

[1] Compt. Rend., 138, 1494. 1904. Journ. Chim. Phys., 3, 537. 1905.
[2] Journ. Chem. Soc., 87, 1601. 1905.

then reduced by electric heating over finely divided metallic nickel. The gain in weight of the nickel represented the amount of oxygen absorbed. In some of the experiments the liberated nitrogen was condensed, at the temperature of liquid air, in cocoa-nut charcoal, and its weight also was determined. Two series of determinations were made, on nickel from different sources, but for present purposes these may be treated as one. For three of the measurements corrections are given for the nitrogen occluded by the mixed nickel and nickel oxide, which corrections I have applied in the following table of Gray's results:

Weight NO.	Weight O.	Weight N.
.31384	.16729	. . . . .
.64304	.34300	.30010
.50672	.27025	. . . . .
.54829	.29221	. . . . .
.61862	.32981	.28885
.62622	.33401	.29234
.62128	.33111	. . . . .
.54469	.29029	.25432
.52001	.27715	.24270
.62103	.33103	.28998

From these weights the subjoined values for N are derived.

$NO:O_2.$	$N_2:O_2.$	$NO:N_2.$
14.0164	. . . . . .	. . . . . .
13.9960	13.9988	13.9996
14.0001	. . . . . .	. . . . . .
14.0217	. . . . . .	. . . . . .
14.0110	14.0129	14.0146
13.9997	14.0039	14.0094
14.0217	. . . . . .	. . . . . .
14.0218	14.0174	14.0136
14.0204	14.0112	14.0031
14.0169	14.0159	14.0151
Mean, 14.0126, $\pm$ .0022	14.0100, $\pm$ .0020	14.0092, $\pm$ .0018

The general mean of the three series is

$$N = 14.0104, \pm .0011$$

The accurate calculation of molecular and atomic weights from gaseous densities is really an affair of very recent times. The gases, as measured, show divergencies from Avogadro's law, and the crude density ratios therefore require correction, as we have already seen in reference to the atomic weight of hydrogen. It seems best, however, to assemble the actual measurements first, and to apply the corrections to the entire mass of data afterwards.

For nitrogen there are abundant measurements made upon the element itself, and also good data for nitrous oxide, nitric oxide and ammonia.

The earlier determinations of the density of nitrogen were all made upon nitrogen derived from the atmosphere. But the supposed nitrogen contained, as we now know, the heavier argon, and the value obtained was therefore incorrect. It is, however, worth while to examine the data, and to see whether a correction for argon may not be advantageously made. The very early work of Biot and Arago, Thomson, Dulong and Berzelius, Lavoisier and others can be neglected, and, as in the case of oxygen, we need consider only the results obtained by Dumas and Boussingault, Regnault, and several more recent investigators.

Taking air as unity, Dumas and Boussingault[1] found the density of atmospheric nitrogen to be—

.970
.972
.974

Mean, .972, ± .00078

For oxygen, as was seen in our discussion of the O : H ratio, the same investigators found a mean of $1.10567, \pm.00006$. The ratio between this and the nitrogen figure is $16 : 14.0657, \pm.0113$.

By Regnault[2] much closer work was done. He found the density of atmospheric nitrogen to be as follows:

.97148
.97148
.97154
.97155
.97108
.97108

Mean, .97137, ± .000062

For oxygen, Regnault's mean value is $1.105633, \pm.000008$. Hence, combining as before, $N = 14.057, \pm.0009$.

Both of the preceding values are affected by a correction for the difference in volume between the weighing globes when full and when empty. This correction, in the case of Regnault's data, was measured by Crafts,[3] who gives 1.10562 for the density of oxygen, and 0.97138 for that of nitrogen. The changes are so small that the ratio remains practically unaltered. The correction in this particular instance, is negligible.

Von Jolly,[4] working with electrolytic oxygen and with nitrogen pre-

[1] Compt. Rend., 12, 1005. 1841.
[2] Compt. Rend., 20, 975. 1845.
[3] Compt. Rend., 106, 1664.
[4] Annalen der Physik. (2), 6, 529. 1879.

pared by passing air over hot copper, compared the weights of equal volumes of the two gases, with results as follows:

Oxygen.	Nitrogen.
1.442470	1.269609
1.442579	1.269389
1.442489	1.269307
1.442570	1.269449
1.442571	1.269515
1.442562	1.269443
1.442478	1.269478
Mean, 1.442545, ± .000013	Mean, 1.269455, ± .000024

The ratio, when O=16, is N=14.0802,±.0003. Corrected by Rayleigh, the ratio between the weights becomes 14.0805.

The next determination in order of time is Leduc's.[1] He made nine measurements of the density of atmospheric nitrogen, giving a mean of .97203, with extremes of .9719 and .9721; but he neglected to cite the intermediate values. Taking the three figures given as representative, and assuming a fair distribution of the other values between the indicated limits, the probable error of the mean is not far from 0.00002. For oxygen he found 1.10514,±.000032. The ratio between the two densities is 16:14.0729,±.0005.

Lord Rayleigh,[2] who prepared nitrogen from the atmosphere by several methods, and weighed it in a standard globe in direct comparison with oxygen, obtained the following weights:

Oxygen.	Nitrogen.
2.6272	2.31035
2.6271	2.31026
2.6269	2.31024
2.6269	2.31012
2.6271	2.31027
Mean, 2.62704, ± .00004	2.31025, ± .000025

In a later paper[3] Rayleigh gives the following additional weights for atmospheric nitrogen, which are directly comparable with the foregoing series.

2.31017
2.30986
2.31010
2.31001
2.31024
2.31010
2.31028
2.31163
2.30956

[1] Compt. Rend., 113, 186. 1891.
[2] Proc. Roy. Soc., 53, 134. 1893.
[3] Proc. Roy. Soc., 55, 340. 1894.

Including these figures with those of the first series, the mean of all becomes 2.31023, ±.00008. Correcting these data for the compression of the empty globes, the mean weights become, for oxygen, 2.6276, ±.00004, and for nitrogen, 2.31079, ±.00008. The ratio between them is 16 : 14.0704, ±.0005.

The combination of these determinations is as follows:

Dumas and Boussingault............	14.0657, ± .0113
Regnault	14.0570, ± .0009
Von Jolly	14.0805, ± .0003
Leduc	14.0729, ± .0005
Rayleigh	14.0704, ± .0005
General mean	14.0758, ± .00022

Now, to correct this mean for the argon contained in the nitrogen. Good measurements have shown that normal air contains, by volume, 0.937 per cent of argon, and 78.122 of nitrogen. The density of argon, referred to the oxygen standard, is 19.940. Applying these values, the final figure for nitrogen, derived from air, becomes 14.0052, ±.00022, a result which is in harmony with others to be considered presently.

In Rayleigh's investigation of the density of nitrogen it was found that nitrogen from chemical sources was lighter than that extracted from the atmosphere. This led to the discovery of argon, to which reference has already been made. In two of his memoirs[1] Rayleigh has given determinations of the density of "chemical nitrogen" obtained from nitrous oxide, nitric oxide, ammonium nitrite, urea and magnesium nitride, and the gas from all these sources is precisely the same. His weights, given now as one series, and representing the same volume as those previously cited, are as follows:

2.30143	From nitric oxide
2.29890	" " "
2.29816	" " "
2.30182	" " "
2.29869	From nitrous oxide
2.29940	" " "
2.30074	" " "
2.30054	" " "
2.29849	From ammonium nitrite
2.29889	" " "
2.29870	" " "
2.29850	From urea
2.29918	From magnesium nitride

Mean, 2.29949, ± .00024

[1] Proc. Roy. Soc., 55, 340, 1894, and 57, 266, 1895.

Corrected for the compression of the empty globe, this mean becomes 2.30005. The weight of an equal volume of oxygen was found to be 2.62760,±.00004. Hence the ratio is 16 : 14.0055,±.0015.

Two determinations of density for "chemical nitrogen" are given by Leduc.[1] In mean, the value found, referred to air as unity, is 0.96717, ±.00008. This, combined with the figure already cited for oxygen gives, as the value for the ratio under discussion, 16 : 14.0025,±.0012. There are also two determinations by Gray,[2] whose comparative weights at 0° and 760 mm., are as follows :

Nitrogen.	Oxygen.
.32286	.36889
.32275	.36879
Mean, .322805, ± .00004	Mean, .36884, ± .00003

Hence the ratio 16 : 14.0030,±.0021.

It is evident here that the data given by Leduc and Gray are overvalued in comparison with Rayleigh's much larger series of determinations. The general mean, however, as shown in the following combination, cannot be far from the truth :

Rayleigh	14.0055, ± .0015
Leduc	14.0025, ± .0012
Gray	14.0030, ± .0021
General mean	14.0036, ± .00085

Hence the normal litre of nitrogen weighs 1.25066 grammes.

For the density of nitrous oxide there are several series of measurements. Leduc[3] gives three figures, as follows, referred to air as unity :

$$1.5304$$
$$1.5298$$
$$1.5301$$

Mean, 1.5301, ± .00012

Combined with Leduc's value for oxygen, this gives the density ratio $O_2 : N_2O :: 32 : 44.3050,±.0037$.

By Rayleigh there are two series of determinations,[4] made at different times. In the earlier series the gas was possibly contaminated by traces of nitrogen, in the second series the nitrous oxide was purified by condensation at the temperature of liquid air. The weights of nitrous oxide filling his standard globe are subjoined.

[1] Ann. Chim. Phys. (7), 15, 33. 1898.
[2] Journ. Chem. Soc., 87, 1601. 1905.
[3] Ann. Chim. Phys. (7), 15, 35. 1898.
[4] Proc. Roy. Soc., 62, 204, 1897, and 74, 181, 1904.

1897 series.	1904 series.
3.6359	3.6368
3.6354	3.6360
3.6364	3.6362
3.6358	3.6363
3.6360	3.6367
——	3.6366
Mean, 3.6359	3.6354
	——
	Mean, 3.6363

These are so nearly together that I venture to treat them as one series, in mean 3.6361,±.000093. The weight of the same volume of oxygen was 2.6276,±.00004. The value of the ratio, therefore, is 32: 44.2819,±.0037.

The measurements by Guye and Pintza [1] are stated so as to show the weight of a normal litre of nitrous oxide. The figures are, in grammes—

$$1.97762$$
$$1.97707$$
$$1.97760$$

Mean, $1.97743, \pm .00015$

The weight of a litre of oxygen, according to Morley, is 1.42896,± .000028. Combining this with Guye and Pintza's figure the ratio becomes 32:44.2824,±.0035.

The three independent values for the density ratio $O_2 : N_2O$, combine as follows:

Leduc .... 44.3050, ± .0037
Rayleigh .... 44.2819, ± .0037
Guye and Pintza............. 44.2824, ± .0035

General mean .... 44.2895, ± .0021

This mean corresponds to a normal litre-weight for nitrous oxide of 1.97775 grammes.

It is convenient at this point to consider the volumetric analysis of nitrous oxide made by Jaquerod and Bogdan. [2] A measured volume of the gas was decomposed by an electrically heated spiral of iron wire, and the volume of the residual nitrogen was measured afterwards. Then, with the known densities of the two gases, the ratio between them was easily calculable. Reduced to uniform conditions, one litre of nitrous oxide gave the following volumes of nitrogen:

---

[1] Compt. Rend., 139, 677. 1904. Corrected in C. R., 141, 51. 1905. The corrected figures are used here.

[2] Journ. Chim. Phys., 3, 562. 1905.

1.00737
1.00698
1.00714
1.00718

Mean, 1.00717, $\pm$ .000054

To this value, however, a correction is yet to be applied; namely, for the increase in volume of the iron wire consequent upon oxidation. This demands a deduction of 0.00030, which reduces the mean to 1.00687. That is, one litre of nitrous oxide, decomposed, yields 1.00687 litres of nitrogen. Hence the following calculation:

1 litre N_2O weighs........................ 1.97775 gramme.[1]
1.00687 N_2 weighs........1.25066 $\times$ 1.00687 $=$ 1.25925   "

Oxygen in N_2O, 0.71850   "

From these data, $O : N_2 :: 0.7185 : 1.25925, = 28.0417$, and $N = 14.0208$, $\pm$.0030. The probable error is computed from the figures already given relative to the densities of the gases.

For the density of nitric oxide there are two modern investigations. First, by Gray;[2] second, by Guye and Davila.[3] Gray gives two series of weights, in which nitric oxide is directly compared with an equal volume of oxygen. Two supplementary determinations are cited as additions to series 2.

Oxygen.	NO, I.	NO, II.
.38230	.35845	.35851
.38229	.35852	.35848
.38227	.35851	· .35852
.38225	.35849	.35850
.38226	.35859	.35848
.38230	.35856	.35855

Mean, .38228, $\pm$ .0000058   Mean of all, .35851, $\pm$ .0000076

From these weights the crude density ratio is

$$O_2 : NO :: 32 : 30.0102, \pm .0007$$

Guye and Davila prepared their nitric oxide by three distinct methods, and obtained the following figures for the normal litre-weight.

---

[1] Jaquerod and Bogdan assume, for the litre-weights of N_2 and N_2O, 1.25045 and 1.97772, respectively. I here use the weights previously computed in this chapter. Jaquerod and Bogdan find $N = 14.015$.

[2] Journ. Chem. Soc., 87, 1601. 1905.

[3] Compt. Rend., 141, 826. 1905.

I.	II.	III.
1.3406	1.3403	1.3399
1.3402	1.3398	1.3403
1.3401	1.3400	
1.3407	1.3408	
1.3398	1.3402	
1.3402	1.3402	

The mean of the 14 determinations, taken as one series, is $1.3402, \pm$ .000056. With Morley's value for oxygen, $1.42896, \pm .000028$, the density ratio becomes—

$$32:30.0124, \pm .00168$$

Combined with Gray's determination, the weighted mean is

$$32:30.0106, \pm .00065$$

The density of gaseous ammonia, according to Leduc,[1] is 0.5971, referred to air as unity. But this figure represents only a single determination, with material of doubtful purity, and need not be considered further. Guye and Pintza,[2] with carefully purified ammonia, made five determinations of density, which gave the subjoined results for the weight of the normal litre:

.77080
.77069
.77073
.77099
.77076
_____
Mean, .77079, $\pm$ .000035

Perman and Davies[3] made three series of determinations, by two methods; but the first series, with commercial ammonia, is to be rejected. The other series gave the following figures for the weight of one litre of the gas:

I.	II.
.7709	.77094
.7711	.77094
.7712	.77090
.7713	.77088
.7711	.77091
.7713	_____
_____	Mean, .77094
Mean, .77115	

---

[1] Ann. Chim. Phys. (7), 15, 39. 1898.
[2] Compt. Rend., 141, 51. 1905.
[3] Proc. Roy. Soc., 78A, 28. 1906. Perman and Davies give still other density determinations for different temperatures and pressures.

Corrected, by reduction to latitude 45°, etc., these two series become nearly identical with each other, and with Guye and Pintza's average; namely, 0.77085 and 0.77086; in mean, as one series, 0.770855, ±.000034. With Guye and Pintza's figure, the general mean becomes 0.77083, ± .000024. Hence, with Morley's weight for a litre of oxygen, the crude density ratio is

$$O_2 : NH_3 :: 32 : 17.2619, \pm .00063$$

The law of Avogadro, that equal volumes of gases contain equal numbers of molecules, is rigorously true only for ideally perfect gases. For gases as they actually occur it is approximately true, but with varying degrees of divergence. The approximation is close for the so-called permanent gases, while those which are easily liquefiable conform less nearly to the law. In order, therefore, to compute molecular weights from observed gaseous densities, it is necessary to apply corrections to the experimental data, or else to employ methods of determination of great manipulative difficulty. By measuring densities at very low pressures, quite close approximations to the truth may be obtained, and observations at high temperatures are also nearly valid. For example, Rayleigh[1] from gaseous densities at very small pressures, obtained the following value for nitrogen, as compared with the standard, oxygen:

$$N_2 = 28.018. \text{ and } N = 14.009$$

On the other hand, by measuring the density of nitrogen at 1067.4°, Jaquerod and Perrot[2] found

$$N_2 = 28.0155, \text{ and } N = 14.0077$$

These values are probably not far from the truth, and are obviously well in accord. At low pressures and at high temperatures gases are more nearly in agreement with Avogadro's law than they are under ordinary conditions.

In the case of the oxygen-hydrogen ratio, the density corrections were determined by actual measurement of the volumes in which the two gases combined, a method which is not always applicable, or at least not conveniently so. It is easier to compute the corrections from physical data, and for this purpose various methods have been proposed.[3]

The following formulæ, based upon the celebrated gas equation of Van der Waals, are, according to Guye,[4] available for the reduction of gaseous densities to true molecular weights:

[1] Proc. Roy. Soc., 73, 153. 1904.
[2] Compt. Rend., 140, 1542. 1905.
[3] See D. Berthelot, Journ. Physique (3), 8, 263. 1899. Leduc, Ann. Chim. Phys. (7), 15, 1. 1898. Guye and Friderich, Arch. Sci. Phys. Nat. (4), 9, 505, and 13, 559. Guye, Journ. Chim. Phys., 3, 321, and 5, 203, also Compt. Rend., 138, 1213, and 140, 241. There is a copious literature upon this subject.
[4] Journ. Chim. Phys., 3, 321. 1905.

$$\text{I} \qquad\qquad\qquad \text{II}$$

$$M = \frac{(R \times mT)L}{(1+a)(1-b)} \qquad\qquad M = \frac{RL}{(1+a_0)(1-b_0)}$$

Equation I applies to the permanent gases, that is, to those which are liquefiable only below 0°. Equation II applies to the easily liquefiable gases. R is the gas constant, and according to Berthelot[1] its value is 22.412. The constant m, of equation I, is given by Guye the value 0.0000623. T represents the critical temperature, on the absolute scale; L is the weight of one litre of gas at 0°, 760 mm., sea level, and latitude 45°; and M is the molecular weight. The symbols a and b are the constants of the Van der Waals equation, which vary for different gases, and in II are brought to the standard temperature and pressure.

In any given case the use of these formulæ requires a knowledge of the constants a and b. These can be deduced from the compressibilities and coefficients of expansion of a gas, or from the critical constants. The latter method is the one adopted by Guye, and with one exception it will be followed here. Guye gives the required data in form ready for use,[2] and they yield results which appear to be trustworthy. Applied to the densities given in the preceding pages they give the following reductions:

Nitrogen, Chemical. L=1.25066. T=127.5°. $(1+a)(1-b)$ = 1.00100. Hence N=14.0058,±.00085. From the figures given for atmospheric nitrogen, N=14.0074,±.00022. The weighted mean is N= 14.0073,±.0002.

Nitrous Oxide. L=1.97775. $(1+a_0)(1-b_0)$ =1.00733. Hence N_2O=44.0028,±.0021. The crude density ratio gives 44.2895,±.0021, showing that the correction is large. This reduced value combines with other values for N_2O as follows:

From density of gas............N_2O = 44.0028, ± .0021
From gravimetric analysis..... " = 44.0150, ± .0066
From volumetric analysis ..... " = 44.0417, ± .0060

General mean ....N_2O = 44.0074, ± .0019

Nitric Oxide. L=1.34012. T=179.5°. a=0.00257. b=0.00115. Hence NO=30.0073,±.00065. Gray's analyses of the gas gave NO= 30.0104,±.0011. The general mean is 30.0083,±.00055.

Ammonia. The crude density ratio gave NH_3=17.2619,±.00065. This has been reduced by means of compressibility data. Perman and Davies, who measured the compressibility, give the multiplying factor

---

[1] Zeitsch. Elektrochem., 1904, 621. In Journ. Physique (3), 8, 527, Berthelot gives values of a and b for several gases.

[2] When Guye gives two or more figures for $(1 + a)(1 - b)$ I take the average.

0.9867, whence $NH_3 = 17.0323$. Jaquerod and Scheuer,[1] by a different formula, and using only the density determinations of Guye and Davila, find $NH_3 = 17.0148$. If $H = 1.0078$, $N = 14.0089$, Perman and Davies' method, or 13.9914 by Jaquerod and Scheuer. The first value is apparently the best and will be adopted here.

There are now four independent values for N, as follows:

From N_2	$N = 14.0073, \pm .00020$
From N_2O	" $= 14.0037, \pm .00095$
From NO	" $= 14.0083, \pm .00055$
From NH_3	" $= 14.0089, \pm .00065$
General mean	$N = 14.0074, \pm .00018$

From compressibility data Rayleigh[2] found from N_2, $N = 14.008$, and from N_2O, $N = 13.998$. His low pressure value, as previously cited, was $N = 14.009$, and Jaquerod and Perrot, at high temperatures, found $N = 14.0077$. To include these values in the general mean would change the final result inappreciably, if at all, and they may therefore be disregarded. They have, however, confirmatory significance.

Some of the determinations utilized in the foregoing combination are evidently overvalued, especially the figure derived from atmospheric nitrogen. The "probable errors," scrutinized in detail, merely show that the density measurements are much more concordant than the gravimetric analyses. Moreover, the errors of the critical constants have not been taken into account, for they can hardly be estimated correctly. Allowances for these uncertainties might be made, but their effect upon the final combination would be trifling. The "probable error" here assigned to N, simply indicates the weight which it should receive in calculating other atomic ratios.[3]

As a check upon the other determinations of the atomic weight of nitrogen, Guye and Pintza[4] have determined the composition of ammonia by volume. The gas was decomposed by a spiral of platinum wire heated to redness, and from the density of the mixed gases, $N_2 + 3H_2$, compared with the known densities of nitrogen and hydrogen, the required datum was calculated. For the weight, in grammes, of a normal litre of the gaseous mixture, the following figures were obtained:

---

[1] Compt. Rend., 140, 1384. 1905. From NO Jaquerod and Scheuer found $N = 14.005$.

[2] Proc. Roy. Soc., 74, 446. 1904.

[3] For a general discussion of the atomic weight of N, see Guye's lecture delivered before the Chemical Society of Paris, June 10, 1905. Also Compt. Rend., 140, 1386, and 144, 1360; and Ber., 39, 1470. Two papers by Berthelot, of a controversial nature, are in Compt. Rend., 144, 76 and 269, and one by Leduc in Compt. Rend., 146, 399.

[4] Compt. Rend., 147, 925. 1908.

$$0.38044$$
$$0.38055$$
$$0.38046$$

Mean, 0.38048, $\pm$ .000024

Corrected for traces of SO_2 and SO_3, this becomes 0.37989. If the weights of the normal litres of N_2 and H_2 are 1.2507 and 0.08987, respectively, the two gases in ammonia are combined in the ratio 1 : 3.00172. Applying this datum to the densities of nitrogen and hydrogen, and assuming $H = 1.0078$, $N = 14.017$, with a probable error, not exactly calculable, greater than $\pm$.0017. To combine this figure with the value already found would change the latter inappreciably. Indeed, Guye and Pintza regard their determinations as inferior to those made by other methods, and publish their results only as a confirmation of the low value for N, as compared with the value 14.04 which had been in general acceptance for many years.

THE CARBON-OXYGEN RATIO.

The ratio between carbon and oxygen, or in other words, the atomic weight of carbon, has been directly determined by several methods. It has also been indirectly computed from analyses of silver salts, such as the acetate; but that group of ratios will be considered under another heading. The early attempts to estimate it from analyses of hydrocarbons, have now only historic value, and can be omitted from the present discussion. The direct measurements of the ratio represent three distinct processes:

First, by the combustion of carbon itself.

Second, by the combustion of carbon monoxide.

Third, by determining the density of gaseous compounds of carbon.

The first of these methods was used by Dumas and Stas[1] in 1840, and a year later by Erdmann and Marchand.[2] 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 determined 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] Compt. Rend., 11, 991. Ann. Chim. Phys. (3), 1, 1.
[2] Journ. prakt. Chem., 23, 159.

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, ± .0005

With artificial graphite:

.992 grm. C gave 3.642 grm. CO_2.	2.6714
.998 " 3.662 "	2.6693
1.660 " 6.085 "	2.6657
1.465 " 5.365 "	2.6621

Mean, 2.6671, ± .0014

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 " 4.517 "	2.6664
1.375 " 5.041 "	2.6662

Mean, 2.6662, ± .0009

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, ±.0007.

With the 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, ± .0009

In more recent years the ratio under consideration has been carefully redetermined by Roscoe, by Friedel, and by Van der Plaats. Roscoe[1] made use of transparent Cape diamonds, and in a sixth experiment he

---

[1] Ann. Chim. Phys. (5), 26, 136. Zeit. anal. Chem., 22, 306. 1883. Compt. Rend., 94, 1180. 1882.

burned carbonado. The combustions were effected in a platinum boat, contained in a tube of glazed Berlin porcelain; and in each case the ash was weighed and its weight deducted from that of the diamond. The results were as follows, with the ratios stated as in the preceding series:

1.2820 grm. C	gave	4.7006	CO_2.	2.6666
1.1254	"	4.1245	"	2.6649
1.5287	"	5.6050	"	2.6665
.7112	"	2.6070	"	2.6656
1.3842	"	5.0765	"	2.6675
.4091	"	1.4978	"	2.6612

Mean, 2.6654, ± .0006

Friedel's work,[1] also upon Cape diamond, was in all essential particulars like Roscoe's. The data, after deduction of ash, were as follows:

.4698 grm. C	gave	1.7208	CO_2.	2.6628
.8616	"	3.1577	"	2.6649

Mean, 2.6638, ± .0004

By Van der Plaats[2] we have six experiments, numbers one to three on graphite, numbers four and five on sugar charcoal, and number six on charcoal made from purified filter paper. Each variety of carbon was submitted to elaborate processes of purification, and all weights were reduced to a vacuum standard. The data, with ash deducted, are subjoined:

1. 5.1217 grm. C	gave	18.7780	CO_2.	2.6664
2. 9.0532	"	33.1931	"	2.6664
3. 13.0285	"	47.7661	"	2.6663
4. 11.7352	"	43.0210	"	2.6660
5. 19.1335	"	70.1336	"	2.6655
6. 4.4017	"	16.1352	"	2.6657

Mean, 2.6660, ± .0001

This combines with the previous series thus:

	Ratio.	Atomic weight C.
Dumas and Stas, first set.........	2.6683, ± .0005	11.9926
Dumas and Stas, second set.......	2.6671, ± .0014	11.9981
Dumas and Stas, third set.........	2.6662, ± .0009	12.0031
Erdmann and Marchand, first set...	2.6636, ± .0007	12.0138
Erdmann and Marchand, second set.	2.6637, ± .0009	12.0134
Roscoe	2.6654, ± .0006	12.0057
Friedel	2.6638, ± .0007	12.0129
Van der Plaats...................	2.6660, ± .0001	12.0030
General mean	2.6660, ± .0001	12.0030, ± .0005

[1] Bull. Soc. Chim., 41, 100. 1884.
[2] Compt. Rend., 100, 52. 1885.

The effect of this combination is to give the work of Van der Plaats overwhelming weight, to which it is perhaps not entitled. The other determinations practically vanish.

According to Scott[1] all of the foregoing determinations are subject to an important correction, namely, a reduction to weight in vacuo. This correction was applied by Van der Plaats, at least partially; but Scott lays emphasis upon the change in volume of the potash solution in which the carbon dioxide was absorbed and weighed. The corrections, as applied by Scott, are given in the following table, in which the total reduced weights of carbon and dioxide are used instead of the individual weights of the separate experiments:

	Total C.	Total CO_2.	Ratio.	Atomic weight.
Dumas and Stas	16.1994	59.4201	2.66804	11.9938
Erdmann and Marchand	12.1636	44.58537	2.66547	12.0054
Roscoe	6.4428	23.6275	2.66727	11.9973
Friedel	1.33185	4.8818	2.66543	12.0056
Van der Plaats	62.5115	229.1836	2.66630	12.0017

If to these figures we assign the relative weights given in the previous combination, the final mean will be identical with that of Van der Plaats as before, and $C = 12.0017, \pm .0005$. Scott adopted the unweighted average of the five series given above, and made $C = 12.0008$.

The second method for determining the atomic weight of carbon was employed by Stas[2] in 1849. Carefully purified carbon monoxide was passed over a known weight 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

[1] Journ. Chem. Soc., 71, 550. 1897.
[2] Bull. Acad. Belg., 1849 (1), 31. Oeuvres Complètes, 1, 287.

Hence $CO = 28.0046$, and $C = 12.0046 ; \pm .0008$.

This work of Stas was also criticised by Scott,[1] in connection with the determinations by the first method. The process employed is subject to several possible errors, two of them being especially serious. First, the carbon monoxide may have contained hydrogen or hydrocarbons. Secondly, the copper oxide, which was prepared by calcining copper nitrate, almost certainly contained occluded nitrogen. The value found for C, however, is probably not very far from the truth, and it is not unlikely that errors in opposite directions tended to compensate one another.

For the density of carbon monoxide there are available determinations by Leduc[2] and Rayleigh.[3] Leduc used a globe which had a capacity of 2.9440 grammes of air. Filled with CO it held the following weights, giving the accompanying densities:

Weight CO.	Density.
2.8470	.96705
2.8468	.96698
2.8469	.96702
	.96702, $\pm$ .000015

This density, combined with Leduc's determination of the density of oxygen, $1.10514, \pm .000032$, gives the crude ratio—

$$O_2 : CO : : 32 : 28.0007, \pm .0010$$

Rayleigh's determinations may be stated in the following form: A globe which held $2.62760, \pm .00004$ grammes of oxygen, held of carbon monoxide—

2.29843
2.29852
2.29854

Mean, 2.29850, $\pm$ .000024

Corrected for the compression of the globe when empty this becomes $2.29906, \pm .000024$. From these data the crude value for CO is 27.9989, $\pm .0012$. Combining this with Leduc's determination, the general mean becomes—

$$CO = 28.0000, \pm .00077$$

Rayleigh, it must be observed, prepared his three samples of carbonic oxide by three distinct methods, and the concordance in their weights gives strong assurance of their purity.

[1] *Loc. cit.* See also Richards, Amer. Chem. Journ., 20, 701. 1898.
[2] Compt. Rend., 115, 1072. 1893.
[3] Proc. Roy. Soc., 62, 204. 1897.

For the calculation of the true molecular weight of carbon monoxide from this crude density ratio, the critical data cited by Guye[1] are available. The mean of two sets of critical constants gives $(1+a)$ $(1-b)=1.00109$, and $T=132.7°$. Applying these figures by the formula given under nitrogen, the molecular weight becomes

$$CO = 12.0031, \pm .00077.$$

The density of carbon dioxide has been determined by many investigators,[2] but the earliest measurements have now only historical interest. In 1845 Regnault[3] published five determinations of the density, referred to air as unity, and they were the first to be worth consideration now His figures are as follows:

$$1.52915$$
$$1.52900$$
$$1.52915$$
$$1.52906$$
$$1.52915$$

Mean, $1.52910, \pm .000032$

Corrected by Crafts,[4] for compression of the empty globe, this becomes $1.52897, \pm .000032$. For the density of oxygen, Regnault's corrected value is $1.10562, \pm .000008$.

Hence $O_2 : CO_2 :: 32 : 44.2530, \pm .00098.$

In three concordant measurements, which are not given separately, Leduc[5] found for CO_2 the density 1.52874. This figure, combined with his value for oxygen, already cited, gives for CO_2 the density ratio $32 : 44.2667$. Rayleigh[6] gives a single figure for the density of CO_2, namely, 1.52909. For oxygen he found 1.10535. Hence the ratio $32 : 44.2673$. The three determinations by Guye and Pintza[7] are stated in the form of normal litre-weights, as follows:

$$1.97684$$
$$1.97676$$
$$1.97681$$

Mean, $1.97680, \pm .0000176$

With Morley's figure for the weight of a litre of oxygen, $1.42896, \pm .000028$, the ratio becomes

$$O_2 : CO_2 :: 32 : 44.2683, \pm .00097.$$

[1] Journ. Chim. Phys., 3, 342. 1905.
[2] The early determinations are well summarized in Van Geun's monograph.
[3] Compt. Rend., 20, 993. 1845.
[4] Compt. Rend., 106, 1664.
[5] Ann. Chim. Phys. (7), 15, 34. 1898.
[6] Proc. Roy. Soc., 62, 204. 1897.
[7] Compt. Rend., 141, 51. 1905.

To the values deduced from Leduc's and Rayleigh's data we may arbitrarily assign equal weight with the mean of Regnault's series. The four determinations then combine thus:

Regnault .... 44.2530, $\pm$ .00098
Leduc .... 44.2667, $\pm$ .00098
Rayleigh .... 44.2673, $\pm$ .00098
Guye and Pintza................... 44.2683, $\pm$ .00097
_____
General mean .... 44.2638, $\pm$ .00050

Regnault's figure is probably too low. Its omission would raise the general mean to 44.2674; but such a procedure is questionable. I prefer therefore to leave the combination unchanged, except for the necessary reduction by means of the critical constants. For these, based on the mean of determinations by Amagat and Keesom, Guye[1] deduces $(1+a_0)$ $(1-b_0) = 1.00687$. Applying this value we have for the molecular weight under consideration,

$$CO_2 = 43.9972, \pm .0005.$$

The four independent values for carbon now combine as follows:

By combustion of C, corrected....$C = 12.0017, \pm .0005$
By combustion of CO.............$C = 12.0046, \pm .0008$
From density of CO..............$C = 12.0031, \pm .0008$
From density of CO_2..............$C = 11.9972, \pm .0005$
_____
General mean ....$C = 12.0007, \pm .0003$

In short, the oxygen-carbon ratio may be written

$$O:C::16:12$$

within the limits of experimental uncertainty.

There are a few other data relative to carbon yet to be considered. Rayleigh[2] has compared the density of carbon monoxide at atmospheric pressure with its density at pressures between 75 and 150 millimetres of mercury. The molecular weights deduced are, for normal pressure, $CO = 28.000$, for low pressures, 28.006, when $O = 16$. Hence $C = 12.006$.

A comparison of the gases at high temperatures has been made by Jaquerod and Perrot.[3] They measured the expansion of the two carbon oxides up to $1067.4°$, applied their results to the mean densities found by Leduc and Rayleigh, and obtained the following molecular values:

$CO = 28.009$, and $C = 12.009$.
$CO_2 = 43.992$, and $C = 11.992$.

_____

[1] Journ. Chim. Phys., 3, 337. 1905.
[2] Proc. Roy. Soc., 73, 153. 1904.
[3] Compt. Rend., 140, 1542. 1905.

These figures are interesting for comparison with those previously discussed, but can hardly be used in a general combination.

Another group of data from which the carbon-oxygen ratio can be deduced is found in the density determinations of certain organic compounds. The older measurements need not be considered, but two recent investigations have some real value.

First, the density of methyl oxide $(CH_3)_2O$, as determined by Baume.[1] Two series are given, with the subjoined values for the weight of a normal litre:

I.	II.
2.10912	2.10925
2.10886	2.10941
2.11045	2.11026
2.10920	2.10936
2.10948	2.11005
2.11003	2.10977
2.10947	
	Mean, 2.10968, $\pm$ .00011
Mean, 2.10951, $\pm$ .00014.	

A small correction raises these means by 0.00001. Combined, the final value is 2.10961, $\pm$ .000084. With the critical data given by Baume, $a_0 = 0.03111$, and $b_0 = 0.00382$. Applying these figures by means of the formula already cited, and assigning to the weight of oxygen the probable error found from Morley's observations, the molecular weight of methyl oxide becomes 46.0306, $\pm$ .0021. Hence, with $H = 1.0078$,

$$C = 11.9919, \pm .0010$$

a value which is almost certainly too low.

For the weight of a normal litre of methane, CH_4, Baume and Perrot[2] find the following values:

0.71690
0.71657
0.71633
0.71669
0.71751
0.71636
0.71672
0.71678
0.71725

Mean, 0.71689, $\pm$ .000098

---

[1] Journ. Chim. Phys., 6, 46. 1908. Baume also gives data for methyl chloride, but they are not available for a good determination of molecular weight.
[2] Compt. Rend., 148, 39. 1909.

Reducing this with the critical constants determined by Guye, $CH_4 = 16.034, \pm .0022$.

Hence

$$C = 12.0028, \pm .0022$$

Combining this with the value from methyl oxide, the weighted mean becomes

$$C = 11.9937, \pm .00091$$

From the oxide ratios $C = 12.0007, \pm .0003$. The two values combined give $C = 12.0000, \pm .00029$.

In this combination the actual variation from the whole number 12 is only 4 in the sixth decimal place; a variation quite without significance. Later, in the discussion of all the fundamental ratios, the value for carbon is modified by other values derived from silver compounds; but the change is not very large.

From the density of toluene, Leduc[1] has recently deduced the value 12.003, which is notably higher than that computed here. The determination, however, is not sufficiently explicit in detail to admit of its use for present purposes. Another value is calculable from Parson's glucinum ratios;[2] namely, $C = 12.007$.

Addenda. The determinations by Baume and Perrot[3] of the density of ethane appeared too late for use in the general discussion of the fundamental ratios. Two series of measurements were made, giving the subjoined figures for the weight of the normal litre:

I.	II.
1.35671	1.35600
1.35679	1.35610
1.35671	1.35653
1.35652	1.35640
1.35700	1.35590
1.35640	1.35640

Mean of all as one series, $1.356455, \pm .000065$. Reducing their data by means of the critical constants, the authors find $C_2H_6 = 30.119$, and $C = 12.036$. This value is evidently too high.

There is also a preliminary note, by Scott,[4] which gives, without details, the results of combustions of naphthalene and cinnamic acid. In six analyses, 17.6175 grammes of naphthalene gave 60.5355 of CO_2.

[1] Compt. Rend., 148, 832. 1909.
[2] See section on glucinum, later.
[3] Journ. Chim. Phys., 7, 369. 1909.
[4] Proc. Chem. Soc., 25, 310.

Hence C=11.999. In two analyses, 8.6153 grammes of cinnamic acid gave 23.0413 of CO_2. Hence 12.0015.

SYNTHESES AND DENSITY OF HYDROCHLORIC ACID.

The quantitative synthesis of hydrochloric acid, with reference to the atomic weight of chlorine, was first effected by Dixon and Edgar.[1] Chlorine, prepared by the electrolysis of fused silver chloride, was weighed in liquid form. Hydrogen, obtained electrolytically from barium hydrate, was occluded by palladium, and so weighed. A combustion globe was filled with the chlorine, and the hydrogen, ignited by a spark, was burned in it. The excess of chlorine was determined by absorption in potassium iodide, and subsequent titration of the liberated iodine with thiosulphate solution. With corrected weights the following results were obtained:

Weight H.	Weight Cl.	Ratio Cl:H.
0.9993	35.1666	35.191
1.0218	35.9621	35.195
.9960	35.0662	35.207
1.0243	36.0403	35.185
1.0060	35.4144	35.203
.9887	34.8005	35.198
1.0159	35.7639	35.204
1.1134	39.1736	35.184
1.0132	35.6527	35.188

Mean, 35.195, ± .0019

The determinations by Noyes and Weber[2] were differently conducted. The hydrogen was weighed in palladium; but the chlorine was taken in the form of potassium chloroplatinate. That salt was heated in a stream of hydrogen, and the loss in weight gave the weight of chlorine taken. The hydrochloric acid produced was also collected and weighed.

Two series of experiments were made, differing in detail. In series I, the hydrogen was prepared by electrolysis of sulphuric acid, and in series II from barium hydroxide. The hydrochloric acid of series I was collected in water directly; but in series II it was first condensed to a solid by cooling with liquid air. The two series, however, were concordant, and may therefore be treated here as one. The data obtained, reduced to a vacuum basis, were as follows:

[1] Phil. Trans., 205A, 169. 1905.
[2] Journ. Amer. Chem. Soc., 30, 13. 1908.

H.	Cl.	HCl.	Cl:H.	HCl:H.
0.25394	8.93293	9.18695	35.177	36.178
.28004	9.85590	10.13259	35.195	36.183
.51821	18.23468	18.75359	35.188	36.189
.67631	23.79587	24.47123	35.185	36.183
.58225	20.48158	. . . . . .	35.177	. . . . .
.47989	16.88423	17.36310	35.184	36.181
.64132	22.55816	23.20054	35.175	36.176
.81608	28.71691	29.53167	35.188	36.187
.83194	29.28055	30.11207	35.195	36.195
.39074	13.74926	14.14078	35.188	36.188
.75560	26.58427	27.33926	35.183	36.182
.77518	27.26746	28.04110	35.176	36.174

Mean, 35.1843,   36.1835,
± .0014   ± .0013

Edgar's [1] syntheses of hydrochloric acid resembled those of Dixon and Edgar, so far as the preparation and weighing of the initial substances were concerned. The chlorine was then burned in the hydrogen, at the end of a quartz tip, and the hydrochloric acid so produced was condensed to solid form by means of liquid air. It was afterwards allowed to evaporate, and passed through a quartz tube filled with mercury vapor, which removed any free chlorine. The purified hydrochloric acid was finally condensed, either in a steel bomb or by absorption in water, and weighed. The corrected weights and ratios are subjoined:

H.	Cl.	HCl.	Cl:H.	HCl:H.
2.1452	75.5026	77.6469	35.196	36.196
2.0387	71.7504	73.7880	35.194	36.194
1.7762	62.5004	. . . . . .	35.188	. . . . .
1.9935	70.1638	72.1565	35.196	36.196
1.6469	57.9671	. . . . . .	35.198	. . . . .
2.1016	73.9662	. . . . . .	35.195	. . . . .
1.7254	60.7162	62.4401	35.190	36.189
2.0885	73.4991	75.5859	35.192	36.191

Mean, 35.194,   36.193,
± .0008   ± .0009

Upon reducing the HCl: H ratios to the Cl: H form the five sets of determinations combine thus:

Dixon and Edgar, H:Cl.............. 35.195, ± .0019
Noyes and Weber, H:Cl.............. 35.1843, ± .0014
Noyes and Weber, H:HCl........... 35.1835, ± .0013
Edgar, H:Cl .... 35.194, ± .0008
Edgar, H:HCl .... 35.193, ± .0009

General mean, 35.1911, ± .00049

[1] Proc. Roy. Soc., 81A, 216. 1908.

That is, the atomic weight of chlorine, when $H = 1$, is 35.1911. If $O = 16$, then $Cl = 35.4652, \pm .0005$.

For the weight of a normal litre of hydrochloric acid, Guye and Ter Gazarian [1] give the subjoined figures:

$$1.6404$$
$$1.6397$$
$$1.6389$$
$$1.6401$$

Mean, 1.6398, $\pm$ .00007

Reducing these by the method of critical constants, in which the term $(1 + a_0)(1 - b_0) = 1.00773$, the molecular weight of HCl becomes 36.4693, $\pm .0015$. Hence, if $H = 1.0078$, $Cl = 35.4615, \pm .0015$.

In a preliminary note Gray and Burt [2] have given the results of their investigation upon the density and composition by volume of hydrochloric acid. For the weight of the normal litre of the gas, as a mean of twenty experiments, the value 1.63885 grammes was found, $\pm .00004$. By passage over heated aluminum the volume of hydrogen liberated from two volumes of HCl was found to be $1.00790, \pm .00002$; the mean of eight experiments. From these data, with $H = 1.0078$, and with Morley's value and probable error for the density of hydrogen, $HCl = 36.4672, \pm .0009$, and $Cl = 35.4594, \pm .0009$.

The several values for Cl now combine thus:

By syntheses of HCl................. 35.4652, $\pm$ .0005
From density of HCl................. 35.4615, $\pm$ .0015
From volumetric composition of HCl.. 35.4594, $\pm$ .0009

General mean .... 35.4637, $\pm$ .00042

This value is still to be modified by the analyses of nitrosyl chloride, as given in the next section of this work.

Addenda. Since the foregoing pages on the chlorine-hydrogen ratio were written, and after the final mean had been utilized in a large number of other calculations, the complete work of Gray and Burt [3] has appeared. First, three series of determinations of the density of HCl are given, with the weight of one litre of the gas at 0°, 760 mm., and at London, as follows:

[1] Compt. Rend., 143, 1233. 1906.
[2] Proc. Chem. Soc., 24, 215. 1908. For changes and corrections see *addenda* to this section.
[3] Journ. Chem. Soc., 95, 1633. 1909.

I.	II.	III.
1.64053	1.64022	1.63950
1.64004	1.63999	1.64013
1.64020	1.63976	1.63984
1.63986	1.64083	1.64069
———	1.64030	1.64031
Mean, 1.64016,	1.64021	1.64017
± .00010	1.64027	1.64050
	———	1.64051
	Mean, 1.64023,	1.63992
	± .00008	1.64001
		———
		Mean, 1.64016,
		± .00008

The three series represent hydrochloric acid prepared by three distinct methods. Series I and II are to be corrected by -0.00013 gramme, which represents gas adsorbed by the walls of the containing glass bulb. The corrected mean becomes 1.64011, ± .00005 grammes, which, at sea level and latitude 45° is equivalent to 1.63915 grammes, the weight of the normal litre. If we reduce this with the critical constants used by Guye and Ter Gazarian,[1] it gives HCl = 36.4548, and with H = 1.0078, Cl = 35.4470, ± .0011, a very low value.

In order to ascertain the atomic weight of chlorine, Gray and Burt have measured the compressibility of the HCl, and also determined its composition by volume. In the latter case the gas was decomposed by heated aluminum, and the volume of hydrogen liberated from two volumes of hydrochloric acid was measured. The volumes thus found were as follows:

$$1.00797$$
$$1.00795$$
$$1.00790$$
$$1.00790$$
$$1.00781$$
$$1.00779$$
$$1.00787$$
$$1.00798$$

Mean, 1.00790, ± .000017

Using Morley's value for the weight of a litre of hydrogen, 0.089872, ± .0000028 gramme, and with the atomic weight H = 1.00779, ± .00001, the molecular weight of HCl is given by the following equation:

$$\frac{1.63915}{0.089872} \times \frac{2}{1.00790} \times 1.00779 = 36.4735$$

[1] See *ante*. Gray and Burt do not make this calculation. It is useful, however, for purposes of comparison.

and $Cl = 35.4657, \pm .0013$. Gray and Burt, calculating with $H = 1.00762$ (Morley's value), find $Cl = 35.459$.

The data given by Gray and Burt for the compressibilities of oxygen and hydrochloric acid are too complex to admit of detailed reproduction here. The normal litre of oxygen, weighing 1.42900 grammes, gave a limiting density of 1.42762 grammes. That of HCl, 1.63915 grammes, gives a limiting density of 1.62698 grammes. The ratio between these limiting densities is the true ratio between the molecular weights according to Avogadro's law. Hence,

$$\frac{1.62698 \times 32}{1.42762} = \text{Mol. Weight HCl} = 36.4687$$

Hence, assuming the probable errors 0.00005 for HCl, and 0.0000028 for O_2, $Cl = 35.4609, \pm .0011$.

The three values derived from Gray and Burt's determinations, now give the subjoined values for the molecular weight of HCl, when $H = 1.00779$.

By critical constants...........HCl $= 36.4548, \pm .0011$
By volumetric analysis.............. 36.4735, $\pm .0013$
By compressibility measurements.... 36.4687, $\pm .0011$

General mean ....HCl $= 36.4647, \pm .0007$

Hence $Cl = 35.4569, \pm .0007$. Gray and Burt, from their two methods alone, find $Cl = 35.460$. The difference between their figure and the foregoing combination is only one part in 11440, which is less than the actual uncertainty.

Determinations of the density of HCl have also been made, very recently, by Scheuer.[1] By simultaneous weighings of the gas in six globes, 28 values were obtained for the weight of the normal litre, as follows:

1.63935	1.63983	1.63943	1.63941
1.63959	1.63932	1.63943	1.63944
1.63939	1.63887	1.63933	1.63895
1.63940	1.63977	1.63933	1.63928
1.63968	1.63951	1.63931	1.63962
1.63945	1.63892	1.63942	1.63932
1.63987	1.63938	1.63968	1.63928

Mean of all, as one series, $1.63941, \pm .000031$.

Reducing with the critical constants, as given by Guye and Ter Gazarian, $Cl = 35.4528, \pm .0007$.

---

[1] Compt. Rend., 149, 590. 1909. Scheuer's complete memoir (Zeitsch. phys. Chem., 68, 575) was received after this work had gone to the printer. In it he discusses his own measurements, in connection with those of Gray and Burt, and finally concludes that $Cl = 35.466$.

The several values for chlorine, as derived from hydrochloric acid and also from the analyses of nitrosyl chloride, as cited in the next section of this work, now combine thus:

By syntheses of HCl.............Cl = 35.4652, ± .0005
Guye and Ter Gazarian.............. 35.4615, ± .0015
Gray and Burt, revised.............. 35.4569, ± .0007
Scheuer .... 35.4528, ± .0007
From NOCl, Guye and Fluss.......... 35.4680, ± .0010

General mean ....Cl = 35.4630, ± .00032

This varies from the value adopted in the previous discussion, Cl = 35.4647, by one part in 21,000. Its introduction into the final reduction of the fundamental atomic weights would change the latter inappreciably.

ANALYSES OF NITROSYL CHLORIDE.

The analyses of nitrosyl chloride, NOCl, by Guye and Fluss,[1] are of special interest, because they give direct ratios between the three component elements. The carefully purified chloride was first weighed, and then distilled over heated silver, which absorbed the chlorine. The weight of the latter was given by the gain in weight of the silver. It was next passed over heated copper, which retained oxygen, and finally over metallic calcium to fix the nitrogen. The sum of the three components was generally a little less than that of the nitrosyl chloride, but whether the loss represents undetermined impurity, or failure to collect all the products of decomposition, seems to be uncertain. The weights obtained were as follows:

NOCl.	Cl.	O.	N.	Loss.
.5341	.2893	.1305	.1142	.0001
.4284	.2319	.1046	.0916	.0003
.7995	.4331	.1954	.1710	.0000
.5639	.3048	.1375	.1204	.0012
.5121	.2773	.1251	.1095	.0002

From these figures, with O = 16, the atomic weights of N and Cl are directly calculable, by comparison with O = 16. In a third column I also give the value of the ratio Cl : N :: 100 : x, computed from columns 2 and 4.

N.	Cl.	Cl:N.
14.001	35.470	39.475
14.011	35.472	39.500
14.002	35.464	39.483
14.010	35.468	39.501
14.005	35.466	39.488
Mean, 14.006, ± .0017	35.468, ± .0010	39.489, ± .0033

[1] Journ. Chim. Phys., 6, 732. 1908.

Several other ratios are calculable from the data given, and, indeed, were computed by Guye and Fluss; but they are not needed here. They involve to a greater extent the uncertainties due to the losses from the initial substance. The values found in this series of analyses may now be combined with those obtained in the preceding sections of this work, as follows:

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

N.

Previously found ....N = 14.0074, ± .00018
From NOCl ....N = 14.006, ± .0017

General mean ......N = 14.0074, ± .00018

Cl.

Previously found [1] ......Cl = 35.4637, ± .00042
From NOCl ....Cl = 35.468, ± .0010

General mean ......Cl = 35.4643, ± .00039

</div>

THE RATIO HCl : NH₃.

Julius Thomsen,[2] for the purpose of fixing indirectly the ratio $H : O$, has made a series of determinations of the ratio $HCl : NH_3$, which may properly be used toward establishing the atomic weight of nitrogen. First, pure, dry, gaseous hydrochloric acid is passed into a weighed absorption apparatus containing pure distilled water. After noting the increase in weight, pure ammonia gas is passed in until a very slight excess is present, and the apparatus is weighed again. The excess of NH_3, which is always minute, is measured by titration with standard hydrochloric acid. In weighing, the apparatus is tared by one of similar form, and containing about the same amount of water. Three series of determinations were made, differing only in the size of the absorption apparatus; so that for present purposes the three may be taken as one. Thomsen considers them separately, and so gives greatest weight to the experiments involving the largest masses of material. I give his weighings, and also, as computed by him, the ratio $\dfrac{HCl}{NH_3}$.

	HCl.	*NH₃.*	*Ratio.*
First series	5.1624	2.4120	2.1403
	3.9425	1.8409	2.1416
	4.6544	2.1739	2.1411
	3.9840	1.8609	2.1409
	5.3295	2.4898	2.1406
	4.2517	1.9863	2.1405

---

[1] Not including addenda.
[2] Zeitsch. physikal. Chem., 13, 398. 1894. For a criticism of Thomsen's work, see Acree and Brunel, Amer. Chem. Journ., 36, 117. The ratio, as determined, is of small value.

	4.8287	2.2550	2.1414
	6.4377	3.0068	2.1411
	4.1804	1.9528	2.1407
	5.0363	2.3523	2.1410
	4.6408	2.1685	2.1411
	——	——	——
Second series	11.8418	5.5302	2.14130
	14.3018	6.6808	2.14073
	12.1502	5.6759	2.14067
	11.5443	5.3927	2.14073
	12.3617	5.7733	2.14118
	——	——	——
Third series	19.3455	9.0360	2.14094
	19.4578	9.0890	2.14081

Mean of all, 2.14093, $\pm$ .000053
Reduced to vacuo, 2.1394

From the sums of the weights Thomsen finds the ratio to be 2.14087, or 2.13934 in vacuo.

ANALYSES OF CHLORATES.

Until recent times the fundamental values for the atomic weights of silver, chlorine and potassium, were best determined by analyses of chlorates. Modern, direct determinations of the chlorine-hydrogen and nitrogen-oxygen ratios have in great measure supplanted the chlorate work, which, however, must still be taken into account, and may even regain some of the lost ground.

The first good series of analyses of potassium chlorate was made by Berzelius.[1] 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 benefited 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, $\pm$ .0006

---

[1] Poggend. Annalen, 8, 1. 1826.

The next series was made by Penny,[1] 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

In 1842 Pelouze[2] made three estimations by the ignition of the chlorate, with these results:

$$60.843$$
$$60.857$$
$$60.830$$

Mean, 60.843, $\pm$ .0053

Marignac, in 1842,[3] 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

Mean, 60.8392, $\pm$ .0013

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.

[1] Phil. Trans., 1839, p. 20.
[2] Compt. Rend., 15, 959.
[3] Ann. Chem. Pharm., 44, 18. Oeuvres Complètes, 1, 57.

In 1845 two series of experiments were published by Gerhardt.[1] The first, made in the usual way, gave these results:

<div align="center">

60.871
60.881
60.875
———
Mean, 60.8757, ± .0020

</div>

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—

<div align="center">

60.947
60.947
60.952
———
Mean, 60.9487, ± .0011

</div>

These last results were afterwards sharply criticised by Marignac,[2] who seriously questioned their value.

The next series, in order of time, is due to Maumené.[3] 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:

<div align="center">

60.788
60.790
60.793
60.791
60.785
60.795
60.795
———
Mean, 60.791, ± .0009

</div>

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,[4] giving certain mean results. According to this chemist, when potassium

[1] Compt. Rend., 21, 1280.
[2] Suppl. Biblio. Univ. Gèneve, Vol. 1.
[3] Ann. Chim. Phys. (3), 18, 71. 1846.
[4] Ann. Chim. Phys. (3), 18, 80. 1846.

chlorate is ignited slowly, we get 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.[1] In the first series are 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:

<p align="center"><i>First Series.</i></p>

<p align="center">60.8380
60.8395
60.8440
60.8473
60.8450</p>

<p align="center">Mean, 60.84276, ± .0012</p>

<p align="center"><i>Second Series.</i></p>

<p align="center">60.850
60.853
60.844</p>

<p align="center">Mean, 60.849, ± .0017</p>

In these experiments every conceivable precaution was taken to avoid error and insure 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.

According to Guye and Ter Gazarian,[2] potassium chlorate tends to retain a constant impurity of chloride. The average amount of chloride, they say, is 2.7 parts in 10,000, but they give no detailed figures in support of their assertion. It can therefore be given only provisional consideration, the existence of the impurity being not fully established. Leaving their correction temporarily out of account, the different series of determinations of KCl from $KClO_3$ combine as follows:

Berzelius	60.851, ± .0006
Penny	60.8225, ± .0014
Pelouze	60.843, ± .0053
Marignac	60.8392, ± .0013
Gerhardt, 1st	60.8757, ± .0020
" 2d	60.9487, ± .0011
Maumené	60.791, ± .0009
Stas, 1st	60.8428, ± .0012
" 2d	60.849, ± .0017
General mean	60.846, ± .00038

[1] Oeuvres Complètes, 1, 395-405.
[2] Compt. Rend., 143, 411.

Hence, with $3O=48$, $KCl=74.593, \pm .00086$.

The percentage of oxygen in sodium chlorate has been determined only by Penny,[1] who used the same method which he applied to the potassium salt. Four experiments gave the following results:

<div align="center">

45.060
45.075
45.080
45.067
_____
Mean, 45.0705, $\pm$ .0029

</div>

Hence, $NaCl=54.500, \pm .0048$.

For the composition of silver chlorate there are analyses by Marignac[2] and by Stas.[3] Marignac's series is as follows:

$AgClO_3$.	$AgCl$.	Per cent. $AgCl$.
24.540	18.363	74.920
25.809	19.336	74.913
30.306	22.709	74.932
28.358	21.247	74.924
28.287	21.185	74.893
57.170	42.840	74.934

<div align="center">

Mean, 74.9193, $\pm$ .0041

</div>

Corrected to a vacuum this becomes 74.917.

The determinations by Stas are only two in number, giving the subjoined percentages of AgCl in $AgClO_3$:

<div align="center">

74.919
74.922
_____
Mean, 74.9205, $\pm$ .0010

</div>

Combining this with Marignac's figure the general mean becomes $74.9203, \pm .0010$. Hence $AgCl=143.390, \pm .0060$.

ANALYSES OF BROMATES AND IODATES.

Accurate analyses of bromates and iodates, available for atomic weight determinations, are few in number, and from a modern point of view, not satisfactory. Potassium bromate was analyzed by Marignac,[4] by

_____

[1] Phil. Trans., 1839, p. 25.
[2] Oeuvres Complètes, 1, 80.
[3] Oeuvres Complètes, 1, 635.
[4] Oeuvres Complètes, 1, 84. From the sum of his weights Marignac computes that $KBrO_3$ contains 28.723 of oxygen. This calculation gives the fourth analysis excessive weight.

careful calcination, with all the precautions taken to avoid loss. His figures are subjoined:

$KBrO_3$.	KBr.	Per cent. O.
6.801	4.849	28.7016
3.480	2.483	28.6494
6.320	4.506	28.7025
23.186	16.521	28.7458

Mean, 28.6998, ± .0133

Hence $KBr = 119.249, \pm .0596$.

Marignac attempted to analyze silver bromate, but found difficulties in drying the salt. He also made some experiments upon the precipitation of silver bromate by potassium chloride, but published no details of his determinations. He merely states that from 31.32 to 31.47 parts of KCl were needed to precipitate the silver from 100 parts of bromate.

Stas[1] effected the analysis of silver bromate by reduction with sulphurous acid, its content in water having been previously determined. After applying all corrections the subjoined percentages of oxygen were found from the weight of the bromate and that of the residual silver bromide:

20.351
20.347

Mean, 20.349, ± .0014

Hence $AgBr = 187.884, \pm .0133$.

The percentage of oxygen in potassium iodate has been determined by Millon.[2] In three experiments he found:

22.46
22.49
22.47

Mean, 22.473, ± .005

Hence $KI = 165.590, \pm .0384$.

According to Marignac[3] potassium iodate loses iodine when calcined, and is therefore unsuited to atomic weight determinations.

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

17.05
17.03
17.06

Mean, 17.047, ± .005

[1] Oeuvres Complètes, 1, 635.
[2] Ann. Chim. Phys. (3), 9, 400. 1843.
[3] Oeuvres Complètes, 1, 85.

The analysis of silver iodate has also been performed with extreme care by Stas.[1] From 76 to 157 grammes were used 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:

<div align="center">

16.976

16.972

16.9761

Mean, 16.9747, ± .0009

</div>

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

Hence $AgI = 234.734, ± .0126$.

<div align="center">

THE IODINE PENTOXIDE-SILVER RATIO.

</div>

The ratio between iodine pentoxide and silver has been measured by Baxter and Tilley.[2] The oxide was prepared by the careful dehydration of iodic acid, the latter having been made from purified iodine. After weighing, the pentoxide was dissolved in water, and the acid so formed was reduced to hydriodic acid by means of hydrazine. By final titration of the solution with a solution of pure silver, the ratio in question was determined. The ultimate data, with vacuum weights and all corrections applied, are as follows:

<div align="center">

Series I.   Tilley.

</div>

Weight I_2O_5.	Weight Ag.	Ratio.
6.06570	3.92027 [3]	64.6234
9.48035	6.12611	
7.73052	4.99564	64.6223
12.63909	8.16777	64.6231
9.49913	6.13841	64.6208
8.34369	5.39202	64.6239
8.83155	5.70715	64.6223
6.77487	4.37803	64.6216

<div align="right">

Mean, 64.6225, ± .0003

</div>

---

[1] Oeuvres Complètes, 1, 628.

[2] Journ. Amer. Chem. Soc., 31, 201. 1909.

[3] These analyses were inadvertently mixed, and hence are combined in the table.

Series II. Baxter.

Weight I_2O_5.	Weight Ag.	Ratio.
12.09036	7.81320	64.6234
6.29744	4.00957	64.6226
10.89880	7.04309	64.6226
9.33895	6.03505	64.6222
10.15370	6.56169	64.6236
11.00453	7.11141	64.6226
7.01649	4.53431	64.6236
9.33573	6.03304	64.6231
8.72163	5.63619	64.6231
9.01524	5.82591	64.6229

Mean, 64.6230, $\pm$ .0001

Combining both series, the mean value for the ratio is

$$I_2O_5 : 2Ag :: 100 : 64.2229, \pm .0001$$

THE SILVER-CHLORINE RATIO.

For the ratio between silver and chlorine there are many series of determinations, some direct and some indirect. As with numerous other ratios, the first work entitled to any consideration was done by Berzelius.[1]

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:

132.700
132.780
132.790

Mean, 132.757, $\pm$ .019

Turner's work[2] 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.

---

[1] Thomson's Annals of Philosophy, 15, 89. 1820.
[2] Phil. Trans., 1829, 291.

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.[1] 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[2] found that 100 parts of silver formed 132.74 of chloride, but gave no available details. Later,[3] in another series of determinations, he was more explicit. Silver was dissolved in nitric acid, and precipitated by hydrochloric acid. The precipitate was washed several times with boiling water, by decantation, and the chloride was finally dried and fused in the same flask in which it had been formed. The figures are as follows:

Ag.	AgCl.	Ratio.
79.853	106.080	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

Corrected for weighing in air the mean becomes 132.854.

The above series all represent the synthesis of silver chloride. Maumené[4] made analyses of the compound, reducing it to metal in a current of hydrogen. His experiments make 100 parts of silver equivalent to chloride:

[1] Phil. Trans., 1839, 28.
[2] Ann. Chem. Pharm., 44, 21.
[3] Oeuvres Complètes, 1, 79.
[4] Ann. Chim. Phys. (3), 18, 49. 1846.

132.734
132.754
132.724
132.729
132.741

Mean, 132.7364, ± .0077

By Dumas[1] 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

Next in order are seven determinations by Stas.[2] 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, 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. Treating Stas' determinations as a single series, his figures are as follows:

Ag.	*AgCl.*	*Ratio.*
91.462	121.4993	132.841
69.86735	92.8145	132.843
101.519	134.861	132.843
108.549	144.207	132.849
399.651	530.920	132.846
99.9925	132.8382	132.848
98.3140	130.602	132.8417

Mean, 132.8445, ± .0008

[1] Ann. Chem. Pharm., 113, 21. 1860.
[2] Oeuvres Complètes, 1, 333-341.

According to Richards and Wells,[1] who made two very careful series of syntheses, the work of Stas on the silver-chlorine ratio was subject to constant errors. His silver probably contained occluded oxygen, and perhaps alkalies also, and his glass vessels were attacked and changed in weight by the acids used in his operations. These errors were avoided by Richards and Wells, who precipitated and fused their silver chloride either in porcelain or quartz vessels, generally the latter, and who employed silver of the highest possible purity. A number of minute corrections were also applied to their determinations, but these cannot be considered in detail now. The results obtained appear in the two following tables:

Preliminary Series.

Ag.	AgCl.	Ratio.
9.06843	12.04365	132.861
8.39217	11.14985	132.860
5.37429	7.14056	132.865
8.08222	10.73869	132.868
7.08517	9.41362	132.864
7.97715	10.59837	132.859
8.11978	10.78767	132.857
8.53452	11.33907	132.861
6.73284	8.94511	132.858
8.91366	11.84240	132.857
9.72295	12.91769	132.858
8.63961	11.47862	132.860
11.13795	14.79849	132.865

Mean, 132.8610, ± .00065

Final Series.

Ag.	AgCl.	Ratio.
7.24427	9.62508	132.865
8.30502	11.03484	132.870
7.29058	9.68676	132.867
8.58472	11.40614	132.866
8.01318	11.64648	132.862
9.77160	12.98335	132.868
7.98170	10.60528	132.870
11.49983	15.27964	132.868
6.25318	8.30834	132.866
7.72479	12.26360	132.866

Mean, 132.8668, ± .0005

The foregoing nine series of determinations are to be classed as *direct;* that is, they were made for the express purpose of measuring the ratio

---

[1] Publ. Carnegie Inst., Washington, No. 28, 1905.

between silver and chlorine, and were not complicated by other considerations. Arranged in the order of ascending magnitude, and expressed in the form $Ag : Cl :: 100 : x$, these combine as follows:

Maumené	32.736,	± .0077
Berzelius	32.757,	± .0190
Turner	32.832,	± .0038
Penny	32.836,	± .0012
Stas	32.8445,	± .0008
Marignac	32.854,	± .0024
Richards and Wells, preliminary	32.861,	± .00065
Richards and Wells, final	32.8668,	± .0005
Dumas	32.8755,	± .0044
General mean	32.8582,	± .00042

This general mean falls within, but near the lower limit of Richards and Wells' preliminary series.

A second group of determinations of the silver-chlorine ratio may be termed *incidental*. A chloride is balanced against silver, and the silver chloride produced is also weighed, and this procedure, intended to fix other atomic weights, also gives values for the ratio now under consideration. The following determinations, thus obtained, are all useful. I limit myself, however, to work done by individual authorities, and do not attempt to combine observations, say of $RCl : Ag$ by one chemist, and $RCl : AgCl$ by another, into determinations of the ratio $Ag : AgCl$. The details of the several investigations will be found in subsequent chapters of this work, in relation to what I may term the several collateral elements.

The first series of this incidental kind to be now considered is due to Lenher,[1] and is derived from his data on the atomic weight of selenium. Silver selenite was converted into silver chloride, and the latter was afterwards reduced to metal by heating in hydrogen. The vacuum weights and the derived ratio appear in the next table.

AgCl.	Ag.	Ratio.
.21897	.16480	132.870
.48522	.36534	132.813
.58999	.44417	132.830
.67532	50821	132.882
.82232	.61882	132.885
1.08350	.81562	132.844
1.36288	1.02588	132.850
1.67234	1.25884	132.848
	Mean,	132.853, ± .0060

---

[1] Journ. Amer. Chem. Soc., 20, 555. 1898.

Similar data are furnished by Ebaugh's [1] analyses of silver arsenate, which were designed to determine the atomic weight of arsenic. The weights are all reduced to a vacuum standard.

AgCl.	Ag.	Ratio.
.21547	.162175	132.863
.44615	.33583	132.850
.48820	.367525	132.844
.74517	.56099	132.831
.88083	.66318	132.819
.94830	.71400	132.815
.98014	.73771	132.863

Mean, 132.841, ± .0050

In their memoir upon the atomic weight of cæsium, Richards and Archibald [2] give analyses of cæsium and potassium chloride, balancing each salt against silver and silver chloride. In the following table the first two determinations are derived from the potassium salt, and the others from the cæsium compound. The weights refer to the vacuum standard, as do all the others in this group of determinations.

Ag.	AgCl.	Ratio.
3.61747	4.80600	132.855
3.62283	4.81325	132.859
2.45600	3.26240	132.834
2.53351	3.36532	132.832
1.45686	1.93555	132.858
1.94244	2.58003	132.824
2.05023	2.72382	132.854
1.50720	2.00253	132.864
1.32251	1.75678	132.837
1.29434	1.71972	132.864
1.13743	1.51093	132.837
1.97590	2.62484	132.835
2.00760	2.66720	132.855
3.24850	4.31570	132.852

Mean, 132.847, ± .0024

Figures of the same order are given by Archibald in his research upon the atomic weight of rubidium,[3] and again in his memoir upon potassium.[4]

---

[1] Doctoral thesis, University of Pennsylvania, 1901.
[2] Proc. Amer. Acad., 38, 443. 1903.
[3] Journ. Chem. Soc., 85, 786. 1904.
[4] Trans. Roy. Soc., Canada, 1904, Sec. III, p. 47.

Rubidium Series.

Ag.	AgCl.	Ratio.
1.78454	2.37070	132.842
1.84241	2.44778	132.858
2.04710	2.71960	132.851
.97702	1.29796	132.849
1.91316	2.54118	132.826
2.58550	3.43475	132.847
1.96076	2.60452	132.832
1.91462	2.54386	132.865
1.89346	2.51557	132.856
2.01515	2.67685	132.836
1.94594	2.58528	132.855
2.07668	2.75878	132.846
3.56998	4.74233	132.842
2.17233	2.88613	132.862

Mean, 132.848, ± .0020

Potassium Series.

Ag.	AgCl.	Ratio.
3.20598	4.25916	132.850
2.88479	3.83250	132.852
4.19557	5.57396	132.853
6.85280	9.10362	132.845

Mean, 132.850, ± .0012

The analyses of cobalt chloride, by Baxter and Coffin,[1] furnish the subjoined figures:

Ag.	AgCl.	Ratio.
1.82671	2.42676	132.846
2.45398	3.26095	132.884
6.38081	8.47735	132.857
4.92244	6.54019	132.865
5.78815	7.69084	132.872
5.47410	7.27284	132.859
2.61905	3.48012	132.877

Mean, 132.8657, ± .0034

From the analyses, by Baxter and Hines,[2] of manganese chloride we have—

---

[1] Zeitsch. anorg. Chem., 51, 171. 1906.
[2] Journ. Amer. Chem. Soc., 28, 1560. 1906.

Ag.	AgCl.	Ratio.
7.93740	10.54641	132.870
6.05041	8.03868	132.862
5.67279	7.53731	132.868
6.11818	8.12932	132.871
5.91637	7.86129	132.873
7.67995	10.20372	132.862
6.72227	8.93140	132.863

Mean, 132.8670, ± .0012

Baxter and Wilson,[1] analyzing lead chloride, obtained the following data:

Ag.	AgCl.	Ratio.
3.62987	4.82273	132.862
3.21408	4.27016	132.858
3.97568	5.28272	132.876
2.99456	3.97949	132.891
2.40837	3.19909	132.832
3.33407	4.42982	132.865

Mean, 132.864, ± .0054

These incidental series of values for the ratio $Ag : Cl :: 100 : x$ now combine thus:

Ebaugh. As series....................	32.841,	± .0050
Richards and Archibald, Cs series....	32.847,	± .0024
Archibald, Rb series.................	32.848,	± .0020
Archibald, K series..................	32.850,	± .0012
Lenher, Se series....................	32.853,	± .0060
Baxter and Wilson, Pb series.........	32.864,	± .0054
Baxter and Coffin, Co series..........	32.8657,	± .0034
Baxter and Hines, Mn series..........	32.8670,	± .0012
General mean	32.8562,	± .00071

A third group of determinations is to be classed as *indirect*. When two ratios, $RCl : Ag$ and $RCl : ÅgCl$ have been measured by the same investigator, but independently of each other, the cross ratio, $Ag : Cl :: 100 : x$ is easily calculable from them. The examples to be given presently are almost self-explanatory; but the details of the determinations must be sought for in the later sections of this work, on titanium, magnesium, barium, cadmium, etc.

---

[1] Journ. Amer. Chem. Soc., 30, 187. 1908.

In his determinations of the atomic weight of titanium, Thorpe gives data from which the subjoined ratios are derived:

$$4Ag:TiCl_4::100:43.999, \pm .0032$$
$$4AgCl:TiCl_4::100:33.118, \pm .0019$$
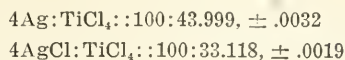
Hence $Ag:Cl::100:32.855, \pm .0092$.

From Richards' analyses of barium chloride we have—

$$2Ag:BaCl_2::100:96.525, \pm .0010$$
$$2AgCl:BaCl_2::100:72.653, \pm .0014$$
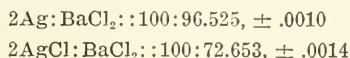
Hence $Ag:Cl::100:32.8575, \pm .0029$.

Ratios computed from the analyses of magnesium chloride by Richards and Parker:

$$2Ag:MgCl_2::100:44.138, \pm .0003$$
$$2AgCl:MgCl_2::100:33.226, \pm .0013$$
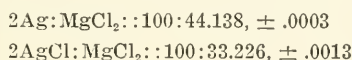
Hence $Ag:Cl::100:32.842, \pm .0054$.

Data for cadmium chloride are given by Baxter and Hines, and also, later, by Baxter, Hines and Frevert. Their series, combined together, give—

$$2Ag:CdCl_2::100:84.9677, \pm .0008$$
$$2AgCl:CdCl_2::100:63.9523, \pm .0004$$
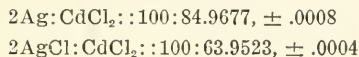
Hence $Ag:Cl::100:32.861, \pm .0016$.

For sodium chloride the analyses of Richards and Wells give the following ratios:

$$Ag:NaCl::100:54.1854, \pm .00015$$
$$AgCl:NaCl::100:40.7797, \pm .00028$$
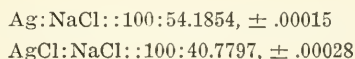
Hence $Ag:Cl::100:32.873, \pm .0010$.

The potassium chloride ratios of Richards and Staehler are—

$$Ag:KCl::100:69.1073, \pm .00032$$
$$AgCl:KCl::100:52.0118, \pm .00025$$
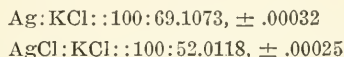
Hence $Ag:Cl::100:32.869, \pm .0009$.

This group of indirect estimates combines as follows:

Richards and Parker, Mg ratios..............	32.842,	$\pm$ .0054
Thorpe, Ti ratios.............................	32.855,	$\pm$ .0092
Richards, Ba ratios..........................	32.8575,	$\pm$ .0029
Baxter, Hines and Frevert, Cd ratios.........	32.861,	$\pm$ .0016
Richards and Staehler, K ratios..............	32.869,	$\pm$ .0009
Richards and Wells, Na ratios................	32.873,	$\pm$ .0010
General mean	32.8684,	$\pm$ .0006

Combining the three groups of determinations, the final value for the ratio $Ag : Cl :: 100 : x$ is obtained.

Direct determinations	32.8582, $\pm$ .00042
Incidental determinations	32.8562, $\pm$ .00071
Indirect determinations	32.8684, $\pm$ .00060
General mean	32.8606, $\pm$ .00031

This value is almost identical with that found by Richards and Wells in their preliminary series of determinations, namely, 32.8610.

Addenda. The following indirect determinations of the silver-chlorine ratio appeared too late to be used in the general discussion of the fundamental ratios.

In Archibald's work on the atomic weight of platinum the subjoined ratios appear:

$$Ag : Pt :: 100 : 180.965, \pm .0034$$
$$AgCl : Pt :: 100 : 136.203, \pm .0031$$

Hence $Ag : Cl :: 100 : 32.864, \pm .0039$.

The final series of determinations by Richards and Willard of the atomic weight of lithium, give these data:

$$Ag : LiCl :: 100 : 39.2992, \pm .00014$$
$$AgCl : LiCl :: 100 : 29.5786, \pm .00014$$

Hence $Ag : Cl :: 100 : 32.8637, \pm .00077$.

From the strontium chloride ratios of Thorpe and Francis I find:

$$2Ag : SrCl_2 :: 100 : 73.490, \pm .0008$$
$$2AgCl : SrCl_2 :: 100 : 55.311, \pm .0009$$

Hence $Ag : Cl :: 100 : 32.867, \pm .0026$.

THE SILVER-BROMINE RATIO.

The measurements of the silver-bromine ratio resemble those of the ratio between silver and chlorine, and fall into three groups. First in order are the *direct* determinations.

Marignac,[1] 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 ratio $Ag : Br :: 100 : x$ is given in the third column:

---

[1] Oeuvres Complètes, 1, 83.

Ag.	AgBr.	Ratio.
25.000	43.518	74.072
20.120	35.020	74.055
15.000	26.110	74.066

Mean, 74.064, ± .003

Corrected for weighing in air the mean becomes 74.077.

Much more elaborate determinations of this ratio are due to Stas.[1] 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 reduced to a vacuum. The data are as follows:

Ag.	AgBr.	Ratio.
53.1958	92.6042	74.0830
51.3436	89.3780	74.0790
55.0615	95.8505	74.0795
55.8040	97.1450	74.0805
43.3620	84.1904	74.0830

Mean, 74.0810, ± .0006

In his paper on the atomic weight of cadmium,[2] Huntington gives three syntheses and three analyses of silver bromide. The data are as follows, with the usual ratio given in the last column:

1.4852 grm. Ag gave	2.5855 AgBr.	74.084
1.4080 "	2.4510 "	74.077
1.4449 "	2.5150 "	74.060
4.1450 grm. AgBr gave	2.3817 Ag.	74.035
1.8172 "	1.0437 "	74.111
4.9601 "	2.8497 "	74.057

Mean, 74.071, ± .0072

Similar synthetic data are also given by Richards, incidentally to his work on copper.[3] There are two sets of three experiments each, which can here be treated as one series, thus:

[1] Oeuvres Complètes, 1, 587, 603.
[2] Proc. Amer. Acad., 17, 28. 1881.
[3] Proc. Amer. Acad., 25, 199, 210, 211. 1890.

1.11235 grm. Ag gave	1.93630 AgBr.		74.073
1.57620	"	2.74335 "	74.044
2.16670	"	3.77170 "	74.076
.9664	"	1.68205 "	74.053
.9645	"	1.6789 "	74.069
.9639	"	1.6779 "	74.074

Mean, 74.065, ± .0035

In their research upon the electrochemical equivalents of copper and silver, Richards, Collins and Heimrod[1] give the following syntheses of silver bromide from electrolytic silver:

Ag.	AgBr.	Ratio.
.71585	1.24567	74.013
5.43807	9.46557	74.061
3.76993	6.56216	74.066
2.29649	3.99820	74.100
2.15701	3.75473	74.071
2.37893	4.14187	74.106
2.97120	5.17218	74.077

Mean, 74.0706, ± .0078

It is only fair to state in this connection that the foregoing series was intended to determine the purity of the silver, and not as an accurate measure of the ratio.

Scott,[2] in his analyses of ammonium bromide, titrated the compound with silver. He afterwards collected and weighed the silver bromide, in order to determine the silver bromide ratio. The subjoined weights refer to the vacuum standard:

Ag.	AgBr.	Ratio.
6.82315	11.87733	74.074
9.66809	16.82816	74.090*
5.41906	9.43315	74.0735
5.51258	9.59596	74.074
5.70686	9.93346	74.062
5.33191	9.28093	74.064
5.62572	9.79254	74.067

Mean, 74.072, ± .0023

The starred figure is corrected for a trace of impurity.

In his paper on the atomic weight of iron Baxter[3] gives three direct comparisons of silver with silver bromide, with vacuum weights, as follows:

[1] Proc. Amer. Acad., 35, 139. 1899.
[2] Journ. Chem. Soc., 79, 147. 1901.
[3] Proc. Amer. Acad., 39, 250. 1904.

Ag.	AgBr.	Ratio.
4.77783	8.31754	74.086
5.87977	10.23533	74.077
4.82995	8.40809	74.082

Mean, 74.082, ± .0018

A much more thorough and conclusive set of syntheses was published by Baxter[1] in 1906. The purest silver was dissolved in nitric acid, and precipitated by ammonium bromide. The silver bromide, before weighing, was fused in an atmosphere containing bromine vapor. With vacuum weights, Baxter's figures are as follows:

Ag.	AgBr.	Ratio.
4.71853	8.21363	74.072
5.01725	8.73393	74.078
5.96818	10.38932	74.079
5.62992	9.80039	74.077
8.13612	14.16334	74.080
5.07238	8.82997	74.079
4.80711	8.36827	74.081
4.27279	7.43776	74.072
5.86115	10.20299	74.078
7.91425	13.77736	74.083
6.40765	11.15468	74.084
6.38180	11.10930	74.078
6.23696	10.85722	74.079
9.18778	15.99392	74.078
8.01261	13.94826	74.079
10.48638	18.25452	74.078
8.59260	14.95797	74.079
8.97307	15.62022	74.079

Mean, 74.0785, ± .00047

The direct determinations of the ratio Ag : Br combine thus:

Richards	74.065, ± .0035
Richards, Collins and Heimrod.......	74.0706, ± .0078
Huntington	74.071, ± .0072
Scott	74.072, ± .0023
Marignac	74.077, ± .0030
Baxter, 1906	74.0785, ± .00047
Stas	74.081, ± .0006
Baxter, 1904	74.082, ± .0018
General mean	74.0797, ± .00035

Analyses of various metallic bromides have furnished many incidental determinations of the silver-bromine ratio, like those already described

---

[1] Journ. Amer. Chem. Soc., 28, 1322. 1906.

for silver and chlorine. In his work on titanium bromide, intended to determine the atomic weight of titanium, Thorpe[1] gives the following equivalent weights of silver and silver bromide:

Ag.	AgBr.	Ratio.
3.66122	6.375391	74.133
5.55097	9.663901	74.094
8.17645	14.227716	74.008
7.83493	13.639956	74.092

Mean, 74.082, ± .0176

Thorpe and Laurie[2] compared gold with silver and silver bromide, and give equivalent weights as follows:

Ag.	AgBr.	Ratio.
3.38451	5.89199	74.087
2.60896	4.54261	74.113
2.28830	3.98288	74.054
2.26415	3.94309	74.153
1.97147	3.43015	73.989
2.01292	3.50207	73.980
2.50334	4.35736	74.062
2.93608	5.11045	74.057

Mean, 74.062, ± .0143

In Richards'[3] memoir upon the atomic weight of barium, the sub-joined vacuum weights of Ag and AgBr are given as equivalent to each other. Two additional determinations are rejected by Richards as inaccurate:

Ag.	AgBr.	Ratio.
1.71323	2.98230	74.075
2.13584	3.71809	74.081
1.52921	2.66191	74.071
2.11740	3.68615	74.089
1.72276	2.99868	74.063
1.34175	2.33530	74.049
4.11360	7.16120	74.086
2.56010	4.45670	74.083
2.51415	4.37669	74.082

Mean, 74.075, ± .0029

From the analyses of nickel bromide, by Richards and Cushman,[4] the following figures are derived. These, and all the subsequent series, represent vacuum weights:

[1] Journ. Chem. Soc., 47, 126. 1885.
[2] Journ. Chem. Soc., 51, 565. 1887.
[3] Proc. Amer. Acad., 28, 1. 1893.
[4] Proc. Amer. Acad., 33, 97. 1897.

Ag.	AgBr.	Ratio.
3.23910	5.63892	74.089
2.66636	4.64208	74.098
3.33990	5.81391	74.074
1.31787	2.29435	74.088
1.23482	2.14963	74.085
1.30629	2.27384	74.069
2.21652	3.85805	74.059

Richards and Cushman also give one direct determination of the ratio, in which 2.10289 grammes of silver yielded 3.66066 of bromide. Ratio, 74.078. Including this in the foregoing series, the mean becomes 74.080, $\pm$.0030.

Similar data appear in the memoirs of Richards and Baxter [1] on the atomic weight of cobalt. Their analyses of cobalt bromide gave the following equivalent figures:

Ag.	AgBr.	Ratio.
1.31702	2.29296	74.102
2.54585	4.43095	74.046
2.80449	4.88135	74.055
1.81170	3.15368	74.073
2.64879	4.61046	74.059
2.84891	4.95943	74.086
2.29593	3.99706	74.093
1.89033	3.29053	74.072

There are also in these two memoirs by Richards and Baxter, three direct determinations of the ratio, as follows:

Ag.	AgBr.	Ratio.
2.18679	3.80679	74.081
2.91386	5.07226	74.073
2.97097	5.17170	74.074

Taking these with the previous eight determinations as one series, the mean value for the ratio is 74.074, $\pm$.0033.

From the analyses of uranium bromide, by Richards and Merigold,[2] the following figures are obtained:

Ag.	AgBr.	Ratio.
1.39365	2.42588	74.066
.82559	1.43713	74.073
1.43617	2.50009	74.080

Mean, 74.073, $\pm$ .0027

---

[1] Proc. Amer. Acad., 33, 115, 1897; and 34, 351, 1899.
[2] Proc. Amer. Acad., 37, 393. 1902.

The following figures are derived from the analyses, by Richards and Archibald,[1] of cæsium bromide:

Ag.	AgBr.	Ratio.
1.77402	3.08815	74.076
3.14606	5.47673	74.082
3.63740	6.33213	74.084

Mean, 74.081, ± .0017

Archibald's[2] analyses of rubidium bromide give a similar series of comparisons, as follows:

Ag.	AgBr.	Ratio.
1.74930	3.04578	74.114
1.35230	2.35401	74.075
1.37061	2.38589	74.076
1.70300	2.96462	74.081
2.50590	4.36215	74.075
2.46502	4.29084	74.069
2.83340	4.93210	74.070

Mean, 74.080, ± .0040

Baxter, Hines and Frevert,[3] in order to determine the atomic weight of cadmium, analyzed cadmium bromide. Their silver figures are subjoined:

Ag.	AgBr.	Ratio.
9.08379	15.81319	74.081
5.40724	9.41267	74.075
5.35277	9.31830	74.084
5.61597	9.77649	74.088
4.07226	7.08933	74.088
4.63072	8.06130	74.083
4.68200	8.15070	74.086
4.75259	8.27360	74.086

Mean, 74.084, ± .0010

Baxter and Hines[4] also analyzed manganese bromide, and give the following equivalent weights of Ag and AgBr:

[1] Proc. Amer. Acad., 38, 443. 1903.
[2] Journ. Chem. Soc., 85, 776. 1904.
[3] Journ. Amer. Chem. Soc., 28, 770. 1906.
[4] Journ. Amer. Chem. Soc., 28, 1560. 1906.

Ag.	AgBr.	Ratio.
6.56765	11.43300	74.080
4.83238	8.41206	74.077
4.90354	8.53642	74.087
5.65813	9.85008	74.087
5.82600	10.14206	74.083
3.61478	6.29271	74.083
5.18711	9.02959	74.077
3.94042	6.85968	74.085
4.51250	7.85571	74.088
3.61736	6.29740	74.088
4.79620	8.34915	74.078
3.59319	6.25569	74.098
5.72641	9.96840	74.078

Mean, 74.084, $\pm$ .0011

The incidental determinations of the silver-bromine ratio now combine thus:

Thorpe and Laurie, Au series................ 74.062, $\pm$ .0143
Richards and Marigold, U series............. 74.073, $\pm$ .0027
Richards and Baxter, Co series.............. 74.074, $\pm$ .0033
Richards, Ba series......................... 74.075, $\pm$ .0029
Richards and Cushman, Ni series............. 74.080, $\pm$ .0030
Archibald, Rb series........................ 74.080, $\pm$ .0040
Richards and Archibald, Cs series........... 74.081, $\pm$ .0017
Thorpe, Ti series........................... 74.082, $\pm$ .0176
Baxter, Hines and Frevert, Cd series........ 74.084, $\pm$ .0010
Baxter and Hines, Mn series................. 74.084, $\pm$ .0011

General mean .... 74.082, $\pm$ .0006

Several indirect determinations of the silver bromine ratio, as in the case of the chlorides, are deducible from analyses of metallic bromides.[1]

In Cooke's determinations of the atomic weight of antimony, the ratios are as follows:

$$3Ag:SbBr_3::100:111.114, \pm .0014$$
$$3AgBr:SbBr_3::100:63.830, \pm .008$$
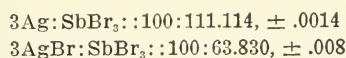
Hence Ag: Br :: 100 : 74.078, $\pm$ .0219.

From Huntington's analyses of cadmium bromide we have—

$$2Ag:CdBr_2::100:126.076, \pm .0052$$
$$2AgBr:CdBr_2::100:72.4216, \pm .0028$$
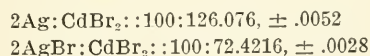
Hence Ag: Br :: 100 : 74.086, $\pm$ .0098.

The work of Richards on strontium bromide gives—

$$2Ag:SrBr_2::100:114.689, \pm .0012$$
$$2AgBr:SrBr_2::100:65.884, \pm .0006$$
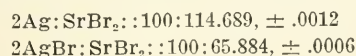
Hence Ag: Br :: 100 : 74.077, $\pm$ .0024.

---

[1] For details, see later sections of this work, on Sb, Cd, Sr, Zn, Cd, Fe, etc.

The ratios deduced from analyses of zinc bromide by Richards and Rogers are—

$$2Ag:ZnBr_2::100:104.380, \pm .0007$$
$$2AgBr:ZnBr_2::100:59.962, \pm .0004$$

Hence $Ag:Br::100:74.077, \pm.0016$.

Analyses by Baxter of ferrous bromide yield the following ratios:

$$2Ag:FeBr_2::100:99.960, \pm .0027$$
$$2AgBr:FeBr_2::100:57.4195, \pm .00044$$

Hence $Ag:Br::100:74.087, \pm.0049$.

Richards and Mueller studied potassium bromide with the subjoined results:

$$Ag:KBr::100:110.319, \pm :0004$$
$$AgBr:KBr::100:63.3727, \pm .0003$$

Hence $Ag:Br::100:74.981, \pm.0012$.

The combination of all these estimates is as follows:

Richards, Sr series....................	74.077,	± .0024
Richards and Rogers, Zn series.......	74.077,	± .0016
Cooke, Sb series....................	74.078,	± .0219
Richards and Mueller, K series.......	74.081,	± .0012
Huntington, Cd series...............	74.086,	± .0098
Baxter, Fe series....................	74.087,	± .0049
General mean	74.0795,	± .00098

Finally, combining the three groups of figures for the ratio $Ag:Br::100:x$ we have—

Direct determinations	74.0797,	± .00035
Incidental determinations	74.082,	± .0006
Indirect determinations	74.0795,	± .00098
General mean	74.0802,	± .00029

Addenda. The determinations by Archibald of the atomic weight of platinum give the following ratios:

$$Ag:Pt::100:180.965, \pm .0034$$
$$AgBr:Pt::100:103.955, \pm .0037$$

Hence $Ag:Br::100:74.080, \pm.0070$.

From the work of Thorpe and Francis on strontium bromide we have—

$$2Ag:SrBr_2::100:114.703, \pm .0040$$
$$2AgBr:SrBr_2::100:65.892, \pm .0011$$

Hence $Ag:Br::100:74.077, \pm.0067$.

These figures were received too late to be used in the final reductions of the fundamental ratios.

THE SILVER-IODINE RATIO.

The composition of silver iodide, first thoroughly investigated by Marignac and Stas, has recently been the subject of elaborate researches.

Marignac[1] dissolved weighed quantities of silver in nitric acid, and precipitated the silver iodide with a solution of potassium iodide. He gives the following weights, and the ratio of AgI to 100 parts of Ag:

Ag.	AgI.	Ratio.
15.000	32.625	217.500
14.790	32.170	217.512
18.545	40.339	217.520

Mean, 217.511, ± .0036

Corrected for weighing in air this becomes 217.5335.

Three series of determinations are given by Stas,[2] all with weights corrected to a vacuum standard.

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. His figures are as follows:

Ag.	AgI.	Ratio.
97.5915	212.2905	217.529
43.5281	94.6984	217.536

Mean, 217.5325, ± .0024

In the second series a complete synthesis of silver iodide from known weights of iodine and metal was effected. 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 were 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

---

[1] Oeuvres Complètes, 1, 86.
[2] Oeuvres Complètes, 1, 548-583.

7

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:

> 117.5390
> 117.5380
> 117.5318
> 117.5430
> 117.5420
> 117.5300

Mean, 117.5373, $\pm$ .0015

From the weight of silver iodide actually collected the following figures are given for the ratio Ag : I. The third experiment in the foregoing column has no equivalent here:

> 117.529
> 117.531
> 117.539
> 117.538
> 117.530

Mean, 117.5334, $\pm$ .0014

These determinations, by Marignac and Stas, are remarkably concordant, and yet, as shown by later investigations, they are affected by constant errors. Silver iodide, precipitated from nitrate solutions, occludes silver nitrate, a fact which must be taken into account in two of the preceding series. The concordance between the second and third series of Stas, however, remains unexplained, if we suppose them to be in error also. That the errors in four sets of determinations, by two observers and four methods, should be so exactly alike in direction and magnitude, is difficult to understand.

With Ag = 107.93, the Marignac-Stas determinations of this ratio make I = 126.85. This value was accepted for many years, until Ladenburg, in 1902, showed that it was about one-tenth of a unit too low. Ladenburg[1] depended upon the ratio Ag : AgCl to establish this conclusion, but he also gave one measurement of the ratio now under consideration, as follows: 50.3147 grammes Ag gave 109.4608 AgI, whence the ratio Ag : AgI = 217.552; a figure higher than those in the foregoing tables, but not strikingly so.

Soon after the publication of Ladenburg's memoir, Scott[2] announced two syntheses of silver iodide, as follows, with weights corrected to a vacuum:

---

[1] Ber. Deutsch. chem. Ges., 35, 2275. 1902.
[2] Proc. Chem. Soc., 18, 112. 1902.

Ag.	AgI.	Ratio.
4.6240	10.0634	117.6340
6.39978	13.92913	117.6502

Mean, 117.6421, ± .0054

Koethner and Aeuer,[1] who also studied what might be called the Ladenburg ratio, succeeded in proving the occlusion of silver nitrate by silver iodide, to which allusion has already been made. They effected two syntheses of silver iodide, however, avoiding this error, and by two methods. First, silver iodide was precipitated from solution with pure hydriodic acid. Secondly, silver was directly combined with iodine, by heating in a stream of iodine vapor. The two syntheses are subjoined, with the ratio stated in the form Ag: AgI, and the weights corrected to a vacuum:

Ag.	AgI.	Ratio.
34.51789	75.12752	217.6347
11.37544	24.75691	217.6480

Mean, 217.6413, ± .0045

The very thorough and careful experiments by Baxter [2] fall into several series, and represent several distinct methods of procedure. First, pure silver was converted into nitrate, and precipitated by a solution of ammonium iodide in presence of an excess of ammonia. All weighings in Baxter's experiments were reduced to a vacuum standard, and various minor corrections were applied, concerning which the original memoirs must be consulted. Two series of determinations are given, as follows:

Preliminary Series.

Ag.	AgI.	Ratio.
5.23123	11.38531	217.6411
3.57039	7.77033	217.6325
4.60798	10.02804	217.6233
4.52467	9.84822	217.6561
4.66256	10.14591	217.6039

Mean, 217.6314, ± .0059

[1] Liebig's Annalen, 337, 123. 1904.
[2] Two memoirs. First, Proc. Amer. Acad., 40, 419. 1904. Second, ibid., 41, 73. 1905.

Final Series.[1]

Ag.	AgI.	Ratio.
4.77244	10.38698	217.645
4.82882	10.50981	217.648
4.04262	8.79755	217.620
1.64711	3.58515	217.663
4.85804*	10.57318	217.643
4.83482	10.52241	217.638
4.97120	10.81800	217.613
3.53858	7.70136	217.640
3.89693	8.48187	217.655
5.33031	11.60111	217.644
5.08748	11.07259	217.644

Mean, 217.6412, ± .0029

Mean, rejecting the seventh value, 217.6440, ± .0024

Secondly, pure iodine was weighed, converted into hydriodic acid by means of sulphurous acid, and then transformed into ammonium iodide with pure ammonia. As nearly as possible the exact equivalent of silver was dissolved in nitric acid, and added to the iodine solution. The trifling excess of silver or iodine was finally determined by titration. The following results were thus obtained:

Ag.	I.	Ratio.
5.54444	6.52288	117.6473
6.27838	7.38647	117.6493
4.57992	5.38814	117.6470

Mean, 117.6479, ± .0005

In Baxter's second memoir the ratio just given was redetermined with variations in the process. Iodine was converted into hydriodic acid, and precipitated by a solution of silver, taking care to avoid an excess of the latter. The final adjustment was effected by titration, as before. In five of the experiments the silver iodide so produced from a known weight of iodine was collected and weighed. In the following table both ratios are expressed in the form Ag : I :: 100 : x ; A representing the direct comparisons, and B the silver iodide syntheses.

---

[1] The starred figure is erroneously given in the original. The corrected figure was kindly furnished me by Professor Baxter. The seventh experiment in the series Baxter rejects.

I.	Ag.	AgI.	Ratio A.	Ratio B.
3.29308	2.79897	. . . . . .	117.6533	. . . .
3.70132	3.14584	. . . . .	117.6576	. . . .
3.75641	3.19258	6.94913	117.6607	117.6555
3.24954	2.76186	6.01137	117.6576	117.6589
4.12541	3.50639	7.63204	117.6543	117.6460
3.53166	3.00165	6.53351	117.6573	117.6494
2.99835	2.54842	5.54682	117.6552	117.6529
2.00015	1.69991	. . . . . .	117.6621	. . . .

Mean, 117.6573, ± .0007   117.6525, ± .0015

In a final series of experiments, based upon the silver used in the preceding set, the ratio Ag : AgI was redetermined, as follows :

Ag.	AgI.	Ratio.
3.19249	6.94877	217.6600
2.76175	6.01110	217.6555
3.00189	6.53399	217.6628
2.54833	5.54659	217.6558

Mean, 217.6585, ± .0012

The determinations of the silver-iodine ratio by Gallo,[1] although numerous, are not as concordant as the foregoing series. Silver was deposited electrolytically, and in the same circuit iodine was liberated from a solution of potassium iodide, and determined afterwards by thiosulphate titration. With vacuum weights the results obtained are as follows :

Ag.	I.	Ratio.
.18054	.21230	117.5917
.21360	.251309	117.6541
.23103	.27181	117.6513
.24005	.28213	117.5291
.15454	.18167	117.5553
.2597	.30515	117.5010
.16229	.19080	117.5673
.300988	.35411	117.6490
.26819	.31528	117.5584
.25877	.30425	117.5755
.24422	.28703	117.5293
.20838	.24516	117.6505
.25047	.29445	117.5599
.20266	.23826	117.5664
.18316	.21533	117.5639
.37278	.43809	117.5197
.28221	.33207	117.6677

[1] Atti Accad. Lincei (5), 15, 24. 1906. Gazz. Chim. Ital., 36, 116.

.2582	.30356	117.5677
.33963	.39923	117.5485
.33461	.39345	117.5846
.3360	.39502	117.5655
.37025	.43526	117.5584
.30824	.36233	117.5480
.36390	.42789	117.5845

Mean, 117.5770, ± .0074

Neglecting the single determination by Ladenburg, and reducing all the series to the common form of $Ag : I :: 100 : x$, the various means combine thus:

Marignac	117.5335, ± .0036
Stas, first	117.5325, ± .0024
Stas, second	117.5373, ± .0015
Stas, third	117.5334, ± .0014
Scott	117.6421, ± .0054
Koethner and Aeuer........	117.6413, ± .0045
Baxter, 1904, preliminary ..	117.6314, ± .0059
Baxter, 1904, Ag:AgI	117.6412, ± .0029
Baxter, 1904, Ag:I	117.6479, ± .0005
Baxter, 1905, Ag:I	117.6573, ± .0007
Baxter, 1905, I:AgI	117.6525, ± .0015
Baxter, 1905, Ag:AgI	117.6585, ± .0012
Gallo	117.5770, ± .0074

General mean .... 117.6351, ± .00034

If we reject the determinations of Marignac, Stas and Gallo the general mean becomes 117.6515, ±.00037. The 1905 determinations by Baxter are probably the best, but they are not absolute and not entitled to exclusive consideration. The two general means correspond to a difference of 0.018 in the atomic weight of iodine.

RATIOS CONNECTING THE SILVER HALIDES.

The three ratios between the silver halides, $AgCl : AgBr$, $AgCl : AgI$, and $AgBr : AgI$, have all been measured with a high degree of accuracy, and by essentially the same process.

When silver bromide is heated in chlorine gas, silver chloride is formed. In 1860 Dumas [1] employed this method 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:

---

[1] Ann. Chem. Pharm., 113, 20.

AgBr.	AgCl.	Ratio.
2.028	1.547	131.092
4.237	3.235	130.974
5.769	4.403	131.024

Mean, 131.030, ± .023

The two series of determinations by Baxter [1] are much more elaborate, and far more conclusive. Before being weighed, the silver bromide was fused in a current of air saturated with bromine. The figures given below are for vacuum weights, which is true for all of Baxter's data as cited in this section.

1905 Series.

AgBr.	AgCl.	Ratio.
10.92091	8.33538	131.019
13.88062	10.59457	131.016
8.21484	6.27006	131.017
7.87887	6.01352	131.020
6.90106	5.26735	131.016
9.53704	7.27926	131.017

Mean, 131.0175, ± .00045

1906 Series.

AgBr.	AgCl.	Ratio.
8.03979	6.13642	131.0176
8.57738	6.54677	131.0170
13.15698	10.04221	131.0168
12.71403	9.70413	131.0167
13.96784	10.66116	131.0162
13.08168	9.98469	131.0174
12.52604	9.56059	131.0175
11.11984	8.48733	131.0170
8.82272	6.73402	131.0172
11.93192	9.10721	131.0162
12.53547	9.56767	131.0190
17.15021	13.09009	131.0167
10.31852	7.87572	131.0168

Mean, 131.0171, ± .00013

The three series combine as follows:

Dumas	131.030,	± .023
Baxter, 1905	131.0175,	± .00045
Baxter, 1906	131.0171,	± .00013
General mean	131.0172,	± .00012

[1] Proc. Amer. Acad., 41, 82. 1905. *Ibid.*, 42, 201. 1906.

Dumas' figures might be rejected altogether without changing the final mean.

Silver iodide, heated in chlorine, is similarly converted into chloride. This ratio has been repeatedly investigated, first by Berzelius.[1] His figures are subjoined, with the ratio $AgCl : AgI :: 100 : x$ in the last column :

AgI.	AgCl.	Ratio.
5.000	3.062	163.292
12.212	7.4755	163.360

Mean, 163.326, $\pm$ .023

There are also two early experiments by Dumas,[2] as follows :

AgI.	AgCl.	Ratio.
3.520	2.149	163.793
7.011	4.281	163.770

Mean, 163.782, $\pm$ .008

The modern work upon this ratio began with an investigation by Ladenburg[3] in 1902, which showed that the previously accepted value for the atomic weight of iodine was at least a tenth of a unit too low. Ladenburg made two series of determinations, with vacuum weights; one preliminary, the other conducted with greater care. His figures are as follows :

Preliminary Series.

AgI.	AgCl.	Ratio.
31.2558	19.0817	163.800
33.7357	20.5930	163.821
49.88229	30.4525	163.804
47.8830	29.2262	163.836
60.1435	36.7154	163.810
41.3649	25.2448	163.855
50.8916	31.0664	163.816
41.3233	25.2200	163.851
80.8139	49.3181	163.863
89.5071	54.6367	163.822

Mean, 163.8278, $\pm$ .0048

---

[1] Ann. Chim. Phys. (2), 40, 430. 1829.
[2] Ann. Chem. Pharm., 113, 28. 1860.
[3] Ber. Deutsch. chem. Ges., 35, 2275. 1902.

Final Series.

AgI.	AgCl.	Ratio.
62.6658	38.2526	163.821
63.8402	38.9687	163.824
74.7576	45.6324	163.826

Mean, 163.8237, ± .00103

Ladenburg was followed, in the measurement of this ratio, by Koethner and Aeuer;[1] whose observations are of the highest significance. In a number of preliminary experiments they found that silver iodide, precipitated from solutions of silver nitrate, was liable to contain occlusions of the latter salt; a fact which accounts for the low values for iodine found by Marignac and Stas. Their final determinations of the chloride-iodide ratio are as follows, with vacuum corrections:

AgI.	AgCl.	Ratio.
24.88066	15.18914	163.8056
10.24699	6.25564	163.8036
12.57020	7.67389	163.8048
25.18868	15.37678	163.8098
9.62006	5.87285	163.8057
12.26770	7.48901	163.8093
22.60660	13.80056	163.8093
20.98601	12.81160	163.8048
22.47667	13.72119	163.8099

Mean, 163.8070, ± .00057

Two series of measurements of this ratio are due to Baxter,[2] who verified the occlusion of silver nitrate by silver iodide. This source of error he obviated by fusing the iodide in an atmosphere containing iodine. In one series, the silver iodide was first converted into bromide and afterwards into chloride; in the other series the conversion was direct. Baxter's determinations appear in the two following tables:

Bromide Series.

AgI.	AgCl.	Ratio
13.65457	8.33538	163.815
17.35528	10.59457	163.813
10.27105	6.27006	163.811
8.62870	5.26735	163.815
11.92405	7.27926	163.809

Mean, 163.8126, ± .00079

---

[1] Liebig's Annalen, 337, 123 and 367. 1904. *Ibid.*, 338, 362. See also Ladenburg, *ibid.*, 338, 259. A preliminary paper by Koethner and Aeuer is in Ber., 37, 2536. 1904.

[2] Proc. Amer. Acad., 40, 431. 1904. *Ibid.*, 41, 73. 1905. Journ. Amer. Chem. Soc., 26, 1593, and 27, 879.

Direct Series.

AgI.	AgCl.	Ratio.
9.26860	5.65787	163.818
6.72061	4.10259	163.814
11.31825	6.90912	163.816
10.07029	6.14754	163.810
13.49229	8.23649	163.811

Mean, 163.8138, ± .00101

The seven series for the ratio AgCl : AgI, arranged in the order of ascending magnitude, now combine thus:

Berzelius .... 163.326, ± .023
Dumas .... 163.782, ± .008
Koethner and Aeuer....... 163.8070, ± .00057
Baxter, bromide series..... 163.8126, ± .00079
Baxter, direct .... 163.8138, ± .00101
Ladenburg, final .... 163.8237, ± .00103
Ladenburg, preliminary ... 163.8278, ± .0048

General mean .... 163.8118, ± .00038

For the ratio AgI : AgBr :: 100 : x there is one set of determinations by Baxter.[1] Silver iodide was converted into bromide by heating in bromine vapor. The data are as follows:

AgI.	AgBr.	Ratio.
13.65457	10.92091	79.9799
17.35528	13.88062	79.9792
9.70100	7.75896	79.9812
10.27105	8.21484	79.9805
9.85688	7.88351	79.9798
8.62870	6.90106	79.9780
11.92405	9.53704	79.9816
7.56933	6.05389	79.9792

Mean, 79.9799, ± .00028

THE POTASSIUM CHLORIDE-SILVER RATIOS.

The ratios between silver, potassium chloride and silver chloride have been repeatedly measured. First, let us consider the ratio Ag : KCl :: 100 : x. Marignac[2] dissolved pure silver in nitric acid, and determined the ratio by titration with a solution of potassium chloride. The data are as follows:

---

[1] Proc. Amer. Acad., 41, 73.   Journ. Amer. Chem. Soc., 27, 878.   1905.
[2] Oeuvres Complètes, 1, 77.

Ag.	*KCl.*	*Ratio.*
4.7238	3.2626	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

Corrected for weighing in air this becomes 69.098, ± .0017.

The work of Stas falls into several series, widely separated in point of time. His earlier experiments [1] upon this ratio may be divided into two sets, as follows: In the first set 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 puri-fied 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.

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

---

[1] Oeuvres Complètes, 1, 363, 364.

69.1034
69.104
69.103
69.102
69.104
69.104
69.105
69.103
69.101
69.105
69.103

Mean, 69.1033, ± .0003

In these determinations Stas did not take into account the slight solubility of precipitated silver chloride in the menstrua employed in the experiments. Accordingly, in 1882,[1] he published a new series, in which by two methods he remeasured the ratio, guarding against the indicated error, and finding the following values:

69.1198
69.11965
69.121
69.123

Mean, 69.1209, ± .0003

Corrected for a minute trace of silica contained in the potassium chloride, this mean becomes

69.11903, ± .0003 [2]

Still later, in order to establish the absolute constancy of the ratio in question, Stas made yet another series of determinations,[3] in which he employed potassium chloride prepared from four different sources. One lot of silver was used throughout. The values obtained were as follows:

69.1227
69.1236
69.1234
69.1244
69.1235
69.1228
69.1222
69.1211
69.1219
69.1249
69.1238
69.1225
69.1211

[1] Oeuvres Complètes, 1, 762-767, 775-777.
[2] Ann. Chim. Phys. (6), 7, 513. 1886.
[3] Oeuvres Complètes, 3, 516, 539.

A series was also begun in which one sample of potassium chloride was to be balanced against silver from various sources, but only one result is given, namely, 69.1240. This, with the previous series, gives a mean of 69.1230, ±.0002.

The difference between the highest and the lowest of Stas' series corresponds to a difference of 0.021 in the atomic weight of potassium. The rejection of the earlier work might be quite justifiable, but would exert a very slight influence upon our final result.

In 1903, incidentally to their work on cæsium, Richards and Archibald [1] published two analyses of potassium chloride, in which both ratios were determined. That is, the silver chloride was weighed, giving data for the second ratio, AgCl : KCl :: 100 : x. The results, with vacuum weights, follow :

KCl.	AgCl.	Ag.	Ag ratio.	AgCl ratio.
2.50019	4.80600	3.61747	69.114	52.022
2.50391	4.81325	3.62283	69.115	52.021
		Mean,	69.1145,	52.0215,
			± .0003	± .0003

In 1904 Archibald [2] gave an additional series of determinations of these ratios, also with vacuum weights, as follows :

KCl.	AgCl.	Ag.	Ag ratio.	AgCl ratio.
2.21586	4.25946	3.20598	69.116	52.026
1.99379	3.83250	2.88479	69.114	52.023
2.89977	5.57396	4.19557	69.115	52.024
4.73606	9.10362	6.85280	69.111	52.024
		Mean,	69.114,	52.024,
			± .0007	± .00055

The measurements of these ratios by Richards and Staehler [3] are probably the most conclusive, for every care was taken to detect and avoid constant errors, such as the authors believe were present, despite all precautions, in the work of Stas. The occlusion of silver nitrate by silver chloride is an error of this kind. The figures for the silver ratio are as follows, with vacuum weights :

[1] Proc. Amer. Acad., 38, 456. 1903.
[2] Trans. Roy. Soc. Canada, 1904, Section III, p. 47.
[3] Publ. Carnegie Inst., Washington, No. 69, p. 7. 1907. An advance publication in Ber. Deutsch. chem. Ges., 39, 3611, contained also the figures of some preliminary experiments, which the authors discard in their final report.

KCl.	Ag.	Ratio.
3.88074	5.61536	69.109
7.44388	10.77156	69.107
5.00681	7.24514	69.106
5.04833	7.30515	69.107
8.19225	11.85412	69.109
4.99795	7.23230	69.106
5.16262	7.47042	69.107

Mean, 69.1073, ± .00032

For the silver chloride ratio Richards and Staehler give the subjoined figures:

KCl.	AgCl.	Ratio.
4.36825	8.3986	52.012
5.56737	10.7038	52.013
6.41424	12.3323	52.012
3.27215	6.2913	52.011
4.83028	9.2870	52.011

Mean, 52.0118, ± .00025

Several earlier measurements of the silver chloride ratio remain to be mentioned. First, Berzelius [1] found that 100 parts of KCl were equivalent to 192.4 of AgCl, a value which, corrected for weighing in air, becomes 192.32. Hence AgCl : KCl : : 100 : 51.997.

In 1842 Marignac [2] published two determinations, as follows:

KCl.	AgCl.	Ratio.
17.034	32.761	51.995
14.427	27.749	51.991

Mean, 51.993,

Four years later, Marignac [3] published a second series of determinations. The new figures are:

KCl.	AgCl.	Ratio.
15.028	28.910	51.982
15.131	29.102	51.993
15.216	29.271	51.983

Mean, 51.986,

---

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

[2] Oeuvres Complètes, 1, 60.

[3] Oeuvres Complètes, 1, 78. The figures of the first set are republished in this series, but not repeated here. Marignac treats the five experiments as one series.

The mean of both series, taken as one, is 51.989; which, corrected to a vacuum standard, becomes 52.011,±.0018.

In three determinations Maumené[1] obtained the following figures:

KCl.	AgCl.	Ratio.
10.700	20.627	51.874
10.5195	20.273	51.892
8.587	16.556	51.868

Mean, 51.878, ± .0049

These figures seem to represent weights in air, but they are hardly worth correcting.

Two other analyses, with vacuum reductions, were made by Thiel[2] incidentally to his research upon indium:

KCl.	AgCl.	Ratio.
7.4314	14.2903	52.003
7.4321	14.2939	51.995

Mean, 51.999, ± .0027

Assembling the data for both ratios, we now have the following combinations:

Ratio Ag : KCl :: 100 : x.

Marignac	69.098,	± .0017
Stas, first	69.1036,	± .0003
Stas, second	69.1033,	± .0003
Stas, third	69.1190,	± .0003
Stas, fourth	69.1230,	± .0002
Richards and Archibald......	69.1145,	± .0003
Archibald	69.114,	± .0007
Richards and Staehler.......	69.1073,	± .00032

General mean .... 69.1138, ± .00011

Ratio AgCl : KCl :: 100 : x.

Berzelius	51.997,	± .0049
Marignac	52.011,	± .0018
Maumené	51.878,	± .0049
Richards and Archibald......	52.0215,	± .0003
Thiel	51.999,	± .0027
Archibald	52.024,	± .00055
Richards and Staehler........	52.0118,	± .00025

General mean .... 52.0163, ± .00018

[1] Ann. Chim. Phys. (3), 18, 41. 1846.
[2] Zeitsch. anorg. Chem., 40, 313. 1904.

In the last combination the single experiment by Berzelius is given equal weight with Maumené's series. Both general means differ from Richards and Staehler's averages by less than one part in 10,500, or 0.01 per cent.

POTASSIUM BROMIDE AND IODIDE RATIOS.

The ratio between silver and potassium bromide was first accurately determined by Marignac.[1] I give, with his weighings, the quantity of KBr proportional to 100 parts of Ag:

Ag.	KBr.	Ratio.
2.131	2.351	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, 110.313, ± .005

Corrected to a vacuum this becomes 110.343, ± .005.

Stas,[2] working in essentially the same manner as when he compared potassium chloride and silver, and with bromide from several distinct sources, found the following values for this ratio:

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, ± .0020

In his paper on the atomic weight of nitrogen, Dean[3] gives three measurements of the Ag : KBr ratio, but with a bromide which was sup-

---

[1] Oeuvres Complètes, 1, 82. Four preliminary analyses are discarded.
[2] Oeuvres Complètes, 1, 747.
[3] Journ. Chem. Soc., 77, 177. 1900.

posed to be not quite pure. His results, however, are so close to later determinations that they are worth citing:

Ag.	KBr.	Ratio.
8.52439	9.40336	110.311
7.83113	8.63900	110.316
8.92432	9.84450	110.312

Mean, 110.313, ± .0010

The recent measurements of this ratio by Richards and Mueller [1] differ considerably from the concordant results of Stas and Marignac. The modern work was probably based upon purer materials, especially in the case of the silver employed. For details upon this side of the discussion the original memoirs must be consulted. The figures, with vacuum weights, given by Richards and Mueller, are as follows:

KBr.	Ag.	Ratio.
4.33730	3.93164	110.318
4.18763	3.79587	110.320
4.15849	3.76943	110.321
3.67867	3.33450	110.321
3.60484	3.26776	110.315
4.78120	4.33387	110.322
5.67997	5.14860	110.321
6.41587	5.81571	110.320
2.88134	2.61184	110.318
3.64383	2.30309	110.316
3.12757	2.83504	110.318

Mean, 110.319, ± .0004

This combines with the former determinations thus:

Marignac	110.343,	± .0050
Stas	110.3463,	± .0020
Dean	110.313,	± .0010
Richards and Mueller.......	110.3190,	± .0004
General mean	110.3193,	± .00033

Richards and Mueller also determined the second ratio, AgBr : KBr :: $100 : x$. Their figures are—

KBr.	AgBr.	Ratio.
2.19027	3.45617	63.3728
4.19705	6.62285	63.3723
2.06723	3.26206	63.3719
2.58494	4.07889	63.3736

Mean, 63.3727, ± .0003

---

[1] Publ. Carnegie Inst., Washington, No. 69, p. 27. 1907.

8

When applied to the determination of the atomic weight of potassium, the Richards and Mueller ratios yield almost absolutely identical results, which also coincide with the figures obtained by Richards and Staehler with the chloride. This agreement is strong evidence in favor of the new determinations.

The ratio between silver and potassium iodide seems to have been measured only by Marignac,[1] but without remarkable accuracy. The figures are as follows:

Ag.	KI.	Ratio.
1.616	2.483	153.651
2.503	3.846	153.665
3.427	5.268	153.720
2.141	3.290	153.667
10.821	16.642	153.794

Mean, 153.6994, $\pm$ .0178

Corrected to a vacuum by Marignac, this becomes 153.800.

THE SODIUM HALIDE-SILVER RATIOS.

The ratio between silver and sodium chloride has been fixed by several investigators. Pelouze[2] 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:

54.158
54.125
54.139

Mean, 54.141, $\pm$ .0063

By Dumas[3] we have seven experiments, with results as follows:

NaCl.	Ag.	Ratio.
2.0535	3.788	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, $\pm$ .0096

[1] Oeuvres Complètes, 1, 86.
[2] Compt. Rend., 20, 1047. 1845.
[3] Ann. Chem. Pharm., 113, 31. 1860.

Stas,[1] applying the method used in establishing the similar ratio for potassium chloride, and working with salt from 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

As in the case of the corresponding ratio for potassium chloride, these data needed to be checked by others which took into account the solubility of silver chloride. Such data are given in Stas' paper of 1882,[2] and four results are as follows:

$$54.2065$$
$$54.20676$$
$$54.2091$$
$$54.2054$$

Mean, 54.20694, $\pm$ .00045

Corrected for a trace of silica in the sodium chloride, this mean becomes 54.2047, $\pm$ .00045.

The elaborate research of Richards and Wells[3] upon this ratio, gave a lower value than that found by Stas. According to Richards and Wells, the silver used by Stas probably contained occluded oxygen, and his silver chloride carried down occlusions of sodium salts. The new data, with vacuum weights as usual, are as follows, the last two experiments forming a small supplementary series:

---

[1] Oeuvres Complètes, 1, 370.
[2] Oeuvres Complètes, 1, 768, 778.
[3] Publ. Carnegie Inst., Washington, No. 28, pp. 52, 56. 1905.

NaCl.	Ag.	Ratio.
3.96051	7.30896	54.187
2.32651	4.29355	54.186
5.36802	9.90699	54.184
4.00548	7.39210	54.186
4.69304	8.66101	54.186
3.27189	6.03842	54.185
5.08685	9.38795	54.185
3.66793	9.76952	54.183
5.48890	10.12993	54.185
3.55943	6.56909	54.185
3.38684	6.25046	54.185
4.68529	8.64634	54.188

Mean, 54.1854, $\pm$ .00025

The five series of determinations combine thus:

Pelouze	54.141,	$\pm$ .0063
Dumas	54.172,	$\pm$ .0096
Stas, earlier	54.2078,	$\pm$ .0002
Stas, later	54.2047,	$\pm$ .00045
Richards and Wells	54.1854,	$\pm$ .00025
General mean	54.1995,	$\pm$ .00015

In this combination the work of Pelouze and Dumas counts for almost nothing. Stas' determinations carry high weight, and it is not easy to understand how their supposed systematic errors could have been so uniform in magnitude. Such errors should vary from experiment to experiment, and so tend to increase the " probable error " of the mean.

In their research upon the atomic weight of boron, Ramsay and Aston[1] converted borax into sodium chloride. In the latter the chlorine was afterwards estimated gravimetrically by weighing as silver chloride on a Gooch filter. Hence the ratio, AgCl : NaCl :: 100 : x, as follows:

NaCl.	AgCl.	Ratio.
3.0761	7.5259	40.874
2.7700	6.7794	40.859
2.8930	7.0804	40.859
2.7360	6.6960	40.860
1.9187	4.6931	40.863

Mean, 40.867, $\pm$ .0033

The same ratio was also measured, much more exactly, by Richards and Wells. The occlusion of sodium salts by the silver chloride was especially considered and guarded against. The figures obtained are as follows:

---

[1] Chem. News, 66, 92. 1892.

NaCl.	AgCl.	Ratio.
3.27527	8.03143	40.781
5.56875	13.65609	41.779
4.18052	10.25176	40.779
4.54319	11.14095	40.779
1.97447	4.84196	40.778
3.97442	9.74547	40.782
6.69495	16.41725	40.780
2.88692	7.07955	40.778
5.56991	13.65833	40.780
5.85900	14.36693	40.781

Mean, 40.7797, $\pm$ .00028

This mean, combined with that of Ramsay and Aston, gives a general mean of 40.7803, $\pm$.00028, which falls within the limits of variation of Richards and Wells' series.

For the ratio between silver and sodium bromide we have one set of measurements by Stas.[1] The bromide was prepared by saturating Na_2CO_3 with HBr. The NaBr proportional to 100 parts of silver was—

95.4420
95.4383
95.4426
95.4392

Mean, 95.4405, $\pm$ .0007

The second bromide ratio, AgBr : NaBr, is represented by two experiments, made by Richards and Wells[2] in a research upon the transition temperature of sodium bromide. With vacuum weights the figures are—

NaBr.	AgBr.	Ratio.
5.49797	10.03253	54.8014
3.64559	6.65248	54.8005

Mean, 54.8010, $\pm$ .0005

THE AMMONIUM HALIDE-SILVER RATIOS.

Ratios connecting silver with the chloride and bromide of ammonium have been repeatedly determined, by methods essentially the same as those adopted in the similar analyses of potassium and sodium halides.

For the ammonium chloride equivalent to 100 parts of silver, Pelouze[3] found:

49.556
49.517

Mean, 49.5365, $\pm$ .013

[1] Oeuvres Complètes, 1, 796.
[2] Proc. Amer. Acad., 41, 443.
[3] Compt. Rend., 20, 1047. 1845.

Marignac[1] obtained the following results. The usual ratio for 100 parts of silver is given also:

Ag.	NH₄Cl.	Ratio.
8.063	3.992	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

Corrected to a vacuum this becomes 49.556, ± .0055.

Stas[2] made three series of determinations of this important ratio, at different times and under varying conditions. All of his weights, as usual, were reduced to a vacuum standard. The third series, published in 1882, was undertaken in order to correct for the solubility of silver chloride, which was not sufficiently guarded against in the earlier work. The values found for the ratio $Ag: NH_4Cl :: 100 : x$ are as follows:

First series.	Second series.[3]	Third series.
49.568	49.598	49.599
49.581	49.597	49.600
49.572	49.593	49.597
49.577	49.597	49.5987
49.595	49.5974	49.597
49.588	49.602	———
49.591	49.597	Mean, 49.598, ± .0005
49.593	49.598	
49.600	49.592	
49.599	———	
49.598	Mean, 49.597, ± .0006	
49.597		
49.591		
49.592		

Mean, 49.589, ± .0018

The first four determinations in the first series are rejected by Stas as unsatisfactory.

By Scott[4] two determinations of this ratio are available, with vacuum weights, as follows:

[1] Oeuvres Complètes, 1, 89.
[2] Oeuvres Complètes, 1, 378, 478, 781.
[3] Excluding three determinations repeated from the first series.
[4] Journ. Chem. Soc., 79, 147. 1901.

Ag.	NH₄Cl.	Ratio.
9.64484	4.78257	49.587
11.12810	5.51744	49.581

Mean, 49.584, $\pm$ .0020

Scott also made one determination of the ratio $AgCl:NH_4Cl$. 4.7850 grammes NH_4Cl balance 12.82048 of Ag. The ratio, therefore, is 100 : 37.3234.

The several values for the ratios $Ag:NH_4Cl::100:x$ now combine as follows:

Pelouze	49.5365,	$\pm$ .0130
Marignac	49.556,	$\pm$ .0055
Stas, first series	49.589,	$\pm$ .0018
Stas, second series	49.597,	$\pm$ .0006
Stas, third series	49.594,	$\pm$ .0005
Scott	49.584,	$\pm$ .0020
General mean	49.5965,	$\pm$ .00038

For the ratio between ammonium chloride and silver chloride there is a series of nine determinations by Richards, Koethner and Tiede.[1] The values found are as follows:

NH₄Cl.	AgCl.	Ratio.
2.02087	5.41469	37.3220
2.23894	5.99903	37.3217
1.55284	4.16076	37.3211
1.36579	3.65959	37.3209
1.61939	4.33914	37.3205
1.93795	5.19219	37.3243
2.89057	7.74498	37.3219
1.31405	3.52082	37.3223
1.82091	4.87921	37.3198

Mean, 37.3217

---

[1] Journ. Amer. Chem. Soc., 31, 6. 1909. The actual analyses were made by Tiede. Professor Richards has kindly furnished me with the three following determinations of this ratio, which were made by Tiede, but not used in the published memoir:

NH₄Cl.	AgCl.	Ratio.
1.10489	2.9607	37.3185
.95997	2.5723	37.3195
.75331	2.0186	37.3184

Mean, 37.3188, $\pm$ .00025

These figures were received too late for use in the systematic discussion. If included in the main series they would tend to lower the atomic weight of nitrogen by 0.001.

Scott's single determination of this ratio, 37.3234, falls within the limits of variation of the foregoing series. Including it in the computation, the ratio becomes

$$AgCl:NH_4Cl::100:37.3218, \pm .0003$$

All weights were reduced to a vacuum basis.

For the ratio $Ag:NH_4Br::100:x$ there are determinations by Stas and Scott.

Stas[1] obtained the following values for x:

> 90.831
> 90.831
> 90.8297
> 90.823
> 90.8317
> 90.8311
> 90.8302
> _____
>
> Mean, 90.8297, $\pm$ .0008

Scott's[2] data, rejecting three preliminary experiments in which the ammonium bromide was distinctly acid, are as follows, with vacuum weights:

$Ag.$	$NH_4Br.$	Ratio.
4.92273	4.46957	90.795
4.20661	4.63303	90.796
4.23664	4.66644	90.790
4.31464	4.75175	90.801
6.19233	6.82047	90.790
8.77664	9.66708	90.789
10.47233	11.53416	90.794
4.91997	5.41834	90.802
5.00442	5.51164	90.797
5.17914	5.70390	90.800
4.84099	5.33177	90.795
5.10677	5.62515	90.784

Mean, 90.7944, $\pm$ .0011

Combining this with the series by Stas, the general mean is 90.8175, $\pm$ .00065.

THE SILVER NITRATE RATIOS.

The quantity of silver nitrate which can be formed from a known weight of metallic silver has been determined by several investigators.

---

[1] Oeuvres Complètes, 1, 801.

[2] Journ. Chem. Soc., 79, 147. 1901. For a criticism by Richards, see Proc. Amer. Phil. Soc., 43, 116. 1904.

Penny [1] dissolved silver in nitric acid in a flask, evaporated to dryness without transfer, and weighed. One hundred parts of silver thus gave of nitrate:

$$
\begin{array}{c}
157.430 \\
157.437 \\
157.458 \\
157.440 \\
157.430 \\
157.455 \\
\hline
\end{array}
$$

Mean, 157.4417, ± .0033

Marignac's [2] 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

Corrected for weighing in air this becomes 157.449.

Stas,[3] 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:

[1] Phil. Trans., 1839.
[2] Oeuvres Complètes, 1, 88. From the sum of the weights, corrected to a vacuum, Marignac computes the ratio 1 : 157.455.
[3] Oeuvres Complètes, 1, 346, 724.

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

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

The reverse ratio, namely, the amount of silver obtainable from a weighed quantity of nitrate, has been determined electrolytically by Hardin.[1] The data obtained, however, are reducible to the same form as in the preceding series, and all are properly combinable together. Pure silver was dissolved in pure aqueous nitric acid, and the crystalline salt thus formed was dried, fused and used for the determinations. The silver nitrate, mixed with an excess of pure potassium cyanide solution, was electrolyzed in a platinum dish. The results obtained, reduced to vacuum weights, were as follows:

$AgNO_3$.	Ag.	Ratio.
.31202	.19812	157.490
.47832	.30370	157.498
.56742	.36030	157.485
.57728	.36655	157.490
.69409	.44075	157.479
.86367	.54843	157.479
.86811	.55130	157.466
.93716	.59508	157.485
1.06170	.67412	157.494
1.19849	.76104	157.477

Mean, 157.484, ± .0020

The most thorough and recent investigation of this ratio is that by Richards and Forbes.[2] They effected the synthesis of the nitrate from the purest silver, the nitrate having been fused and tested for such

---

[1] Journ. Amer. Chem. Soc., 18, 995. 1896.
[2] Publ. Carnegie Inst., Washington, No. 69, p. 47. 1907.

impurities as dissolved air, retained water and ammonia, and nitric or nitrous acids. Only two of these were found, and in minute traces, between 0.001 and 0.002 per cent. in all. The final data, with vacuum weights, are as follows:

Ag.	AgNO₃.	Ratio.
6.14837	9.68249	157.481
4.60825	7.25706	157.480
4.97925	7.84131	157.480
9.07101	14.28503	157.480
9.13702	14.38903	157.481
9.01782	14.20123	157.480

Mean, 157.480, ± .0001

The impurities above mentioned may lower this value to 157.478, their maximum effect. The authors accept the intermediate figure, 157.479. Combining the several determinations, we have—

Penny	157.4417,	± .0033
Marignac	157.449,	± .0061
Stas, earlier	157.474,	± .0014
Stas, later	157.486,	± .0003
Hardin	157.484,	± .0020
Richards and Forbes	157.479,	± .0001
General mean	157.479,	± .000095

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 [1] found of chloride from 100 parts of nitrate:

84.357
84.389

Mean, 84.373, ± .011

Penny,[2] 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.

[1] Phil. Trans., 1833. 537.
[2] Phil. Trans., 1839.

The ratio directly connecting silver nitrate with ammonium chloride has been determined only by Stas.[1] The 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, ± .0006

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

Marignac[2] gives the following weights. I add the quantity of KCl proportional to 100 parts of $AgNO_3$:

KCl.	$AgNO_3$.	Ratio.
1.849	4.218	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, ± .0044

Corrected to a vacuum this becomes 43.874, ± .0044.

Stas'[3] 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, ± .0005

[1] Oeuvres Complètes, 1, 382.
[2] Oeuvres Complètes, 1, 88.
[3] Oeuvres Complètes, 1, 381.

Second Series.

43.864
43.869
43.876

———

Mean, 43.8697, ± .0023

Third Series.

43.884
43.878
43.885

———

Mean, 43.8823, ± .0015

Combining all four series we have—

Marignac .... 43.874, ± .0044
Stas, first series............ 43.8755, ± .0005
Stas, second series.......... 43.8697, ± .0023
Stas, third series............ 43.8823, ± .0015

———————

General mean .... 43.8759, ± .00046

POTASSIUM AND SODIUM NITRATE RATIOS.

Ratios connecting the alkaline nitrates, chlorates and chlorides have been determined by Penny, Stas and Hibbs.

The general method of working upon these ratios is due to Penny.[1] 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 have reduced both series to one standard, namely, so as to express the number of parts of nitrate corresponding to 100 of chloride:

———————————————

[1] Phil. Trans., 1839.

First Series.—KCl treated with HNO₃.

<div align="center">

135.639
135.637
135.640
135.635
135.630
135.640
135.630

</div>

Mean, 135.636, ± .0011

Second Series.—KNO₃ treated with HCl.

<div align="center">

135.628
135.635
135.630
135.641
135.630
135.635
135.630

</div>

Mean, 135.633, ± .0011

Stas,[1] who converted potassium chloride into nitrate, gives the following figures:

KCl.	KNO₃.	Ratio.
50.7165	68.7938	135.643
80.2610	108.8665	135.638
72.1022	99.8050	135.647
50.2175	68.1200	135.649
48.9274	63.3675	135.645
69.8836	94.7900	135.640
14.2578	19.3415	135.655

. Mean, 135.6453, ± .0014

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

The determinations made by Hibbs[2] differ slightly in method from those of Penny and Stas. He converted the nitrate into the chloride by heating in a stream of gaseous hydrochloric acid. His results were as follows, vacuum weights being given:

---

[1] Oeuvres Complètes, 1, 683.

[2] Doctoral dissertation, University of Pennsylvania, 1896. Work done under the direction of Professor Edgar F. Smith.

Weight KNO₃.	Weight KCl.	Ratio.
.11090	.08177	135.624
.14871	.10965	135.622
.21067	.15533	135.627
.23360	.17225	135.620
.24284	.17903	135.642

Mean, 135.627, ± .0026

Now, combining, we have:

Penny, 1st series............	135.636, ± .0011
Penny, 2d series............	135.633, ± .0011
Stas	135.6423, ± .0014
Hibbs	135.627, ± .0026

General mean .... 135.636, ± .0007

By the same general process Penny[1] 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 HNO₃.

145.415
145.408
145.420
145.424
145.410
145.418
145.420

Mean, 145.4164, ± .0015

---

[1] Phil. Trans., 1839.

Second Series.—NaNO₃ treated with HCl.

145.419
145.391
145.412
145.415
145.412
145.412

Mean, 145.410, ± .0026

The sodium chloride to nitrate series of Stas[1] is as follows:

NaCl.	NaNO₃.	Ratio.
120.0110	174.5590	145.453
32.4837	47.2550	145.468
68.1295	99.1045	145.465
47.9226	69.7075	145.459
14.5380	21.1465	145.443

Mean, 145.4576, ± .0030

Reduced to a vacuum basis this becomes 145.4526.

Hibbs'[2] data, obtained by the method employed in the case of the potassium compounds, are as follows, vacuum weights being stated:

Weight NaNO₃.	Weight NaCl.	Ratio.
.01550	.01066	145.403
.20976	.14426	145.404
.26229	.18038	145.410
.66645	.45829	145.429
.93718	.64456	145.399

Mean, 145.407, ± .0026

Combining, we have as follows:

Penny, 1st series............ 145.4164, ± .0015
Penny, 2d series............ 145.410, ± .0026
Stas .... 145.4526, ± .0030
Hibbs .... 145.407, ± .0026

General mean .... 145.418, ± .0012

One other potassium nitrate ratio has been measured by Richards and Archibald.[3] On heating the nitrate with silica, potassium silicate is formed, and the equivalent of N_2O_5 is volatilized. The vacuum weights are given in the following table, together with the ratio $N_2O_5 : K_2O :: 100 : x$:

[1] Oeuvres Complètes, 1, 688.
[2] Dissertation, University of Pennsylvania, 1896.
[3] Proc. Amer. Acad., 38, 462. 1903.

KNO_3 taken.	N_2O_5 lost.	Ratio.
1.81034	0.96692	87.227
3.14564	1.68005	87.235
2.55598	1.36512	87.235

Mean, 87.232, ± .0017

THE SILVER CARBON RATIOS.

The determination of atomic weights by the analysis of organic silver salts has been repeatedly attempted. The measurements of this class may, for present purposes, be conveniently grouped together.

In 1840 Redtenbacher and Liebig[1] sought to determine the atomic weight of carbon, that of silver being assumed as known, by analyses of the acetate, tartrate, racemate and malate of silver. There were five determinations with each compound, the salt being ignited, and the residual silver weighed. 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 64.6006.

In the tartrate the silver was 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, 59.2758

---

[1] Ann. Chem. Pharm., 38, 113. 1841. Mem. Chem. Soc., 1, 9. Phil. Mag. (3), 19, 210.

9

And from the malate:

$$61.996$$
$$61.972$$
$$62.015$$
$$62.059$$
$$62.011$$

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

These results 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 Redtenbacher and Liebig 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 apparently 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 Redtenbacher and Liebig must be decidedly in excess of the true figure.

Strecker,[1] however, discussed the data given by Redtenbacher and Liebig by the method of least squares, using the Berzelian scale, and assuming H = 12.51. Thus treated, they gave C = 75.415, and Ag = 1348.79; or, with O = 16, C = 12.066 and Ag = 107.903. These values of course would change somewhat upon adoption of the modern ratio between O and H.

Observations upon silver acetate, like those of Redtenbacher and Liebig, were also made by Marignac.[2] The salt was prepared by dissolving silver carbonate in acetic acid, and repeatedly recrystallizing. Two experiments gave as follows:

3.3359 grm. acetate gave 2.1561 Ag.   64.633 per cent.
3.0527   "   1.9727 "   64.621   "

Mean, 64.627, ± .0040

Reduced to a vacuum, this becomes 64.609.

---

[1] Ann. Chem. Pharm., 59, 280. 1846.
[2] Ann. Chem. Pharm., 59, 287. 1846. Oeuvres Complètes, 1, 184.

In a second series, conducted with special precautions to avoid mechanical loss by spurting, Marignac found:

24.717 grm. acetate gave	15.983 Ag.	64.665 per cent.
21.202 "	13.709 "	64.661 "
31.734 "	20.521 "	64.666 "

Mean, 64.664, $\pm$ .0010

Other experiments, comparable with the preceding series, have more recently been published by Hardin,[1] who sought to redetermine the atomic weight of silver. Silver acetate and silver benzoate, carefully purified, were subjected to electrolysis in a platinum dish, and the percentage of silver so determined. For the acetate, using vacuum weights, he gives the following data, the percentage column being added by myself:

.32470 grm. acetate gave	.20987 Ag.	64.635 per cent.
.40566 "	.26223 "	64.643 "
.52736 "	.34086 "	64.635 "
.60300 "	.38976 "	64.637 "
.67235 "	.43455 "	64.631 "
.72452 "	.46830 "	64.636 "
.78232 "	.50563 "	64.632 "
.79804 "	.51590 "	64.646 "
.92101 "	.59532 "	64.638 "
1.02495 "	.66250 "	64.637 "

Mean, 64.637, $\pm$ .0011

Combining this series with those of the earlier investigators we have:

Redtenbacher and Liebig.............	64.6006, $\pm$ .0018
Marignac, 1st series.................	64.609, $\pm$ .0040
Marignac, 2d series.................	64.664, $\pm$ .0010
Hardin	64.637, $\pm$ .0011
General mean	64.6434, $\pm$ .0007

With silver benzoate, $C_7H_5AgO_2$, Hardin's results are as follows :

.40858 grm. benzoate gave	.19255 Ag.	47.127 per cent.
.46674 "	.21999 "	47.133 "
.48419 "	.22815 "	47.120 "
.62432 "	.29418 "	47.120 "
.66496 "	.31340 "	47.131 "
.75853 "	.35745 "	47.124 "
.76918 "	.36247 "	47.124 "
.81254 "	.38286 "	47.119 "
.95673 "	.45079 "	47.118 "
1.00840 "	.47526 "	47.130 "

Mean, 47.125, $\pm$ .0012

[1] Journ. Amer. Chem. Soc., 18, 990. 1896.

A different method of dealing with organic silver salts was adopted by Maumené,[1] in 1846, for the purpose of establishing by reference to carbon the atomic weight of silver. 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 Redtenbacher and Liebig. 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 dibasic and the other by a monobasic acid, it is well to reduce both to a common standard. Doing this, we have for the ratio between carbon dioxide and 100 parts of silver the following combination:

From the acetate.............. 40.724, $\pm$ .0076
From the oxalate.............. 40.718, $\pm$ .0185

General mean .... 40.723, $\pm$ .0071

That is, Ag : CO_2 :: 100 : 40.723, $\pm$ .0071.

[1] Ann. Chim. Phys. (3), 18, 41. 1846.

The experiments of Dean[1] on silver cyanide, may be conveniently summarized here, although they involve nitrogen as well as carbon. Dean's object was to determine the atomic weight of nitrogen, the values for silver and carbon being supposedly known. The cyanide was dissolved in nitric acid, or, in the last experiment in sulphuric acid, and its content of silver was determined by titration with a standard solution of potassium bromide. The silver equivalent of the latter compound was previously fixed by titration against a definite solution of silver. The weights obtained, corrected to a vacuum, are subjoined, together with a column giving the percentages of silver:

Weight AgCN.	Weight Ag.	Per cent. Ag.
6.2671	5.0490	80.564
17.60585	14.18496	80.570
17.1049	13.7801	80.561
17.9210	14.43881	80.569
12.11215	9.75875	80.570
14.6672	11.81727	80.569

Mean, 80.567, $\pm$ .0010

Still another pair of ratios, involving bromine, were measured by Scott.[2] Tetraethylammonium bromide, purified with great care, was titrated with silver solutions of known strength. The results obtained, with vacuum weights, were as follows:

$(C_2H_5)_4NBr.$	Ag.	Ratio.
5.07039	2.60146	194.906
5.26380	2.70142	194.853
7.10662	3.64683	194.876
6.79951	3.48976	194.842
2.72225	1.39695	194.871
6.24530	3.20481	194.873
5.74581	2.94853	194.870
5.21663	2.67699	194.869

Mean, 194.870, $\pm$ .0045

A single experiment with the corresponding tetramethyl compound was also made. 8.64585 grammes of $(CH_3)_4NBr$ are equivalent to 6.05348 of silver. Ratio, 142.824, $\pm$ .0123, when the probable error is assumed equal to that of one experiment in the ethyl series. From these figures Scott deduces a value for the atomic weight of carbon much higher than that given by the direct $O : C$ ratio.

---

[1] Journ. Chem. Soc., 77, 117. 1900.
[2] Journ. Chem. Soc., 95, 1200. 1909.

In a criticism of Scott's work, Thorpe [1] has pointed out the possibility of errors due to the vacuum reductions; errors discussed long ago by Marignac, and recently, in more detail, by Guye and Zachariades.[2] The substances analyzed were weighed in powder, under which conditions they are liable to condense and occlude air. A probable correction, applied to Scott's weighings, reduced the atomic weight of carbon to 12.008, in harmony with other good determinations. To this criticism Scott [3] published a rejoinder, seeking to show, on the basis of experimental evidence, that the supposed errors do not, in fact, exist. According to Guye and Zachariades, the errors noted by them in the study of 26 compounds may amount to as much as, or even more than, 3 parts in 10,000.

Since silver tartrate and silver racemate are isomeric compounds, their figures may be consolidated into one series. We then have the following ratios in this group, to be discussed in connection with other ratios later:

$$AgC_2H_3O_2 : Ag : : 100 : 64.6434, \pm .0007$$
$$Ag_2C_4H_4O_6 : 2Ag : : 100 : 59.2778, \pm .0009$$
$$Ag_2C_4H_4O_5 : 2Ag : : 100 : 62.0016, \pm .0096$$
$$AgC_7H_5O_2 : Ag : : 100 : 47.125, \pm .0012$$
$$Ag : CO_2 : : 100 : 40.723, \pm .0071$$
$$AgCN : Ag : : 100 : 80.567, \pm .0010$$
$$Ag : (C_2H_5)_4NBr : : 100 : 194.870, \pm .0045$$
$$Ag : (CH_3)_4NBr : : 100 : 142.824, \pm .0123$$

THE SULPHUR RATIOS.

The atomic weight of sulphur has been determined by means of several ratios connecting it with silver, chlorine, oxygen, hydrogen, sodium and carbon. Other ratios have also been measured, but they are hardly available 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 toward ascertaining the atomic weights of the metals just named.

First in order let us take up the composition of silver sulphide, as directly determined by Dumas, Stas and Cooke. Dumas' [4] 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

---

[1] Proc. Chem. Soc., 25, 285.
[2] Compt. Rend., 149, pp. 593 and 1122.
[3] Proc. Chem. Soc., 25, 286.
[4] Ann. Chem. Pharm., 113, 24. 1860.

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:

Weight Ag.	Weight S.	Ratio.
9.9393	1.473	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, ± .0029

Dumas used from ten to thirty grammes of silver in each experiment. Stas,[1] however, in his work employed much larger quantities. Three of Stas' determinations were made by Dumas' method, while in the other two the sulphur was replaced by pure sulphuretted hydrogen. In all cases the excess of sulphur was expelled by carbon dioxide, purified with scrupulous care. Impurities in the dioxide may cause serious error. The data are as follows, with vacuum weights:

Weight Ag.	Weight Ag_2S.	Ratio.
59.4225	68.24823	114.854
104.139	119.6078	114.853
191.9094	220.4158	114.854
150.000	172.2765	114.851
249.076	286.061	114.849

Mean, 114.8522, ± .0007

The experiments made by Professor Cooke[2] 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 volatility of silver, and they represent, not syntheses, but reductions 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 concordant and at the same time plainly erroneous figures were obtained, the error being eventually traced to the fact that some of the reduced silver, although not heated to its melting 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:

---

[1] Oeuvres Complètes, 1, 349.
[2] Proc. Amer. Acad., 13, 47-52. 1877.

7.5411 grm. Ag$_2$S. 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

Mean, 114.888, ± .0012

1.1357 grm. Ag$_2$S. lost	.1465 S.	Ratio,	114.810
1.2936 "	.1670 "	"	114.823

Mean, 114.8165, ± .0044

Now, combining all four series, we have—

Dumas .... 114.8234, ± .0029
Stas .... 114.8522, ± .0007
Cooke's 2d .... 114.888, ± .0012
Cooke's 3d .... 114.8165, ± .0044

General mean .... 114.8581, ± .0006

The percentage of silver in silver sulphate has been determined by Struve and by Stas. Struve[1] reduced the sulphate by heating in a current of hydrogen, and obtained these results:

Ag_2SO_4.	Ag.	Per cent. Ag.
5.1860	3.5910	69.244
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, ± .004

Stas,[2] working by essentially the same method obtained the following figures, which imply vacuum weights:

Ag_2SO_4.	Ag.	Per cent. Ag.
72.137	49.919	69.200
60.251	41.692	69.197
81.023	56.071	69.204
33.115	57.523	69.209
55.716	38.5595	69.207
63.922	44.2355	69.202

Mean, 69.203, ± .0012

Combining this mean with that of Struve, the general mean becomes 69.205, ± .0011.

---

[1] Ann. Chem. Pharm., 80, 203. 1851.
[2] Oeuvres Complètes, 1, 410.

The third sulphur ratio to be considered 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[1] 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 discover the cause of the mistake, I must exclude the figures 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$_2$S.			86.478
9.2523	"	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.[2] 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.

The work done by Richards[3] relative to the atomic weight of sulphur is of a different order from any of the preceding determinations. Sodium carbonate was converted into sodium sulphate, fixing the ratio Na$_2$CO$_3$: Na$_2$SO$_4$ :: 100 : x. The data are as follows, with vacuum weights:

Na$_2$CO$_3$.	Na$_2$SO$_4$.	Ratio.
1.29930	1.74113	134.005
3.18620	4.26790	133.950
1.01750	1.36330	133.985
2.07680	2.78260	133.985
1.22427	1.63994	133.952
1.77953	2.38465	134.005
2.04412	2.73920	134.004
3.06140	4.10220	133.997

Mean, 133.985, $\pm$ .0055

---

[1] Berzelius' Lehrbuch, 5 Aufl., 3, 1187.
[2] Journ. prakt. Chem., 44, 320. 1848.
[3] Proc. Amer. Acad., 26, 268. 1891. Incidental to work on the atomic weight of copper.

Still another method for fixing the atomic weight of sulphur was adopted by Richards and Jones.[1] Silver sulphate was converted into chloride by heating in a current of pure, dry hydrochloric acid gas. The data obtained, with vacuum weights, were as follows:

Ag_2SO_4.	$AgCl$.	Per cent. $AgCl$.
5.21962	4.79859	91.934
5.27924	4.85330	91.932
5.08853	4.67810	91.934
5.36381	4.93118	91.934
5.16313	4.74668	91.934
5.08383	4.67374	91.933
5.13372	4.71946	91.931
5.16148	4.74490	91.929
5.19919	4.77992	91.936
5.37436	4.94088	91.934

Mean. 91.933, $\pm$ .0004

In recent years attempts have been made to deduce the atomic weight of sulphur from the density of sulphur dioxide, for which there are several modern determinations. Leduc,[2] in a series of measurements, found the density to range between 2.2638 and 2.2641; in mean, 2.2639. If we take these three values for the entire series the probable error of the mean becomes $\pm$.000067. For oxygen Leduc's density figures give 1.10514,$\pm$.0000321. Hence the crude density ratio $O_2 : SO_2 :: 32 : 65.553$, $\pm$.0020. From these figures, with the aid of the compressibilities and critical constants of the gases, Leduc[3] determines $SO_2 = 64.056$. From the density of H_2S he finds a molecular weight of 34.071. Hence $S = 32.056$. By the method of limiting densities, D. Berthelot,[4] from Leduc's figures, finds $S = 32.050$.

Jaquerod and Pintza[5] give for the weight of a normal litre of SO_2, 2.92664 grammes. For the corresponding volume of oxygen their weight is 1.4292 grammes. Hence the crude molecular ratio $32 : 65.528$. Since individual determinations are not given, the probable error of this ratio cannot be calculated, and I shall assign it equal weight with Leduc's determinations. Jaquerod and Pintza also measured the density of SO_2 at pressures lower than the normal, namely, at 570 and 380 mm. Then extrapolating to zero pressure they deduce $SO_2 = 64.01$, and $S = 32.01$.

---

[1] Publ. Carnegie Inst., Washington, No. 69, p. 69. 1907. Richards and Jones give a thorough criticism of the previous work on sulphur.

[2] Compt. Rend., 117, 219. 1893.

[3] Ann. Chim. Phys. (7), 15, 94. 1898. Leduc here puts the density of O = 1.1052. See also *ante*, p. 33.

[4] Journ. Physique (3), 8, 263. 1899.

[5] Compt. Rend., 139, 129. 1904.

Jaquerod and Scheuer,[1] from the same density figures, but with measurements of compressibility, found $S = 32.036$.

The density determinations by Baume [2] are much more elaborate. Two series were made, in globes of different capacity, and at pressures varying slightly from the normal. His crude figures for the weight of a litre of sulphur dioxide are as follows:

Series I.	Series II.
2.92836	2.92662
2.92592	2.92718
2.92683	2.92632
2.92500	2.92711
	2.92623

Mean of both series as one, $2.92667, \pm .00030$. As corrected by Baume the normal litre of SO_2 weighs 2.92661 grammes. Morley's value for the normal litre of oxygen is $1.42896, \pm .000028$ grammes. Hence the ratio $O_2 : SO_2 :: 32 : 65.538, \pm .0067$. This combines with the previous series thus:

Leduc .... $65.553, \pm .0020$
Jaquerod and Pintza.......... $65.528, \pm .0020$
Baume .... $65.538, \pm .0067$

General mean .... $65.540, \pm .0014$

Guye,[3] in his recalculation of the density ratio for SO_2, assigns to the weight of the normal litre of oxygen the value 1.4290, and to SO_2 the value 2.9266. Hence the crude ratio is 65.536, which is close to Baume's figure and also near the general mean as given above. In reducing this by means of the critical constants he assumes $a_0 = 0.02644$, and $b_0 = 0.00255$. Baume, on the other hand, finds $a_0 = 0.02837$, and $b_0 = 0.00267$. The formula for reduction, as employed in relation to the carbon and nitrogen gases, is

$$\frac{22.412L}{(1 + a_0)(1 - b_0)}$$

Hence, using Guye's value for L, which is sensibly identical with that of Baume, we have—

By Guye's critical data.......... $SO_2 = 64.065$
By Baume's critical data......... $SO_2 = 63.952$

The difference between these figures shows the uncertainty of the method as applied to sulphur dioxide. If we accept Guye's figures, as

[1] Compt. Rend., 140, 1384. 1905.
[2] Journ. Chim. Phys., 6, 43. 1908.
[3] Journ. Chim. Phys., 3, 321. 1905.

yielding results more nearly in harmony with the chemical methods of determination, the general mean for sulphur dioxide gives $SO_2 = 64.069$, $\pm .0014$, and $S = 32.069, \pm .0014$.

Another value for the atomic weight of sulphur is derivable from the density of hydrogen sulphide, as determined by Baume and Perrot.[1] Their crude values for the weight of a litre of the gas are as follows:

1.53934	1.53860
1.54126	1.53943
1.53843	1.53900
1.53862	1.53917
1.53789	1.53921
1.53843	1.53960
1.53798	1.53938
1.53890	1.53964
1.53929	1.54069

Mean, 1.53916, ± .00013

Corrected to the usual standards, the weight of the normal litre becomes 1.5392 grammes. With the critical constants determined by Olzewski, $a_0 = .01438$, and $b_0 = .00240$. Hence the molecular weight of H_2S is 34.0893, and $S = 32.074, \pm .0030$. This, combined with the value deduced from the density of sulphur dioxide, gives a general mean of $S = 32.070, \pm .0013$.

GENERAL DISCUSSION.

There are now before us, as developed in the preceding pages, 55 ratios, from which the atomic weights of ten elements are to be computed. These elements are hydrogen, silver, chlorine, bromine, iodine, nitrogen, carbon, sulphur, sodium and potassium. The first twelve " ratios " are really positive values, referred to $O = 16$, which can be regarded as first approximations to the true quantities. These values are applicable to the reduction of the remaining ratios, by which they are themselves to be adjusted in turn.

The rigorous method of dealing with such a mass of data is well understood.[2] The several ratios should be transformed into linear equations, and each one weighted inversely as the square of its " probable error." The 55 equations should then be combined into 10 normal equations, which, when solved, would give the 10 atomic weights now under consideration. But that method of reduction is exceedingly laborious, and would possibly be premature. There is great activity at present in the measurement of fundamental ratios, and for that reason the rigorous dis-

---

[1] Journ. Chim. Phys., 6, 610. 1908. Baume and Perrot reduce their data with the aid of the constant 22.410, instead of the 22.412 adopted here. Leduc's single determination of the density (Ann. Chim. Phys. (7), 15, 35) may be neglected. His gas was not certainly pure.

[2] See Clarke, Am. Chem. Journ., 27, 321. 1902.

cussion of them may well be deferred. There is, moreover, one practical disadvantage in it; namely, that the specific influence of each individual ratio is more or less obscured, except to the computer himself. The extent to which a given ratio affects the final results is not readily seen in a general combination of all the data, whereas for present purposes some such insight is likely to be helpful in guiding future work. An approximate method of reduction is therefore adopted here, which will give highly probable values for the several atomic weights, even if it does not yield the " most probable values " of the method of least squares. The uncertainties will not be large, and perhaps no larger in reality than if the rigid mathematical procedure were followed implicitly.

The 55 ratios may now be tabulated, and numbered for reference, as follows:

(1). $H = 1.00779, \pm .00001$
(2). $C = 12.0000, \pm .00029$
(3). $N = 14.0074, \pm .00018$
(4). $S = 32.070, \pm .0013$
(5). $Cl = 35.4643, \pm .00039$
(6). $NaCl = 58.500, \pm .0048$
(7). $KCl = 74.593, \pm .00086$
(8). $KBr = 119.249, \pm .0596$
(9). $KI = 165.590, \pm .0384$
(10). $AgCl = 143.390, \pm .0060$
(11). $AgBr = 187.884, \pm .0133$
(12). $AgI = 234.734, \pm .0126$
(13). $I_2O_5 : 2Ag :: 100 : 64.6229, \pm .0001$
(14). $Ag : Cl :: 100 : 32.8606, \pm .00031$
(15). $Ag : Br :: 100 : 74.0802, \pm .00029$
(16). $Ag : I :: 100 : 117.6351, \pm .00034$
(17). $AgCl : AgBr :: 100 : 131.0172, \pm .00012$
(18). $AgCl : AgI :: 100 : 163.8118, \pm .00038$
(19). $AgI : AgBr :: 100 : 79.9799, \pm .00028$
(20). $Ag : KCl :: 100 : 69.1138, \pm .00011$
(21). $AgCl : KCl :: 100 : 52.0163, \pm .00018$
(22). $Ag : KBr :: 100 : 110.3193, \pm .00033$
(23). $AgBr : KBr :: 100 : 63.3727, \pm .0003$
(24). $Ag : KI :: 100 : 153.800, \pm .0178$
(25). $Ag : NaCl :: 100 : 54.1995, \pm .00015$
(26). $AgCl : NaCl :: 100 : 40.7803, \pm .00028$
(27). $Ag : NaBr :: 100 : 95.4405, \pm .0007$
(28). $AgBr : NaBr :: 100 : 54.8010, \pm .0005$
(29). $Ag : NO_3 :: 100 : 57.479, \pm .000095$
(30). $AgNO_3 : AgCl :: 100 : 84.3743, \pm .0025$
(31). $AgNO_3 : KCl :: 100 : 43.8759, \pm .00046$
(32). $AgNO_3 : NH_4Cl :: 100 : 31.488, \pm .0006$
(33). $Ag : NH_4Cl :: 100 : 49.5965, \pm .00038$
(34). $AgCl : NH_4Cl :: 100 : 37.3218, \pm .0003$
(35). $Ag : NH_4Br :: 100 : 90.8175, \pm .00065$
(36). $NH_3 : HCl :: 100 : 213.934, \pm .0053$
(37). $Cl : N :: 100 : 39.489, \pm .0033$

(38). $N_2O_5:K_2O::100:87.232, \pm .0017$

(39). $KCl:KNO_3::100:135.636, \pm .0007$

(40). $KClO_3:KNO_3::100:82.500, \pm .0012$

(41). $NaCl:NaNO_3::100:145.418, \pm .0012$

(42). $NaClO_3:NaNO_3::100:79.8823, \pm .0029$

(43). $AgC_2H_3O_2:Ag::100:64.6434, \pm .0007$

(44). $Ag_2C_4H_4O_6:2Ag::100:59.2778, \pm .0009$

(45). $Ag_2C_4H_4O_5:2Ag::100:62.0016, \pm .0096$

(46). $AgC_7H_5O_2:Ag::100:47.125, \pm .0012$

(47). $Ag:CO_2::100:40.723, \pm .0071$

(48). $AgCN:Ag::100:80.567, \pm .0010$

(49). $Ag:C_8H_{20}NBr::100:194.870, \pm .0045$

(50). $Ag:C_4H_{12}NBr::100:142.824, \pm .0123$

(51). $2Ag:S::100:14.8581, \pm .0006$

(52). $Ag_2SO_4:2Ag::100:69.205, \pm .0011$

(53). $2AgCl:Ag_2S::100:86.4733, \pm .0011$

(54). $Ag_2SO_4:2AgCl::100:91.933, \pm .0004$

(55). $Na_2CO_3:Na_2SO_4::100:133.985, \pm .0055$

Now, using the formulæ for the calculation of probable error that were given at the beginning of this work, the foregoing ratios yield twenty-nine values for the atomic weight of silver, as follows:

From ratios	9 and 24	$Ag = 107.666, \pm .0279$
"	" 1, 2, and 45	$107.717, \pm .0320$
"	" 1, 2, and 44	$107.742, \pm .0030$
"	" 13 and 16	$107.791, \pm .0011$
"	" 2, 3, and 48	$107.826, \pm .0066$
"	" 5, 12, and 18	$107.831, \pm .0077$
"	" 12 and 16	$107.857, \pm .0058$
"	" 1, 2, and 46	$107.874, \pm .0039$
"	" 1, 3, 5, and 33	$107.876, \pm .0011$
"	" 3 and 29	$107.878, \pm .00036$
"	" 1, 3, 5, and 34	$107.891, \pm .0016$
"	" 1, 3, 5, and 32	$107.908, \pm .0015$
"	" 1, 2, and 43	$107.914, \pm .0027$
"	" 4 and 51	$107.921, \pm .0061$
"	" 5 and 14	$107.923, \pm .0016$
"	" 5 and 10	$107.926, \pm .0060$
"	" 7 and 20	$107.927, \pm .0013$
"	" 11 and 15	$107.930, \pm .0077$
"	" 6 and 25	$107.934, \pm .0089$
"	" 10 and 54	$107.937, \pm .0066$
"	" 3, 10, and 30	$107.938, \pm .0087$
"	" 5, 7, and 21	$107.939, \pm .0014$
"	" 5, 11, and 17	$107.940, \pm .0101$
"	" 4 and 52	$107.948, \pm .0045$
"	" 10 and 53	$107.959, \pm .0055$
"	" 5, 6, and 26	$107.988, \pm .0118$
"	" 3, 7, and 31	$108.002, \pm .0180$
"	" 2 and 47	$108.047, \pm .0189$
"	" 8 and 22	$108.094, \pm .0540$

General mean, $Ag = 107.880, \pm .00029$

This final mean is almost identical with the value derived from ratio 29, which gives the composition of silver nitrate. That ratio, moreover, is presumably the best of all, and has the smallest probable error. It dominates the entire combination; but its rejection would only raise the atomic weight of silver to 107.883. If we should reject all the values for silver dependent upon analyses of chlorates, bromates and iodates, which are generally high, the final mean becomes 107.877. It is clear, therefore, that the true value cannot be very far from the general mean of all, namely,

$$Ag = 108.880, \pm .00029$$

As for the widely aberrant values, especially the first two and the last four, their probable errors are so large that it is a matter of no moment whether they are retained or rejected. Their influence is negligible.

With the aid of the value thus found for silver, we can now compute twenty values for the atomic weight of chlorine, as follows:

From ratios	12, 18, and Ag	Cl = 35.4150,	± .0080
"	"	4, 53, and Ag	35.4186,	± .0058
"	"	1, 3, and 36	35.4269,	± .0029
"	"	3, 31, 38, and Ag	35.4279,	± .0012
"	"	3, 38, and 39	35.4401,	± .0012
"	"	3, 20, 38, and Ag	35.4483,	± .00096
"	"	14 and Ag	35.4502,	± .00035
"	"	1, 3, 32, and Ag	35.4556,	± .0010
"	"	3, 38, and 40	35.4569,	± .0022
"	"	4, 54 and Ag	35.4575,	± .00093
"	"	3, 30, and Ag	35.4610,	± .0043
"	"	5	35.4643,	± .00039
"	"	1, 3, 33, and Ag	35.4661,	± .00051
"	"	3 and 37	35.4717,	± .0030
"	"	3, 10, 21, 38, and Ag	35.4745,	± .0032
"	"	1, 3, 10, and 34	35.4772,	± .0023
"	"	3, 7, and 38	35.4813,	± .0013
"	"	10 and Ag	35.5100,	± .0061
"	"	3, 7, 21, 38, and Ag	35.5235,	± .0018
"	"	11, 17, and Ag	35.5240,	± .0102

General mean, Cl = 35.4584, ± .0002

Here, again, the extreme values are evidently of no real significance, and have practically no effect upon the final result. The rounded-off figure, 35.458, is in good agreement with the determinations made by Noyes and Weber, and also with the ratio between silver and chlorine as measured by Richards and Wells.

For bromine, using the new value for chlorine in place of that given by ratio 5, eleven values are deducible:

From ratios 12, 19, and Ag......Br = 79.8600, ± .0101
"   "   3, 22, 38, and Ag.........79.9008, ± .0011
"   "   15 and Ag...............79.9177, ± .00038
"   "   17, Ag, and Cl..........79.9189, ± .00063
"   "   1, 3, 35, and Ag.........79.9353, ± .00079
"   "   3, 11, 23, 38, and Ag......79.9555, ± .0085
"   "   1, 2, 3, 50, and Ag....... 79.9775, ± .0133
"   "   11 and Ag..............80.0040, ± .0134
"   "   1, 2, 3, 49, and Ag.......80.0624, ± .0054
"   "   3, 8, and 38.............80.1320, ± .0597
"   "   8, 23, and Ag...........80.2910, ± .0940

General mean, Br = 79.9197, ± .0003

From Baxter's measurement of the silver bromine ratio, when Ag = 107.88, Br = 79.916. The difference is less than 1 part in 21,000.

For iodine seven values are computable, thus:

From ratios 3, 9, and 38.........I = 126.478, ± .0385
"   "   3, 24, 38, and Ag........126.807, ± .0192
"   "   12 and Ag..............126.854, ± .0127
"   "   16 and Ag..............126.905, ± .0005
"   "   18, Ag, and Cl..........126.925, ± .0008
"   "   19, Ag, and Br.........126.928, ± .0011
"   "   13 and Ag..............126.938, ± .0006

General mean, I = 126.9204, ± .00033

The first two of these values for iodine are meaningless. The third and fourth involve the determinations made by Stas and Marignac. The final mean, however, agrees with Baxter's determinations to within 1 part in 13,000.

For potassium there are twelve values, as follows:

From ratios 9 and I.............K = 38.6696, ± .0385
"   "   24, Ag, and I...........38.9989, ± .0192
"   "   3, 39, and Cl............39.0420, ± .0017
"   "   1, 3, 31, Ag, and Cl.......39.0812, ± .00089
"   "   22, Ag, and Br...........39.0927, ± .00056
"   "   23, Ag, and Br...........39.0940, ± .00068
"   "   21, Ag, and Cl...........39.1009, ± .00039
"   "   20, Ag, and Cl...........39.1016, ± .00031
"   "   3, 40, and Cl............39.1097, ± .0085
"   "   3 and 38................39.1117, ± .00093
"   "   7 and Cl................39.1346, ± .00095
"   "   8 and Br...............39.3293, ± .0598

General mean, K = 39.0999, ± .0002

This value is in good agreement with the determinations made by Richards and his collaborators in the Harvard laboratory.

The eight values for sodium, which come next, are less satisfactory than any of the preceding figures:

From ratios 26, Ag, and Cl.....Na = 22.9954, ± .00048
"   "   28, Ag, and Br...........22.9963, ± .0011
"   "   3, 41, and Cl..............22.9964, ± .0017
"   "   25, Ag, and Cl............23.0120, ± .0003
"   "   27, Ag, and Br...........23.0415, ± .0009
"   "   6 and Cl.................23.0416, ± .0048
"   "   2, 4, and 55..............23.0675, ± .0088
"   "   3, 42, and Cl.............23.1692, ± .0050

General mean, Na = 23.0108, ± .00024

The first four values, taken by themselves, give a general mean of 23.0072, ±.00025. This harmonizes better with the determinations made by Richards and Wells than the general mean of all. The fifth and sixth values, however, cannot be safely rejected, for their discordance with the others is not explained. The last two values signify little or nothing.

For sulphur there are six values, as follows:

From ratios 52 and Ag...........S = 32.0094, ± .0038
"   "   2, 55, and Na............32.0314, ± .0059
"   "   51 and Ag...............32.0578, ± .0013
"   "   4 ....32.070, ± .0013
"   "   54, Ag, and Cl...........32.0723, ± .0016
"   "   53, Ag, and Cl...........32.1392, ± .0032

General mean, S = 32.0667, ± .00075

For nitrogen, the fundamental ratios give eighteen values, as follows:

From ratios 38 and K............N = 13.9938, ± .0011
"   "   37 and Cl...............14.0022, ± .0012
"   "   1, 32, Ag, and Cl........14.0032, ± .0015
"   "   30, Ag, and Cl...........14.0040, ± .0051
"   "   1, 34, Ag, and Cl........14.0069, ± .0005
"   "   3 ....14.0074, ± .00018
"   "   29 and Ag...............14.0083, ± .00020
"   "   40, K, and Cl...........14.0107, ± .0015
"   "   41, Na, and Cl...........14.0140, ± .0009
"   "   1, 33, Ag, and Cl........14.0151, ± .0005
"   "   2, 48, and Ag...........14.0209, ± .0014
"   "   1, 36, and Cl...........14.0221, ± .00043
"   "   1, 35, Ag, and Br........14.0230, ± .0009
"   "   39, K, and Cl...........14.0279, ± .0007
"   "   42, Na, and Cl...........14.0392, ± .0030
"   "   31, Ag, K, and Cl........14.0500, ± .0020
"   "   1, 2, 50, Ag, and Br......14.0652, ± .0133
"   "   1, 2, 49, Ag, and Br......14.1501, ± .0054

General mean, N = 14.0101, ± .0001

The mean is distinctly higher than the atomic weight of nitrogen as determined directly, or as derived from the study of silver nitrate.

Finally, there are ten values for carbon:

From ratios 47 and Ag...........C = 11.9320, ± .0077
"   "   1, 43, and Ag............11.9957, ± .0004
"   "   2 ....12.0000, ± .00029
"   "   1, 46, and Ag............12.0007, ± .0007
"   "   1, 50, N, Ag, and Br......12.0138, ± .0044
"   "   1, 49, N, Ag, and Br......12.0175, ± .00052
"   "   48, N, and Ag...........12.0197, ± .0014
"   "   55, Na, and S...........12.0270, ± .0044
"   "   1, 44, and Ag...........12.0475, ± .0010
"   "   1, 45, and Ag...........12.0499, ± .0098

General mean, C = $\overline{12.0038}$, ± .0002

That this mean is higher than the atomic weight given in ratio (2) does not prove it to be in error. Scott's recent determinations, the fifth and sixth given above, are even higher, and the cause of the discrepancy is undetermined. The general mean of all determinations agrees well with the results obtained by modern physical methods, and may, therefore, stand, until it is superseded by something of less uncertainty.

As for hydrogen, new values for its atomic weight can be deduced from eleven of the fundamental ratios. The computation has been roughly made, and found to be without significance. The combined values, so obtained, are of such small weight in comparison with ratio (1) that they only modify it in the sixth decimal place, a change which is not worth considering.

To sum up: The subjoined values, referred to O = 16 as the standard, have been computed from all the ratios, old and new, good, bad and indifferent:

H = 1.00779, ± .0001
C = 12.0038, ± .0002
N = 14.0101, ± .0001
Na = 23.0108, ± .00024
S = 32.0667, ± .00075
Cl = 35.4584, ± .0002
K = 39.0999, ± .0002
Br = 79.9197, ± .0003
Ag = 107.880, ± .00029
I = 126.9204, ± .00033

That these values are final, is not to be supposed. That they are, in the strict mathematical sense, the most probable values deducible from the experimental data, is also questionable. But that they are highly probable values, in harmony with the best modern evidence, can safely be asserted. The inferior determinations, low in weight, have practically vanished, one might almost say self-rejected, but not thrown out arbitrarily. The good measurements overwhelm the doubtful ones, whose influence upon the final computations is almost negligible. The nine values as given above, will be used in calculating the atomic weights of all the other elements.

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, Stas, Dittmar and Richards and Willard.

Mallet's experiments [1] 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:

$$7.1885 \text{ grm. LiCl gave } 24.3086 \text{ grm. AgCl.} \qquad 29.606$$
$$8.5947 \qquad " \qquad 29.0621 \qquad " \qquad 29.574$$

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, $29.581, \pm .0087$. Hence $Li = 6.943$.

Diehl,[2] whose paper begins with a good résumé 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, $59.417, \pm .006$

Hence $Li = 7.024$.

Diehl's investigation was quickly followed by a confirmation from Troost.[3] This chemist, in an earlier paper,[4] had sought to fix the atomic

[1] Amer. Journ. Sci., November, 1856. Chem. Gazette, 15, 7.
[2] Ann. Chem. Pharm., 121, 93.
[3] Zeit. Anal. Chem., 1, 402.
[4] Ann. Chim. Phys., 51, 108.

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, $\pm$ .020

Hence Li = 7.003.

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, $\pm$ .0145

Hence Li = 6.959.

Next in order is the work of Stas,[1] which was executed with his usual care. 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

Hence Li = 7.0110.

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

Hence Li = 6.956.

[1] Oeuvres Complètes, 1, 710-716.

The determinations of Dittmar[1] resemble those of Diehl; but the lithium carbonate used was dehydrated by fusion in an atmosphere of carbon dioxide. The carbonate was treated with sulphuric acid, and the CO_2 was collected and weighed in an absorption apparatus, which was tared by a similar apparatus after the method of Regnault. The following percentages of CO_2 in Li_2CO_3 were found:

<div align="center">

59.601
59.645
59.529—rejected
59.655
59.683
59.604
59.517
59.663
60.143—rejected
59.794
59.584

</div>

<div align="center">

Mean of all, 59.674

</div>

Rejecting the two experiments which Dittmar regards as untrustworthy, the mean of the remaining nine becomes 59.638, ± .0173, and $Li = 6.891$. This combines with the work of Diehl and Troost, as follows:

<div align="center">

Diehl ....59.417, ± .0060
Troost ....59.456, ± .0200
Dittmar ....59.638, ± .0173

General mean ....59.442, ± .0054

</div>

The unique merit of the determinations by Richards and Willard[2] is, not only that their work was done with scrupulous accuracy, but that their ratios give simultaneous values for the atomic weights of lithium, silver and chlorine, which are independent of all other data. Analyses of lithium perchlorate gave directly the molecular weight of lithium chloride, with reference to oxygen alone, and with that their other ratios are reducible. The data for the perchlorate are as follows, with vacuum weights:

<div align="center">

Preliminary Series.

</div>

$LiClO_4$.	$LiCl$.	Per cent. $LiCl$.
10.64596	4.24171	39.8434
12.77683	5.09073	39.8435
10.12750	4.03587	39.8506
13.04021	5.19638	39.8489

<div align="center">

Mean, 39.8466, ± .00125

</div>

[1] Trans. Roy. Soc. Edinburgh, 35, II, 429. 1889.
[2] Journ. Amer. Chem. Soc., 32, 4. 1910.

Final Series.

LiClO₄.	LiCl.	Per cent. LiCl.
12.79265	5.09744	39.8466
10.55416	4.20534	39.8453
11.39912	4.54205	39.8456
11.17008	4.45070	39.8448
17.84842	7.11167	39.8448
22.58273	8.99846	39.8466

Mean, 39.8456, ± .00023

The two series combined give a general mean of 39.8457, ± .00023. Hence LiCl = 42.393, and Li = 6.946.

The two other ratios determined by Richards and Willard are those between lithium chloride, silver chloride and silver. With vacuum weights, their data, first for the ratio Ag : LiCl are these:

Preliminary Series.[1]

LiCl.	Ag.	Ratio.
8.99620	22.89013	39.3017
5.25395	13.36777	39.3030

Mean, 39.3023, ± .00048

Hence Li = 6.9409.

Final Series.

LiCl.	Ag.	Ratio.
5.82422	14.82035	39.2988
6.28662	15.99687	39.2991
5.82076	14.81122	39.2996
6.70863	17.07038	39.2998
6.24717	15.89620	39.2998
7.75349	19.72977	39.2984
7.99108	20.33415	39.2988

Mean, 39.2992, ± .00014

Hence Li = 6.9300.

Combining the figures for this ratio we have—

Stas .... 39.358, ± .0011
Richards and Willard 1 ...... 39.3023, ± .00048
Richards and Willard 2 ...... 39.2992, ± .00014

General mean .... 39.3002, ± .00013

[1] The material used in the preliminary series contained a trace of sodium.

For the silver chloride ratio Richards and Willard give the following data:

Preliminary Series.

LiCl.	AgCl.	Ratio.
4.01994	13.59125	29.5774
6.32840	21.39635	29.5770
8.99620	30.41341	29.5797
4.66824	15.78111	29.5812
5.43032	18.35734	29.5812
5.10725	17.26504	29.5815
5.74000	19.40375	29.5819
5.42038	18.32417	29.5805
5.21573	17.63280	29.5797
6.56925	22.20617	29.5817
4.84268	16.37121	29.5805

Mean, 29.5802, ± .00033

Hence Li = 6.9414.

Final Series.

LiCl.	AgCl.	Ratio.
6.28662	21.25442	29.5779
5.82076	19.67875	29.5790
6.70863	22.68030	29.5791
6.24717	21.12073	29.5784
5.50051	18.59600	29.5790
8.34521	28.21438	29.5779
6.65987	22.51564	29.5788

Mean, 29.5786, ± .00014

Hence Li = 6.9391.

Combining the several series for this ratio we have—

Mallet	29.581, ± .0087
Troost	29.5925, ± .0145
Richards and Willard 1......	29.5802, ± .00033
Richards and Willard 2......	29.5786, ± .00014
General mean	29.5789, ± .00013

The older work, with its high probable errors, vanishes.

Summing up, the following ratios are now available, from which to compute the atomic weight of lithium:

$$(1). \ LiClO_4:LiCl::100:39.8457, \pm .00023$$
$$(2). \ Ag:LiCl::100:39.3002, \pm .00013$$
$$(3). \ AgCl:LiCl::100:29.5789, \pm .00013$$
$$(4). \ LiCl:LiNO_3::100:162.5953, \pm .0025$$
$$(5). \ Li_2CO_3:CO_2::100:59.442, \pm .0054$$

To reduce these ratios we have—

$$Ag = 107.880, \ \pm .00029 \qquad N = 14.0101, \pm .0001$$
$$Cl = 35.4584, \pm .0002 \qquad C = 12.0038, \pm .0002$$

Hence—

From ratio 1 ....$Li = 6.9346, \pm .00036$
"   "   " 2 ....6.9387, $\pm$ .00028
"   "   " 3 ....6.9395, $\pm$ .00095
"   "   " 4 ....6.9563, $\pm$ .0056
"   "   " 5 ....7.0122, $\pm$ .0024

General mean, $Li = 6.9379, \pm .00021$

Richards and Willard, from their three *final* series of determinations, deduce

$$Ag = 107.871$$
$$Cl = 35.454$$
$$Li = 6.939$$

The slightly lower value for lithium given in the general combination above is due to the higher value here assigned to chlorine. From the final silver and silver chloride series of Richards and Willard, the ratio $Ag:Cl::100:32.8637$ is derivable. This is a little lower than the value determined by Richards and Wells directly.

RUBIDIUM.

The atomic weight of rubidium has been determined by analyses of the chloride and bromide.

Bunsen,[1] 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

Hence Rb = 85.309.

The work of Piccard[2] 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

Hence Rb = 85.362.

Godeffroy,[3] starting with material containing both rubidium and cæsium, separated the two metals by fractional 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] Zeit. Anal. Chem., 1, 136. Poggend. Annal., 113, 339. 1861.
[2] Journ. prakt. Chem., 86, 454. 1862. Zeit. Anal. Chem., 1, 518.
[3] Ann. Chem. Pharm., 181, 185. 1876.

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

Hence Rb = 85.426.

Heycock[1] worked by two methods, but unfortunately his results are given only in abstract, without details. First, silver solution was added in slight deficiency to a solution of rubidium chloride, and the excess of the latter was measured by titration. The mean of seven experiments gave—

$$Ag:RbCl::107.93:120.801$$

Hence Rb = 85.287.

Two similar experiments with the bromide gave—

$$Ag:RbBr::107.93:165.437$$
$$Ag:RbBr::107.93:165.342$$

Mean, 165.3895, ± .0320

Hence Rb = 85.393.

The determinations by Archibald[2] were made with scrupulously purified materials, and with all of the precautions observed in the best modern investigations. The chloride and bromide were precipitated with known weights of silver, and the silver halide produced was also weighed. Two ratios were thus measured for each salt, and checked by the cross ratios between silver and chlorine or bromine, respectively. The weights, corrected to a vacuum, are given below, and also the four principal ratios:

Weight RbCl.	Weight AgCl.	Weight Ag.	AgCl ratio.	Ag ratio.
1.99966	2.37070	1.78454	84.349	112.054
2.06480	2.44778	1.84241	84.354	112.070
2.29368	2.71960	2.04710	84.339	112.046
1.09495	1.29796	.97702	84.360	112.070
2.14381	2.54118	1.91316	84.364	112.056
2.89700	3.43475	2.58550	84.344	112.047
2.19692	2.60452	1.96076	84.350	112.044
2.14543	2.54386	1.91462	84.338	112.055
2.12164	2.51557	1.89346	84.341	112.052
2.25777	2.67685	2.01515	84.344	112.040
2.18057	2.58528	1.94594	84.346	112.057
2.32699	2.75878	2.07668	84.348	112.053
4.00035	2.74233	3.56998	84.354	112.055
2.43440	2.88613	2.17233	84.348	112.064
		Mean, 84.3485, ± .0014		112.0545, ± .0016

[1] British Association Report, 1882, 449.
[2] Journ. Chem. Soc., 85, 776. 1904.

From the AgCl ratio, Rb $=85.446$.

From the Ag ratio, Rb $=85.426$.

And Ag : Cl : : 100 : 32.847.

The values for the AgCl ratio combine as follows :

Bunsen	84.253,	$\pm$ .031
Piccard	84.290,	$\pm$ .0105
Godeffroy	84.3345,	$\pm$ .0051
Archibald	84.3485,	$\pm$ .0014
General mean	84.3433,	$\pm$ .0013

Heycock's single value for the Ag ratio, reduced to the usual standard, becomes Ag : RbCl : : 100 : 111.926. It is not worth while to combine it with Archibald's values, for its influence would be quite negligible. In the AgCl ratio the older determinations count for something, but the general mean falls within the range of variation of Archibald's series.

The bromide analyses by Archibald are as follows :

Weight RbBr.	Weight AgBr.	Weight Ag.	AgBr ratio.	Ag ratio.
2.68170	3.04578	1.74930	88.047	153.301
2.07280	2.35401	1.35230	88.054	153.280
2.10086	2.38589	1.37061	88.053	153.278
2.61044	2.96462	1.70300	88.053	153.285
3.84082	4.36215	2.50590	88.049	153.272
3.77852	4.29084	2.46502	88.061	153.287
4.34299	4.93210	2.83340	88.056	153.278
			Mean, 88.0533,	153.283,
			$\pm$ .0012	$\pm$ .0024

From the Ag ratio, Rb $=85.442$.

From the AgBr ratio, Rb $=85.444$.

And Ag : Br : : 100 : 74.080.

Heycock's mean for the Ag ratio, reduced, becomes Ag : RbBr : : 100 : 153.238, $\pm$.0300. Its probable error is so high that combination with Archibald's data would be useless.

There are now four ratios from which to compute the atomic weight of rubidium :

(1). Ag:RbCl::100:112.0545, $\pm$ .0016

(2). AgCl:RbCl::100:84.3433, $\pm$ .0013

(3). Ag:RbBr::100:153.283, $\pm$ .0024

(4). AgBr:RbBr::100:88.0533, $\pm$ .0012

Reducing these ratios with Ag $=107.880, \pm.00029$, Cl $=35.4584, \pm$ .0002, and Br $=79.9197, \pm.0003$, we have—

From ratio 1	Rb $=85.426, \pm$ .0018
" " 2	85.438, $\pm$ .0019
" " 4	85.442, $\pm$ .0026
" " 3	85.444, $\pm$ .0023
	General mean, Rb $= 85.436, \pm$ .0010

CÆSIUM.

The atomic weight of cæsium, like that of rubidium, has been computed from analyses of the chloride and bromide, and also from experiments upon the nitrate. The earliest determination, by Bunsen,[1] was incorrect, because of impurity in the material studied. The first trustworthy determinations were published by Johnson and Allen[2] in 1863. 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 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

Hence Cs = 132.963.

Shortly after the results of Johnson and Allen appeared a new series of estimations was published by Bunsen.[3] 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

Hence Cs = 132.917.

Godeffroy's work[4] 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] Zeitsch. Anal. Chem., 1, 137.
[2] Amer. Journ. Sci. (2), 35, 94.
[3] Poggend. Annalen, 119, 1. 1863.
[4] Ann. Chem. Pharm., 181, 185. 1876.

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, $\pm$ .023

Hence Cs $=$ 132.483.

The foregoing investigations may now be regarded as merely preliminary, in comparison with the more elaborate determinations made by Richards and Archibald.[1] Their material was purified by fractional crystallization as cæsium dichloriodide, from which the chloride, bromide and nitrate were afterwards prepared. The chloride and bromide were freed from possible traces of moisture by fusion in an atmosphere of nitrogen, and analyzed by the usual method. That is, they were precipitated by known weights of silver dissolved as nitrate, and the silver chloride or bromide produced was also weighed. All the weights given are reduced to a vacuum standard. The results obtained with cæsium chloride are given in the next table:

Weight CsCl.	Weight AgCl.	Weight Ag.	AgCl ratio.	Ag ratio.
3.83054	3.26240	2.45600	117.415	155.967
3.95120	3.36532	2.53351	117.409	155.958
2.27237	1.93555	1.45686	117.402	155.977
3.02935	2.58003	1.94244	117.415	155.956
3.19774	2.72382	2.05023	117.399	155.970
2.35068	2.00253	1.50270	117.386	155.963
2.06245	1.75678	1.32251	117.399	155.950
2.56372	2.18358	. . . . . .	117.409	. . . . . .
2.01881	1.71972	1.29434	117.392	155.972
1.77391	1.51093	1.13743	117.405	155.958
3.08160	2.62484	1.97590	117.401	155.959
3.13117	2.66720	2.00760	117.395	155.966
5.06656	4.31570	3.24850	117.398	155.966

Mean, 117.402,   155.9635,
      $\pm$ .0016 $\pm$ .0016

From Ag ratio, Cs $=$ 132.795.
From AgCl ratio, Cs $=$ 132.824.
And Ag : Cl : : 100 : 32.846.

The silver chloride ratio combines with previous determinations thus:

Johnson and Allen............ 117.499, $\pm$ .025
Bunsen .... 117.467, $\pm$ .013
Godeffroy .... 117.164, $\pm$ .023
Richards and Archibald...... 117.402, $\pm$ .0016

General mean .... 117.405, $\pm$ .0016

[1] Proc. Amer. Acad., 38, 443. 1903. Zeitsch. anorg. Chem., 34, 353.

The older determinations practically vanish, leaving the Richards and Archibald mean almost unchanged.

The figures for the bromide series are as follows:

Weight CsBr.	Weight AgBr.	Weight Ag.	AgBr ratio.	Ag ratio.
3.49820	3.08815	1.77402	113.278	197.192
6.20409	5.47673	3.14606	113.281	197.202
2.17300	6.33213	2.63740	113.279	197.201
			Mean, 113.279,	197.198,
			± .0007	± .0045

From Ag ratio, Cs = 132.817.
From AgBr ratio, Cs = 132.818.
And Ag : Br : : 100 : 74.078.

When cæsium nitrate is fused with finely powdered silica, cæsium silicate is formed, and the elements of the nitric radicle are expelled. With weighed quantities of the nitrate, the loss of weight is equivalent to N_2O_5. The ratio $N_2O_5 : Cs_2O : : 100 : x$ is thus easily determined. In four experiments Richards and Archibald obtained the following results:

Weight CsNO₃.	Weight N₂O₅.	Ratio.
3.76112	1.04273	260.699
3.33334	.92416	260.689
4.81867	1.33590	260.706
5.04807	1.39960	260.679
	Mean,	260.693, ± .0039

Hence Cs = 132.801.

The five ratios for the atomic weight of cæsium are now as follows:

(1). Ag : CsCl : : 100 : 155.9635, ± .0016
(2). AgCl : CsCl : : 100 : 117.405, ± .0016
(3). Ag : CsBr : : 100 : 197.198, ± .0045
(4). AgBr : CsBr : : 100 : 113.279, ± .0007
(5). N_2O_5 : Cs_2O : : 100 : 260.693, ± .0039

Reducing these ratios with

Ag = 107.880, ± .00029   Br = 79.9197, ± .0003
Cl = 35.4584, ± .0002   N = 14.0101, ± .0039

we have—

From ratio 1 ....Cs = 132.795, ± .0018
"   "   5 ....132.801, ± .0022
"   "   3 ....132.818, ± .0049
"   "   4 ....132.818, ± .0015
"   "   2 ....132.828, ± .0024

General mean, Cs = 132.811, ± .0010

COPPER.

The atomic weight of copper has been chiefly determined by means of the oxide, the sulphate and the bromide, and by direct comparison of the metal with silver.

In dealing with the first-named compound nearly 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,[1] 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

Hence Cu = 63.298.

Erdmann and Marchand,[2] 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

Hence Cu = 63.462.

Still later we find a few analyses by Millon and Commaille.[3] 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 "	.... "	79.770 "

Mean, 79.7787, $\pm$ .0043

Hence Cu = 63.125.

For the third of these analyses the water estimation was not made, but for the other two it yielded results which, in sum, would make the atomic weight of copper 63.165. This figure has so high a probable error that we need not consider it further.

---

[1] Poggend. Annal., 8, 177. 1826.

[2] Journ. prakt. Chem., 31, 380. 1844.

[3] Fresenius' Zeitschrift, 2, 475. 1863.

The results obtained by Dumas [1] 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 $Cu = 63.5$.

In 1873 Hampe [2] published his careful determinations, which were for many years almost unqualifiedly accepted. 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

Hence $Cu = 63.344$.

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. CuSO₄	gave	16.04958 grm. Cu.	39.724	per cent.
44.64280	"	17.73466	"	39.726	"

Mean, 39.725, ± .0007

The last series of data gives $Cu = 63.314$, and is interesting for comparison with results obtained by Richards later.

In all of the foregoing experiments with copper oxide, that compound was obtained by ignition of the basic nitrate. But, as was shown in the chapter upon oxygen, copper oxide so prepared always carries occluded gases, which are not wholly expelled by heat. This point was thoroughly worked up by Richards [3] in his fourth memoir upon the atomic weight of copper, and it vitiates all the determinations previously made by this method.

By a series of experiments with copper oxide ignited at varying temperatures, and with different degrees of heat during the process of reduction, Richards obtained values for Cu ranging from 63.20 to 63.62. In two cases selected from this series he measured the amount of gaseous

---

[1] Ann. Chim. Phys. (3), 55, 129. 1859.

[2] Fresenius' Zeitschrift, 13, 352.

[3] Proc. Amer. Acad., 26, 276. 1891.

impurity, and corrected the results previously obtained. The results were as follows, with a vacuum reduction:

1.06253 grm. CuO gave	.84831 grm. Cu.	79.802 per cent.
1.91656 "	1.5298 "	79.820 "

Mean, 79.811, ± .0061

Correcting for the occluded gases in the oxide, the sum of the two experiments gives 79.901 per cent. of copper, whence Cu = 63.605. Three other indirect results, similarly corrected, gave 79.900 per cent. Cu in CuO, or Cu = 63.603. If we assign all five experiments equal weight, and judge their value by the two detailed above, the mean percentage becomes 79.900, ± .0038.

The recent experiments on copper oxide, by Murmann,[1] are of very doubtful utility. Copper was oxidized by heating in oxygen, and the oxide was also reduced in hydrogen, giving values for Cu varying from 63.513 to 64.397. The five experiments, with all corrections, including reduction to a vacuum, and eliminating the excessively high figure given above, may be stated in the following form:

Weight Cu.	Weight CuO.	Per cent. Cu.
1.13625	1.41856	80.099
2.64333	3.30923	79.878
1.07874	1.35045	79.880
5.12489	6.41350	79.908
3.33515	4.17315	79.919

Mean, 79.937, ± .0278

Hence Cu = 63.749. Murmann himself selected values from his series varying between 63.512 and 63.560.

These figures, by Richards and Murmann, need not be combined with the data given by previous observers, so far as practical purposes are concerned; but as this work is, in part, at least, a study of the compensation of errors, it may not be wasted time to effect the combination, as follows:

Berzelius	79.823,	± .0020
Erdmann and Marchand	79.8645,	± .0038
Millon and Commaille	79.7787,	± .0043
Hampe	79.8347,	± .0013
Richards	79.900,	± .0038
Murmann	79.937,	± .0278
General mean	79.836,	± .0010

[1] Monatsh. Chem., 27, 351. 1906.

This result is practically identical with that of Hampe, whose work receives excessive weight, as does also that of Berzelius. The oxide of copper is evidently of doubtful value in the measurement of this atomic weight.

The composition of copper sulphate has been studied, not only by Hampe, but also by Baubigny[1] and by Richards.[2] Baubigny merely ignited the anhydrous salt, weighing both it and the residual oxide, as follows:

$$4.022 \text{ grm. } CuSO_4 \text{ gave } 2.0035 \text{ CuO.} \quad 49.813 \text{ per cent.}$$
$$2.596 \qquad \text{``} \qquad 1.293 \quad \text{``} \qquad 49.807 \quad \text{``}$$

Mean, 49.810, $\pm$ .002

Hence $Cu = 63.460$.

The same ratio, in reverse—that is, the synthesis of the sulphate from the oxide—was investigated by Richards, who shows that the results obtained are vitiated by the same errors which affect the copper oxide experiments previously cited. The weights given are reduced to vacuum standards. The percentage of oxide in the sulphate is stated in the third column of figures:

$$1.0084 \text{ grm. } CuO \text{ gave } 2.0235 \text{ grm. } CuSO_4. \quad 49.835 \text{ per cent.}$$
$$2.7292 \qquad \text{``} \qquad 5.4770 \qquad \text{``} \qquad 49.830 \quad \text{``}$$
$$1.0144 \qquad \text{``} \qquad 2.0350 \qquad \text{``} \qquad 49.848 \quad \text{``}$$

Mean, 49.838, $\pm$ .0036

Hence $Cu = 63.550$.

The two series combine thus:

Baubigny .... 49.810, $\pm$ .0020
Richards .... 49.838, $\pm$ .0036

General mean .... 49.816, $\pm$ .0017

Here, plainly, the rigorous discussion gives Baubigny's work weight in excess of its merits.

In the memoir by Richards now under consideration, his fourth upon copper, the greater part of his attention is devoted to the sulphate, Hampe being followed closely in order to ascertain what sources of error affected the work of the latter. Crystallized sulphate, $CuSO_4.5H_2O$ was purified with every precaution and made the basis of operations. Three series of experiments were carried out, the water being determined by loss of weight upon heating, and the copper being estimated electrolytically. In the first series the following data were found, the weights being reduced to a vacuum, as in all of Richards' determinations:

[1] Compt. Rend., 97, 906. 1883.
[2] Proc. Amer. Acad., 26, 240. 1891.

	CuSO₄. 5 aq.	CuSO₄ at 250°.	Cu.
1............	2.8815	.....	.7337
2............	2.7152	.....	.6911
3...........	3.4639	2.2184	.8817

Hence the subjoined percentages:

	Water at 250°.	Cu in Cryst. Salt.	Cu in CuSO₄.
1............	.....	25.462	.....
2............	.....	25.452	.....
3............	35.958	25.454	39.745

Mean, 25.456

In the second series of analyses, which are stated with much detail, several refinements were introduced, in order to estimate also the sulphuric acid. These will be considered later. The results, given below, are numbered consecutively with the former series:

	CuSO₄. 5 aq.	CuSO₄ at 260°.	CuSO₄ at 360°.	Cu.
4.................	3.06006	1.9597	1.95637	.77886
5.................	2.81840	1.8048	......	.71740
6.................	7.50490	4.8064	4.79826	1.90973

Hence percentages as follows:

	Water, 260°.	Water, 360°.	Cu in Cryst. Salt.	Cu in CuSO₄, 260°.	Ditto, 360°.
4.....	35.959	36.068	25.452	39.744	39.811
5.....	35.964	.....	25.454	39.750	.....
6.....	35.957	36.065	25.446	39.733	39.799
Mean,	35.960	36.067	25.450	39.742	39.805

Hampe worked with a sulphate dried at 250°, but these data show that a little water is retained at that temperature, and consequently that his results must have been too low. The third of Richards' series resembles the second, but extra precautions were taken to avoid conceivable errors.

	CuSO₄. 5 aq.	CuSO₄ at 260°.	CuSO₄ at 370°.	Cu.
7................	2.88307	......	......	.73380
8...............	3.62913	2.32373	......	.92344
9...............	5.81352	......	3.71680	1.47926

And the percentages are:

	Water at 260°.	At 370°.	Cu in Cryst. Salt.	Cu in CuSO₄.
7..............	.....	.....	25.452	.....
8..............	35.970	.....	25.446	39.740(260°)
9..............	.....	36.067	25.445	39.799(370°)
			25.448	

In this series the determinations of sulphuric acid gave essentially the same results for all three samples of sulphate, although one was not dehydrated, and the others were heated to 260° and 370°, respectively. Hence the loss of weight in dehydration at either temperature represents water only, and does not involve partial decomposition of the sulphate. Between 360° and 400° copper sulphate is at essentially constant weight, but further experiments indicated that even at 400° it retained traces of water, and possibly as much as .042 per cent. The last trace is not expelled until the salt itself begins to decompose.

Richards also effected two syntheses of the sulphate directly from the metal by dissolving the latter in nitric acid, then evaporating to dryness with sulphuric acid, and heating to constant weight at 400°.

.67720 grm. Cu gave 1.7021 grm. $CuSO_4$.   39.786 per cent. Cu.
1.00613   "   2.5292   "   39.781   "

If we include these percentages in a series with the data from analyses 4, 6 and 9, which gave percentages of 39.811, 39.799 and 39.799, respectively, of copper in sulphate dried at 360° and upwards, the mean becomes

$$CuSO_4 : Cu : : 100 : 39.795, \pm .0036$$

Hence $Cu = 63.499$.

Since even this result is presumably too low, the other figures from sulphate dried at 250° must be rejected. Since Hampe's work on the sulphate is affected by the same sources of error, and apparently to a still greater extent, it need not be considered farther. As for Richards' nine determinations of Cu in $CuSO_4.5H_2O$, we may take them as one series giving a mean percentage of 25.451, ±.0011, and $Cu = 63.55$. This salt seems to retain occluded water, for the percentage of copper in it leads to a value for the atomic weight which is inconsistent with the best evidence, as will be seen later.

In the second and third series of Richards' experiments upon copper sulphate, the sulphuric acid was estimated by a method which gave valuable results. After the copper had been electrolytically precipitated, the acid which was set free was nearly neutralized by a weighed amount of pure sodium carbonate, and the slight excess remaining was determined by titration. Thus the weight of sodium carbonate equivalent to the copper was ascertained. The resulting solution of sodium sulphate was then evaporated to dryness, and a new ratio, connecting that salt with copper, was also determined. The cross ratio $Na_2CO_3 : Na_2SO_4$ has already been utilized in a previous chapter. The results, ignoring the weights of hydrated copper sulphate, are as follows, with the experiments numbered as before:

	Cu.	Na_2CO_3.	Na_2SO_4.
4............	.77886	1.2993	1.7411
6............	1.90973	3.1862	4.2679
7............	.73380	1.22427	1.63994
8............	.92344	1.54075	......
9............	1.47926	......	3.30658

Hence,

$Cu:Na_2CO_3::100:x.$	$Cu:Na_2SO_4::100:x$
166.824	223.549
166.840	223.482
166.840	223.538
166.849	223.529
Mean, 166.838, ± .0035	Mean, 223.525, ± .0098

Hence Cu = 63.55.   Hence Cu = 63.571.

In one more experiment the sulphuric acid was weighed as barium sulphate, the latter being corrected for occluded salts. 3.1902 grm. $CuSO_4.5H_2O$ gave 2.9761 $BaSO_4$; hence $CuSO_4.5H_2O : BaSO_4 :: 100 : 93.289$. The sulphate contained 25.448 per cent. of Cu: hence $BaSO_4 : Cu :: 93.289 : 25.448$, and Cu = 63.676. Still other ratios can be deduced from Richards' work on the sulphate, but in view of the uncertainties relative to the water in the salt they are hardly worth computing.

In his third paper upon the atomic weight of copper,[1] Richards studied the dibromide, $CuBr_2$. In preparing this salt he used hydrobromic acid made from pure materials, and further purified by ten distillations. This was saturated with copper oxide prepared from pure electrolytic copper, and the solution obtained was proved to be free from basic salts. As the crystallized compound was not easily obtained in a satisfactory condition, weighed quantities of the solution were taken for analysis, in which, after expulsion of bromine by nitric and sulphuric acids, the copper was determined by electrolysis. In other portions of solution the bromine was precipitated by silver nitrate, and weighed as silver bromide. The first preliminary series of experiments gave the subjoined results, with vacuum weights as usual:

In 25 Grammes of Solution.

Cu.	AgBr.
.4164	2.4599
.4164	2.4605
.4164	2.4605
.4165	2.4599

Hence 2AgBr : Cu :: 100 : 16.927, ± .0013.

[1] Proc. Amer. Acad., 25, 195. 1890.

The second, also preliminary series, was made with more dilute solutions, and came out as follows:

In 25 Grammes of Solution.

Cu.	AgBr.
.26190	1.5478
.26185	1.5477
	1.5479

Hence $2AgBr : Cu :: 100 : 16.919, \pm .0012$.

In the third series, two distinct lots of crystallized bromide were dissolved, and the solutions examined in the same way:

Cu.	AgBr.	Ratio.
.2500	1.4771	16.925
.5473	3.2348	16.919

Mean, $16.922, \pm .0020$

In the final set of analyses, the materials used were purified even more scrupulously than before, and the process was distinctly modified, as regards the determination of the bromine. The solution of the bromide was added to a solution of pure silver in nitric acid, not quite sufficient for complete precipitation. The slight excess of bromine was then determined by titration with a solution containing one gramme of silver to the litre. Thus silver proportional to the copper in the bromide was determined, and the silver bromide was weighed in a Gooch crucible as before. The results are subjoined:

In 50 Grammes of Solution.

Cu.	Ag.	AgBr.
.54755	1.8586	3.2350
.54750	1.8579	3.2340
	1.8583	3.2348

Hence $Cu : 2Ag :: 100 : 339.392, \pm .0108$, and $2AgBr : Cu :: 100 : 16.927, \pm .0012$.

The latter ratio, combined with the results of the three preceding series, gives a general mean of:

$$2AgBr : Cu :: 100 : 16.924, \pm .0007$$

Hence $Cu = 63.566$.

In his two earlier papers [1] Richards determined the copper-silver ratio directly—that is, without the weighing of any compound of either metal. By placing pure copper in an *ice-cold* solution of silver nitrate, metallic

---

[1] Proc. Amer. Acad., 22, 346, and 23, 177. 1886 and 1887.

silver is thrown down, and the weights of the two metals were in equivalent proportions. In the first paper the following results were obtained. The third column gives the value of x in the ratio $Cu : 2Ag :: 100 : x$.

Cu taken.	Ag found.	Ratio.
.53875	1.8292	339.527
.56190	1.9076	339.491
1.00220	3.4016	339.414
1.30135	4.4173	339.440
.99870	3.39035	339.477
1.02050	3.4646	339.500

Mean, 339.475, $\pm$ .0114

In the second paper Richards states that the silver of the fifth experiment, which had been dried at 150°, as were also the others, still retained water, to the extent of four-tenths milligramme in two grammes. If we assume this correction to be fairly uniform, as the concordance of the series indicates, and apply it throughout, the mean value for the ratio then becomes 339.408, $\pm$ .0114. This procedure, however, leaves the ratio in some uncertainty, and accordingly some new determinations were made, in which the silver, collected in a Gooch crucible, was heated to incipient redness before final weighing. Copper from two distinct sources was taken, and three experiments were carried out upon one sample to two with the other. Treating both sets as one series, the results were as follows:

Cu taken.	Ag found.	Ratio.
.75760	2.5713	339.40
.95040	3.2256	339.39
.75993	2.5794	339.42
1.02060	3.4640	339.42
.90460	3.0701	339.39

Mean, 339.404, $\pm$ .0046

a value practically identical with the corrected mean of the previous determinations, and with that found in the later experiments upon copper bromide. Hence $Cu = 63.570$.

In various electrical investigations the same ratio, the electrochemical equivalent of copper, has been repeatedly measured, and the later results of Lord Rayleigh and Mrs. Sidgewick,[1] Gray,[2] Shaw,[3] and Vanni[4] may properly be included in this discussion. As the data are somewhat differently stated, I have reduced them all to the common standard adopted

---

[1] Phil. Trans., 175, 458.
[2] Phil. Mag. (5), 22, 389.
[3] British Assoc. Report, 1886. Abstract in Phil. Mag. (5), 23, 138.
[4] Ann. der Phys. (Wiedemann's) (2), 44. 214.

above. Gray gives two sets of measurements, one made with large and the other with small metallic plates:

Rayleigh and S.	Gray 1.	Gray 2.	Shaw.	Vanni.
340.483	341.297	340.252	339.68	340.483
340.832	341.413	339.674	340.05	340.600
340.367	340.815	340.020	339.84	340.367
———	340.252	339.905	339.71	340.252
340.561,	339.905	339.674	340.04	340.600
± .0935	341.064	339.328	339.94	340.136
	340.832	340.136	340.35	———
	341.297	340.136	339.82	340.406,
	341.064	340.136	340.09	± .0520
	341.413	340.020	339.84	
	———	340.020	339.90	
	340.935,	340.136	339.98	
	± .1072	———	340.14	
		339.953,	340.56	
		± .0521	339.82	
			339.983,	
			± .0411	

The lack of sharp concordance in these data and the consequently high probable errors seem to indicate a distinct superiority of the purely chemical method of determination over that adopted by the physicist. This supposition is strengthened by the electrochemical experiments of Richards, Collins and Heimrod,[1] who precipitated copper and silver simultaneously in the same current of electricity. Their first series, with vacuum weights, is as follows:

Weight Cu.	Weight Ag.	Ratio.
.44478	1.51064	339.64
.31645	1.07473	339.63
.24968	.84792	339.60
1.02186	3.47056	339.63
.66166	2.24538	339.36
.63027	2.14050	339.63
.45919	1.55905	339.72
.39177	1.33071	339.67
1.11030	3.76990	339.54
.67564	2.29655	339.91
.48232	1.63768	339.54
.83092	2.82203	339.63
.63491	2.15735	339.79
.70102	2.37868	339.32
.84469	2.86608	339.55
.87462	2.97114	339.71
.69405	2.35683	339.58

Hence Cu = 63.532.

Mean, 339.615, ± .0230

[1] Proc. Amer. Acad., 35, 123. 1899.

In a second series of experiments the copper was deposited from solutions saturated with cuprous sulphate:

Weight Cu.	Weight Ag.	Ratio.
.71847	2.43935	339.52
.71861	2.43940	339.46
.72019	2.44603	339.64
.97193	3.30100	339.63
.50916	1.72859	339.50
.76188	2.58664	339.51

Mean, 339.543, ± .0200

Hence Cu = 63.544.

In the foregoing series the temperature of the solution was $0°$. Two experiments at higher temperatures, $56°$-$61°$, gave lower values for the ratio, and consequently a higher atomic weight for copper:

Weight Cu.	Weight Ag.	Ratio.
.97295	3.30100	339.28
.76214	2.58664	339.39

Mean, 339.335, ± .0370

Hence Cu = 63.569.

There is also an electrochemical series of determinations by Gallo,[1] of slight importance. The figures with vacuum weights are—

Weight Cu.	Weight Ag.	Ratio.
.21805	.73937	339.083
.27153	.92062	339.049
.19001	.64571	339.829
.39585	1.34578	339.972

Mean, 339.483, ± .164

Hence Cu = 63.555.

The general combination of all the data relative to the copper-silver ratio is as follows:

Richards, first series, corrected.............. 339.408, ± .0114
Richards, second series...................... 339.404, ± .0046
Richards, CuBr$_2$ series....................... 339.392, ± .0108
Richards, Collins, and Heimrod, first......... 339.615, ± .0230
Richards, Collins, and Heimrod, second...... 339.543, ± .0200
Richards, Collins and Heimrod, third........ 339.335, ± .0370
Rayleigh and Sidgewick..................... 340.561, ± .0935
Gray, large plates........................... 340.935, ± .1072
Gray, small plates........................... 339.953, ± .0521
Shaw .... 339.983, ± .0411
Vanni .... 340.406, ± .0520
Gallo .... 339.483, ± .1640

General mean .... 339.423, ± .0038

---

[1] Atti Acad. Lincei (5), 14, 23. 1905.

If we combine Richards' three series into a general mean separately, the value found for the ratio becomes 339.402,±.0040. The other determinations, having high probable errors, affect this mean but slightly, and it makes little difference whether they are retained or rejected.

We now have the following ratios from which to compute the atomic weight of copper:

(1). Percentage of Cu in CuO, 79.836, ± .0010
(2). Percentage of Cu in $CuSO_4$, 39.795, ± .0036
(3). Percentage of Cu in $CuSO_4$, $5H_2O$, 25.451, ± .0011
(4). Percentage of CuO in $CuSO_4$, 49.816, ± .0017
(5). $Cu:Na_2CO_3::100:166.838$, ± .0035
(6). $Cu:Na_2SO_4::100:223.525$, ± .0098
(7). $BaSO_4:Cu::93.289:25.448$
(8). $2AgBr:Cu::100:16.924$, ± .0007
(9). $Cu:2Ag::100:339.423$, ± .0038

Ratio 7 rests upon a single experiment, and must be arbitrarily weighted. For this purpose, the value for copper derived from it may be given double the probable error of the highest among the other determinations. To reduce the ratios we have—

Ag = 107.880, ± .00029   C = 12.0038, ± .0002
Cl = 35.4584, ± .0002   Na = 23.0108, ± .00024
Br = 79.9197, ± .0003   Ba = 137.363, ± .0025
S = 32.0667, ± .00075   H = 1.0079, ± .00001

Hence,

From ratio 1 ....Cu = 63.3493, ± .0032
"   "   4 ....63.4796, ± .0039
"   "   2 ....63.4993, ± .0069
"   "   3 ....63.5497, ± .0033
"   "   5 ....63.5499, ± .0024
"   "   8 ....63.5664, ± .0027
"   "   9 ....63.5667, ± .00075
"   "   6 ....63.5714, ± .0029
"   "   7 ....63.6765, ± .0138

General mean, Cu = 63.5550, ± .00063

This value is possibly, but not certainly, a little too low. The rejection of the first value, derived from copper oxide, raises the general mean to 63.564, which may be nearer the truth.

GOLD.

Among the early estimates of the atomic weight of gold the only ones worthy of consideration are those of Berzelius and Levol.

The earliest method adopted by Berzelius[1] 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 if Hg = 200, Au = 196.397.

In a later investigation[2] Berzelius resorted to the analysis of potassio-auric chloride, $KCl.AuCl_3$. 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:

4.1445 grm.	$KAuCl_4$	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, $\pm$ .026

Hence Au = 196.69.

Still a third series of experiments by Berzelius[3] 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. One hundred parts of P precipitate the quantities of Au given in the third column:

[1] Poggend. Annalen, 8, 177.
[2] Lehrbuch, 5 Aufl., 3, 1212.
[3] Lehrbuch, 5 Aufl., 3, 1188.

.829 grm. P precipitated 8.714 grm. Au.   1051.15

.754   "   7.930   "   1051.73

Mean, 1051.44, ± .196

Hence, if P = 31, Au = 195.568.

Levol's [1] 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 = 196.49.

All these values may be neglected as worthless, except that derived from Berzelius' K_2AuCl_6 series.

In 1886 Krüss [2] published the first of the recent determinations of the atomic weight under consideration, several distinct methods being recorded. First, in a solution of pure auric chloride the gold was precipitated by means of aqueous sulphurous acid. In the filtrate from the gold the chlorine was thrown down as silver chloride, and thus the ratio Au : 3AgCl was measured. I subjoin Krüss' weights, together with a third column giving the gold equivalent to 100 parts of silver chloride:

Au.	AgCl.	Ratio.
7.72076	16.84737	45.828
5.68290	12.40425	45.814
3.24773	7.08667	45.828
4.49167	9.80475	45.811
3.47949	7.59300	45.825
3.26836	7.13132	45.832
5.16181	11.26524	45.821
4.86044	10.60431	45.834

Mean, 45.824, ± .0020

Hence Au = 197.05.

The remainder of Krüss' determinations were made with potassium auribromide, $KAuBr_4$, and with this salt several ratios were measured. The salt was prepared from pure materials, repeatedly recrystallized under precautions to exclude access of atmospheric dust, and dried over phosphorus pentoxide. First, its percentage of gold was determined, sometimes by reduction with sulphurous acid, sometimes by heating in a stream of hydrogen. For this ratio, the weights and percentages are as follows, the experiments being numbered for further reference, and the reducing agent being indicated:

---

[1] Untersuchungen über das Atomgewicht des Goldes. München, 1886. 112 pp., 8vo.

[2] Ann. Chim. Phys. (3), 30, 355. 1850.

	$KAuBr_4$.	Au.	Per cent.
1. SO_2	10.64821	3.77753	35.476
2. SO_2	4.71974	1.67330	35.453
3. H	7.05762	2.50122	35.440
4. H	4.49558	1.59434	35.465
5. SO_2	8.72302	3.09448	35.475
6. SO_2	7.66932	2.71860	35.448
7. SO_2	7.15498	2.53695	35.457
8. H	12.26334	4.34997	35.471
9. H	7.10342	2.51919	35.465

Mean, 35.461, $\pm$ .0028

Hence Au = 197.13.

In five of the foregoing experiments the reductions were effected with sulphurous acid; and in these, after filtering off the gold, the bromine was thrown down and weighed as silver bromide. This, in comparison with the gold, gives the ratio Au : 4AgBr :: 100 : x :

	Au.	$4AgBr$.	Ratio.
1.............	3.77753	14.39542	381.080
2.............	1.67330	6.37952	381.254
5.............	3.09448	11.78993	380.999
6.............	2.71860	10.35902	381.042
7.............	2.53695	9.66117	380.731

Mean, 381.021, $\pm$ .057

Hence Au : AgBr :: 100 : 95.255, $\pm$ .0142, and Au = 197.16.

In the remaining experiments, Nos. 3, 4, 8 and 9, the $KAuBr_4$ was reduced in a stream of hydrogen, the loss of weight, Br_3, being noted. In the residue the gold was determined, as noted above, and the KBr was also collected and weighed. The weights were as follows:

	Au.	Loss, Br_3.	KBr.
3.............	2.50122	3.04422	1.51090
4.............	1.59434	1.93937	.96243
8.............	4.34997	5.29316	2.62700
9.............	2.51919	3.06534	1.52153

From these data we obtain two more ratios, viz., Au : Br_3 :: 100 : x, and Au : KBr :: 100 : x, thus:

	$Au:Br_3$.	$Au:KBr$.
3...................	121.710	60.405
4...................	121.641	60.365
8...................	121.683	60.391
9...................	121.680	60.398

Mean, 121.678, $\pm$ .0100   Mean, 60.390, $\pm$ .0059

Hence Au = 197.04, and 197.08.

From all the ratios, taken together, Krüss deduces a final value of $Au = 197.13$, if $O = 16$. It is obviously possible to derive still other ratios from the results given, but to do so would be to depart unnecessarily from the author's methods as stated by himself.

Thorpe and Laurie,[1] whose work appeared shortly after that of Krüss, also made use of the salt $KAuBr_4$, but, on account of difficulty in drying it without change, they did not weigh it directly. After proving the constancy in it of the ratio $Au : KBr$, even after repeated crystallizations, they adopted the following method: The unweighed salt was heated with gradual increase of temperature, up to about 160°, for several hours, and afterwards more strongly over a small Bunsen flame. This was done in a porcelain crucible, tared by another in weighing, which latter was treated in precisely the same way. The residue, $KBr + Au$, was weighed, the KBr dissolved out, and the gold then weighed separately. The weight of KBr was taken by difference. The ratio $Au : KBr :: 100 : x$ appears in a third column:

Au.	KBr.	Ratio.
6.19001	3.73440	60.329
4.76957	2.87715	60.323
4.14050	2.49822	60.336
3.60344	2.17440	60.342
3.67963	2.21978	60.326
4.57757	2.76195	60.337
5.36659	3.23821	60.326
5.16406	3.11533	60.327

Mean, 60.331, ± .0016

Hence $Au = 197.28$.

This mean combines with Krüss' thus:

Krüss .... 60.390, ± .0059
Thorpe and Laurie................... 60.331, ± .0016

General mean .... 60.338, ± .0015

The potassium bromide of the previous experiments was next titrated with a solution of pure silver by Stas' method, the operation being performed in red light. Thus we get the following data for the ratio $Ag : Au :: 100 : x$, using the weights of gold already obtained:

[1] Journ. Chem. Soc., 51, 565. 1887.

Ag.	Au.	Ratio.
3.38451	6.19001	182.893
2.60896	4.76957	182.813
2.28830	4.18266	182.786
2.26415	4.14050	182.868
1.97147	3.60344	182.775
2.01292	3.67963	182.801
2.50334	4.57757	182.863
2.93608	5.36659	182.780
2.82401	5.16406	182.865

Mean, 182.827, ± .0101

Hence Au = 197.24.

Finally, in eight of these experiments, the silver bromide formed during titration was collected and weighed, giving values for the ratio Au : AgBr :: 100 : x, as follows:

Au.	AgBr.	Ratio.
6.19001	5.89199	95.186
4.76957	4.54261	95.242
4.18266	3.98288	95.224
4.14050	3.94309	95.232
3.60344	3.43015	95.191
3.67963	3.50207	95.175
4.57757	4.35736	95.189
5.36659	5.11045	95.227

Mean, 95.208, ± .0061

Krüss found, 95.255, ± .0142

General mean, 95.222, ± .0056

From Thorpe and Laurie's mean, Au = 197.25.

From the second and third of the ratios measured by Thorpe and Laurie an independent value for the ratio Ag : Br may be computed. It becomes 100 : 74.072, which agrees fairly with the direct determinations made by other chemists. Similarly, the ratios Ag : KBr and AgBr : KBr may be calculated, giving additional checks upon the accuracy of the manipulation, though not upon the purity of the original material studied.

Thorpe and Laurie suggest objections to the work done by Krüss, on the ground that the salt KAuBr$_4$ cannot be completely dried without loss of bromine. This suggestion led to a controversy between them and Krüss, which in effect was briefly as follows:

First, Krüss[1] urges that the potassium auribromide ordinarily contains traces of free gold, not belonging to the salt, produced by the reducing action of dust particles taken up from the air. He applies a correction

---

[1] Ber. Deutsch. chem. Gesell., 20, 2365. 1887.

for this supposed free gold to the determinations made by Thorpe and Laurie, and thus brings their results into harmony with his own. To this argument Thorpe and Laurie[1] reply, somewhat in detail, stating that the error indicated was guarded against by them, and that they had dissolved quantities of from eight to nineteen grammes of the auribromide without a trace of free gold becoming visible. A final note in defense of his work was published by Krüss a little later.[2]

In 1889 an elaborate set of determinations of this constant was published by Mallet,[3] whose experiments are classified into seven distinct series. First, a neutral solution of auric chloride was prepared, which was weighed off in two approximately equal portions. In one of these the gold was precipitated by pure sulphurous acid, collected, washed, dried, ignited in a Sprengel vacuum, and weighed. To the second portion a solution containing a known weight of pure silver was added. After filtering, with all due precautions, the silver remaining in the filtrate was determined by titration with a weighed solution of pure hydrobromic acid. We have thus a weight of gold, and the weight of silver needed to precipitate the three atoms of chlorine combined with it; in other words, the ratio $3Ag : Au :: 100 : x$. All weights in this and the subsequent series are reduced to a vacuum standard, and all weighings were made against corresponding tares:

Au.	Ag.	Ratio.
7.6075	12.4875	60.921
8.4212	13.8280	60.900
6.9407	11.3973	60.898
3.3682	5.5286	60.923
2.8244	4.6371	60.909

Mean, 60.910, ± .0034

Hence $Ag : Au :: 100 : 182.730, \pm .0102$, and $Au = 197.13$.

The second series of determinations was essentially like the first, except that auric bromide was taken instead of the chloride. The ratio measured, $3Ag : Au$, is precisely the same as before. Results as follows:

Au.	Ag.	Ratio.
8.2345	13.5149	60.929
7.6901	12.6251	60.911
10.5233	17.2666	60.945
2.7498	4.5141	60 916
3.5620	5.8471	60.919
3.9081	6.4129	60.941

Mean, 60.927, ± .0038

Hence $Ag : Au :: 100 : 182.781, \pm .0114$, and $Au = 197.18$.

---

[1] Berichte, 20, 3036, and Journ. Chem. Soc., 51, 866. 1887.
[2] Berichte, 21, 126. 1888.
[3] Philosophical Transactions, 180, 395. 1889.

In the third series of experiments the salt $KAuBr_4$ was taken, purified by five recrystallizations. The solution of this was weighed out into nearly equal parts, the gold being measured as in the two preceding series in one portion, and the bromine thrown down by a standard silver solution as before. This gives the ratio $4Ag : Au :: 100 : x$.

Au.	Ag.	Ratio.
5.7048	12.4851	45.693
7.9612	17.4193	45.693
2.4455	5.3513	45.699
4.1632	9.1153	45.673

Mean, 45.689, ± .0040

Hence $Ag : Au :: 100 : 182.756, ± .0160$, and $Au = 197.16$.

The fifth series of determinations, which for present purposes naturally precedes the fourth, was electrolytic in character, gold and silver being simultaneously precipitated by the same current. The gold was in solution as potassium aurocyanide, and the silver in the form of potassium silver cyanide. The equivalent weights of the two metals, thrown down in the same time, were as follows, giving directly the ratio $Ag : Au :: 100 : x$.

Au.	Ag.	Ratio.
5.2721	2.8849	182.748
6.3088	3.4487	182.933
4.2770	2.3393	182.832
3.5123	1.9223	182.713
3.6804	2.0132	182.814

Mean, 182.808, ± .0256

Hence $Au = 197.22$.

This mean may be combined with the preceding means, and also with the determination of the same ratio by Thorpe and Laurie, thus:

Thorpe and Laurie...........	182.827, ± .0101
Mallet, chloride series........	182.730, ± .0102
Mallet, bromide series........	182.781, ± .0114
Mallet, $KAuBr_4$ series........	182.756, ± .0160
Mallet, electrolytic	182.808, ± .0256
General mean	182.778, ± .0055

In Mallet's fourth series a radically new method was employed. Tri-methyl-ammonium aurichloride, $N(CH_3)_3HAuCl_4$, was decomposed by heat, and the residual gold was determined. In order to avoid loss by

12

spattering, the salt was heated in a crucible under a layer of fine siliceous sand of known weight. Several crops of crystals of the salt were studied, as a check against impurities, but all gave concordant values.

Salt.	Residual Au.	Per cent. Au.
14.9072	7.3754	49.475
15.5263	7.6831	49.484
10.4523	5.1712	49.474
6.5912	3.2603	49.464
5.5744	2.7579	49.474

Mean, 49.474, ± .0021

Hence Au = 197.73.

In his sixth and seventh series Mallet seeks to establish, by direct measurement, the ratio between hydrogen and gold. In their experimental details his methods are somewhat elaborate, and only the processes, in the most general way, can be indicated here. First, gold was precipitated electrolytically from a solution of potassium aurocyanide, and its weight was compared with that of the amount of hydrogen simultaneously liberated in a voltameter by the same current in the same time. The hydrogen was measured, and its weight was then computed from its density. The volumes are given, of course, at $0°$ and 760 mm.

Wt. Au.	Vol. H, cc.	Wt. H.
4.0472	228.64	.0205483
4.0226	227.03	.0204046
4.0955	231.55	.0208103

These data, with the weight of one litre of hydrogen taken as 0.89872 gramme, give the subjoined values in the ratio $H : Au :: 1 : x$.

196.960
197.151
196.805

Mean, 196.972, ± .0675

In the last series of experiments a known quantity of metallic zinc was dissolved in dilute sulphuric acid, and the amount of hydrogen evolved was measured. Then a solution of pure auric chloride or bromide was treated with a definite weight of the same zinc, and the quantity of gold thrown down was determined. The zinc itself was purified by fractional distillation in a Sprengel vacuum. From these data the ratio $3H : Au$ was computed by direct comparison of the weight of gold and that of the liberated hydrogen. The results were as follows:

Wt. Au.	Vol. H, cc.	Wt. H.
10.3512	1756.10	.157824
8.2525	1400.38	.125857
8.1004	1374.87	.123565
3.2913	558.64	.050206
3.4835	590.93	.053109
3.6421	618.11	.055551

Hence for the ratio $3H : Au :: 1 : x$ we have:

$$65.587$$
$$65.571$$
$$65.557$$
$$65.556$$
$$65.593$$
$$65.563$$

Mean, $65.571, \pm .00436$

And $H : Au :: 1 : 196.713, \pm .0131$. This, combined with the value found in the preceding series, gives a general mean of $196.722, \pm .0129$. The ratios available for gold are now as follows:

(1). $KCl : Au :: 100 : 263.730, \pm .026$
(2). $3AgCl : Au :: 100 : 45.824, \pm .0020$
(3). $KAuBr_4 : Au :: 100 : 35.461, \pm .0028$
(4). $Au : AgBr :: 100 : 95.222, \pm .0056$
(5). $Au : 3Br :: 100 : 121.678, \pm .0100$
(6). $Au : KBr :: 100 : 60.338, \pm .0015$
(7). $Ag : Au :: 100 : 182.778, \pm .0055$
(8). $NC_3H_{10}AuCl_4 : Au :: 100 : 49.474, \pm .0021$
(9). $H : Au :: 1 : 196.722, \pm .0129$

The antecedent atomic weights are—

$Ag = 107.880, \pm .00029$	$N = 14.0101, \pm .0001$
$Cl = 35.4584, \pm .0002$	$K = 39.0999, \pm .0002$
$Br = 79.9197, \pm .0003$	$C = 12.0038, \pm .0002$
$H = 1.00779, \pm .00001$	

Hence,

From ratio 1 ....$Au = 196.687, \pm .0195$
    "   " 5 ....197.044, $\pm .0163$
    "   " 2 ....197.050, $\pm .0086$
    "   " 3 ....197.131, $\pm .0178$
    "   " 7 ....197.181, $\pm .0060$
    "   " 4 ....197.223, $\pm .0116$
    "   " 6 ....197.255, $\pm .0049$
    "   " 8 ....197.728, $\pm .0118$
    "   " 9 ....198.254, $\pm .0130$

General mean, $Au = 197.269, \pm .0030$

Rejection of the very doubtful values from ratios 1, 8 and 9 lowers the mean to 197.19. The atomic weight of gold is probably not far from 197.2.

The ninth or last value in the foregoing series represents Mallet's ratio between gold and hydrogen, and is peculiarly instructive. In Mallet's paper the several ratios determined were discussed upon the basis of $O = 15.96$, referred to hydrogen as unity. This, on the oxygen scale, is equivalent to $H = 1.0025$. On that basis the determination in question agreed well with the others; but with $H = 1.00779$, the present value, it is enormously raised. The former agreement between the several series of gold values was therefore only apparent, and shows that concordance among determinations may be only coincidence, and no real proof of accuracy. It is probable, furthermore, that direct comparisons of metals with hydrogen cannot give good measurements of atomic weights, for several reasons. First, it is not possible to be certain that every trace of hydrogen has been collected and measured, and any loss tends to raise the apparent atomic weight of the metal studied; secondly, the weight of the hydrogen is computed from its volume, and a slight change in the factors used in reduction of the observations may make a considerable difference in the final result. These uncertainties exist in all determinations of atomic weights hitherto made by the hydrogen method.

CALCIUM.

Much of the older work on the atomic weight of calcium, including the earliest determinations by Berzelius, may be disregarded as having no present value. Baup's [1] analyses of organic salts of calcium are interesting, but carry no weight now. They led to the value $Ca = 39.98$. As for Salvétat's [2] determination, that was merely given as a statement of results, without such details as would make his work available for discussion.

The largest factor in measuring the atomic weight of calcium, is the composition of calcium carbonate, as determined by several investigators. This will be considered first, and the determinations based upon calcium sulphate and calcium chloride follow later.

In 1842 Dumas [3] 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. His figures are as follows:

49.916 grm. $CaCO_3$	gave 28.016 grm. CaO.	56.12 per cent.
50.497 "	28.305 "	56.04 "
64.508 "	36.167 "	56.06 "

Mean, $56.073, \pm .016$

Hence $Ca = 40.111$.

About this same time Erdmann and Marchand [4] began their researches upon the same subject. Two ignitions of spar, containing .04 per cent. of impurity, gave resepectively 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:

$$56.03$$
$$55.98$$
$$56.00$$
$$55.99$$

Mean, $56.00, \pm .007$

Hence $Ca = 40.005$.

[1] Bull. Universelle des Scienc s de Genève, 39, 347. 1842.
[2] Compt. Rend., 17, 318. 1843.
[3] Compt. Rend., 14, 547. 1842.
[4] Journ. prakt. Chem., 26, 472. 1842.

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:

$$56.00$$
$$56.02$$

Mean, 56.01, ± .007

In a still later paper [1] 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:

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

Hence Ca = 40.068.

Six years later Erdmann and Marchand [2] 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 was 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.

Hence Ca = 40.018.

Herzfeld,[3] in his determinations of atomic weight, made use of artificial calcium carbonate. The lime was prepared by ignition of the oxalate, and then converted into bicarbonate by treatment with solid

---

[1] Journ. prakt. Chem., 31, 269. 1844.

[2] Journ. prakt. Chem., 50, 237. 1850.

[3] Zeitschr. Ver. Rübenzucker Industrie, 47, 497. 1897. Partly reproduced in Ber., 34, 559. 1904.

carbon dioxide and water under pressure. By heating in a silver dish
the bicarbonate was converted into the normal salt, which was weighed,
and then ignited at a temperature of 1300°-1400°. The data are as
follows:

3.9772 grm. $CaCO_3$ gave	2.2268 grm. CaO.	55.989 per cent.
2.3614 "	1.3218 "	55.975 "
3.2966 "	1.8456 "	55.985 "

Mean, 55.983, ± .0028

Hence Ca = 39.966.

Hinrichsen,[1] in his two separate communications, gives analyses of spar
from two distinct localities, namely, Iceland and the Crimea. In each
case very small quantities of impurity were present, which were carefully
determined and corrected for. The spar, previously freed from all traces
of moisture, was ignited in an electric furnace, at a temperature between
1200° and 1400°. The results obtained, with all corrections applied,
and vacuum weights, are subjoined:

First Series.

30.72157 grm. $CaCO_3$ gave	17.22354 grm. CaO.	56.0633 per cent.
32.77791 "	18.375587 "	56.0617 "
34.45625 "	19.31698 "	56.0623 "
33.36885 "	18.70723 "	56.0620 "

Second Series.

31.20762 grm. $CaCO_3$ gave	17.49526 grm. CaO.	59.0608 per cent.
22.00588 "	12.33642 "	56.0602 "

Mean of both series as one, 56.0617, ± .0003

Hence Ca = 40.145.

Combining all these determinations, we have for the percentage of
CaO from $CaCO_3$:

Dumas	56.073, ± .016
Erdmann and Marchand, 1............	56.000, ± .007
Erdmann and Marchand, 2............	56.028, ± .0047
Erdmann and Marchand, 3............	56.006, ± .0043
Herzfeld	55.983, ± .0028
Hinrichsen	56.0617, ± .0003
General mean	56.0603, ± .0003

The effect of this combination is practically to discard all of the de-
terminations except that of Hinrichsen. Herzfeld's figures are cer-
tainly too low, and probably because of undetermined impurity in his

---

[1] Zeitschr. physikal. Chem., 39, 311, 1901; and 40, 747, 1902.

artificial carbonate. The extreme difficulty of preparing absolutely pure compounds of calcium is well known.[1]

In the earliest of the three papers by Erdmann and Marchand there is also given a series of determinations of the ratio between calcium carbonate and sulphate. Pure Iceland 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, $136.0525, \pm .0071$

Hence Ca $= 40.025$.

In 1843 the atomic weight of calcium was redetermined by Berzelius,[2] 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, $142.3998, \pm .0518$

Hence Ca $= 40.227$.

The atomic weight of calcium has been several times computed from analyses of the chloride. The earliest determination by Berzelius[3] was based upon this compound, and Marignac[4] also used it in some provisional experiments, to which, however, he assigns little importance. They gave values for Ca far in excess of the truth. Dumas[5] also published a series of determinations of more than questionable value. Supposedly pure

[1] See Stas, Oeuvres Complètes, 3, 337.
[2] Journ. prakt. Chem., 31, 263. Ann. Chem. Pharm., 46, 241.
[3] Poggend. Annalen, 8, 189.
[4] Oeuvres Complètes, 1, 90.
[5] Ann. Chim. Phys. (3), 55, 129. 1859. Ann. Chem. Pharm., 113, 34.

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:

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

Hence $Ca = 40.103$.

Better results were obtained by Richards.[1] Calcium chloride, purified by repeated crystallizations, and fused in a stream of nitrogen, was precipitated by a solution of silver, and the silver chloride so produced was weighed. The data, with vacuum weights, are subjoined:

1.56454 grm. $CaCl_2$ gave	4.0409 AgCl.		Ratio,	38.7177
3.57630	"	9.2361	"	"	38.7209
3.59281	"	9.2788	"	"	38.7206
5.00880	"	12.9364	"	"	38.7187
9.00246	"	23.2506	"	"	38.7197

Mean, 38.7195, ± .0004

Hence $Ca = 40.083$.

There are now five independent ratios for calcium, as follows:

(1). $CaCO_3 : CaO :: 100 : 56.0603$, ± .0003
(2). $CaO : SO_3 :: 100 : 142.3998$, ± .0518
(3). $CaCO_3 : CaSO_4 :: 100 : 136.0525$, ± .0071
(4). $2Ag : CaCl_2 :: 100 : 51.4554$, ± .0230
(5). $2AgCl : CaCl_2 :: 100 : 38.7195$, ± .0004

To reduce these ratios we have—

$Ag = 107.880$, ± .00029 $S = 32.0667$, ± .00075
$Cl = 35.4584$, ± .0002 $C = 12.0038$, ± .0002

Hence,

From ratio 3 ....Ca $= 40.0250$, ± .0200
"   " 5 ....40.0829, ± .0013
"   " 4 ....40.1034, ± .0497
"   " 1 ....40.1421, ± .00055
"   " 2 ....40.2267, ± .0207

General mean, Ca $= 40.1323$, ± .0005

[1] Journ. Amer. Chem. Soc., 24, 374. 1902.

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 smaller amount of work. The early experiments of Stromeyer,[1] 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,[2] who neglected to publish sufficient details.

Taking the ratio between strontium chloride and silver first in order, we have series of figures by Pelouze, Dumas, Marignac and Richards. Pelouze[3] employed the volumetric method to be 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 ± .0050

Hence $Sr = 87.614$.

Dumas,[4] 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

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

[1] Schweigg. Journ., 19, 228. 1816.
[2] Compt. Rend., 17, 318. 1843.
[3] Compt. Rend., 20, 1047. 1845.
[4] Ann. Chim. Phys. (3), 55, 29. 1859. Ann. Chem. Pharm., 113, 34.

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

Mean of all as one series, 73.4079, ± .0170

Hence Sr = 87.468.

The foregoing determinations are now supplanted by the much more recent work of Richards,[1] who fused his strontium chloride in a stream of gaseous hydrochloric acid and nitrogen, and adopted all of the precautions relative to the solubility of silver chloride which modern experience has shown to be necessary. The results, with vacuum weights, follow:

4.2516 grm. SrCl$_2$ =	5.7864 Ag.	Ratio,	73.476
2.4019 "	3.2688 "	"	73.480
3.5184 "	4.7886 "	"	73.475
3.0264 "	4.1189 "	"	73.476

Mean, 73.4767, ± .0008

Hence Sr = 87.616.

Combining this series with the others we have:

Pelouze .... 73.4781, ± .0050
Dumas .... 73.4079, ± .0170
Richards .... 73.4767, ± .0008

General mean .... 73.4766, ± .0008

Dumas' determinations practically vanish, but those of Pelouze are confirmed.

The foregoing figures apply to anhydrous strontium chloride. The ratio between silver and the crystallized salt, SrCl$_2$.6H$_2$O, was determined in two series of experiments by Marignac.[2] Five grammes of the salt were used in each estimation, and, in the second series, the water was also determined. The quantities of the chloride corresponding to 100 parts of silver are given in the last column:

Series A.

5 grm. SrCl$_2$.6H$_2$O =	4.0515 grm. Ag.	Ratio,	123.411
" "	4.0495 "	"	123.472
" "	4.0505 "	"	123.442

Mean, 123.442

---

[1] Proc. Amer. Acad., 40, 603. 1905. Three of the determinations were made by H. G. Parker.
[2] Arch. Sci. Phys. Nat., 1, 220. 1858. Journ. prakt. Chem., 74, 216. Oeuvres Complètes, 1, 568.

Series B.

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

Mean, 123.477

Mean of all as one series, 123.460, ± .0082

Hence $Sr = 87.37$.

From series B, by deducting Marignae's water determinations, 40.563 per cent. in mean, the ratio between silver and the anhydrous chloride can be determined. The value found is $2Ag : SrCl_2 :: 100 : 73.3907$, ± .0065. This is so much lower than the measurements previously cited that it needs no further consideration.

Marignac also determined the ratio between strontium chloride and strontium sulphate. By direct conversion, one hundred parts of the former salt gave the quantities of sulphate shown in the third column of the next table:

5.942 grm. $SrCl_2$ gave 6.887 $SrSO_4$.			Ratio, 115.932
5.941	"	6.8855	"	" 115.949
5.942	"	6.884	"	" 115.927

Mean, 115.936, ± .004

Hence $Sr = 86.90$.

Richards,[1] in his study of strontium bromide, followed pretty much the lines laid down in his work on barium. The properties of the bromide itself were carefully investigated, and its purity established beyond reasonable doubt, and then the two usual ratios were determined. First, the ratio $2Ag : SrBr_2 :: 100 : x$, by titration with standard solutions of silver. For this ratio there are three series of measurements, by varied processes, concerning which full details are given. The data obtained, with weights reduced to a vacuum, are as follows:

First Series.

Wt. Ag.	Wt. $SrBr_2$.	Ratio.
1.30755	1.49962	114.689
2.10351	2.41225	114.677
2.23357	2.56153	114.683
5.3684	6.15663	114.683

Mean, 114.683

[1] Proc. Amer. Acad., 1894, 369.

Second Series.

Wt. Ag.	Wt. SrBr₂.	Ratio.
1.30762	1.49962	114.683
2.10322	2.41225	114.693
4.57502	5.24727	114.694
5.3680	6.15663	114.691

Mean, 114.690

Third Series.

Wt. Ag.	Wt. SrBr₂.	Ratio.
2.5434	2.9172	114.697
3.3957	3.8946	114.692
3.9607	4.5426	114.692
4.5750	5.2473	114.695

Mean, 114.694

Mean of all as one series, 114.689, $\pm$ .0012

Hence $Sr = 87.614$.

For the ratio, measured gravimetrically, $2AgBr : SrBr_2 :: 100 : x$, two series of determinations are given:

First Series.

Wt. AgBr.	Wt. SrBr₂.	Ratio.
2.4415	1.6086	65.886
2.8561	1.8817	65.884
6.9337	4.5681	65.883

Mean, 65.884

Second Series.

Wt. AgBr.	Wt. SrBr₂.	Ratio.
2.27625	1.49962	65.881
3.66140	2.41225	65.883
3.88776	2.56153	65.887
9.34497	6.15663	65.882

Mean, 65.883

Mean of all as one series, 65.884. $\pm$ .0006

Hence $Sr = 87.621$.

From the two bromide ratios the silver bromine ratio can be calculated, with the following result: $Ag : Br :: 100 : 74.077$.

There are now five ratios for strontium, as follows:

(1). $2Ag : SrCl_2 :: 100 : 73.4766$, $\pm$ .0008
(2). $2Ag : SrCl_2.6H_2O :: 100 : 123.460$, $\pm$ .0082
(3). $SrCl_2 : SrSO_4 :: 100 : 115.936$, $\pm$ .0040
(4). $2Ag : SrBr_2 :: 100 : 114.689$, $\pm$ .0012
(5). $2AgBr : SrBr_2 :: 100 : 65.884$, $\pm$ .0006

The atomic weights used in reducing these ratios are:

$$Ag = 107.880, \pm .00029 \qquad Br = 79.9197, \pm .0003$$
$$Cl = 35.4584, \pm .0002 \qquad S = 32.0667, \pm .00075$$
$$H = 1.00779, \pm .00001$$

Hence,

From ratio 3	....	$Sr = 86.899, \pm .0811$
" " 2	....	$87.366, \pm .0178$
" " 4	....	$87.614, \pm .0026$
" " 1	....	$87.616, \pm .0018$
" " 5	....	$87.621, \pm .0024$

General mean, $Sr = 87.616, \pm .0013$

Ratios 2 and 3 evidently count for nothing in this combination. The final value for strontium is practically that of Richards alone.

Addendum. Since the manuscript of this volume went to the printer, Sir Edward Thorpe has kindly sent me, in advance of publication, the work of Thorpe and Francis[1] on the atomic weight of strontium. Six ratios were measured, involving the chloride, bromide, and sulphate of strontium, all with vacuum weights, and with every known precaution to ensure accuracy. For details the published memoir must be consulted.

First.   The ratio $2Ag : SrBr_2$:

$SrBr_2$.	Ag.	Ratio.
1.77884	1.55073	114.710
1.86109	1.62216	114.729
1.85254	1.61511	114.701
1.73801	1.51534	114.694
1.85787	1.61994	114.688
1.70563	1.48707	114.697

Mean, 114.703, $\pm$ .0040

Hence $Sr = 87.644$.

Second.   The ratio $2AgBr : SrBr_2$:

$SrBr_2$.	$AgBr$.	Ratio.
1.86112	2.82438	65.895
1.85261	2.81155	65.893
1.73807	2.63762	65.895
1.85798	2.81999	65.886
1.70571	2.58866	65.892

Mean, 65.892, $\pm$ .0011

Hence $Sr = 87.651$.

---

[1] Proc. Roy. Soc., 83A, 277. 1910.

The two bromide ratios combined give $Ag : Br :: 100 : 74.077, \pm .0067$.
Third. The ratio $2Ag : SrCl_2$:

$SrCl_2$.	Ag.	Ratio.
1.64759	2.24203	73.486
1.66352	2.26356	73.491
1.53462	2.08817	73.491
1.64619	2.24011	73.487
1.76006	2.39486	73.493
1.56224	2.12572	73.492

Mean, 73.490, $\pm$ .0008

Hence $Sr = 87.645$.
Fourth. The ratio $2AgCl : SrCl_2$:

$SrCl_2$.	$AgCl$.	Ratio.
1.64764	2.97899	55.309
1.66357	3.00762	55.312
1.53467	2.77446	55.314
1.64624	2.97653	55.307
1.76010	2.18202	55.314

Mean, 55.311, $\pm$ .0009

Hence $Sr = 87.610$.
The two chloride ratios combined give $Ag : Cl :: 100 : 32.867, \pm .0026$.
Fifth. Ratio $SrBr_2 : SrSO_4$:

$SrBr_2$.	$SrSO_4$.	Ratio.
7.14570	5.30466	74.236
7.64281	5.67326	74.230
9.86072	7.32047	74.239

Mean, 74.235, $\pm$ .0018

Hence $Sr = 87.677$.
Sixth. Ratio $SrCl_2 : SrSO_4$:

$SrCl_2$.	$SrSO_4$.	Ratio.
7.30246	8.46071	115.861
8.71628	10.09868	115.861
8.46493	9.80743	115.859
8.79502	10.18957	115.855

Mean, 115.859, $\pm$ .0010

Hence $Sr = 87.668$.
The arithmetic mean of the six values obtained by Thorpe and Francis is 87.649, a little higher than the value found by Richards. A general combination of all the figures for strontium, however, would fall very near Richards' determinations.

BARIUM.

For the atomic weight of barium we have a series of seven ratios, established by the labors of Berzelius, Turner, Struve, Marignac, Dumas, Richards and Thorpe. Andrews[1] and Salvétat,[2] in their papers upon this subject, gave no details nor weighings, and therefore their work may be properly disregarded. First in order, we may consider the ratio between silver and barium chloride, as determined by Pelouze, Marignac, Dumas and Richards.

Pelouze,[3] 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 carefully ascertained. In the last column I give the quantity of barium chloride proportional to 100 parts of silver:

3.860 grm.	BaCl₂ ppt.	4.002 grm.	Ag.	96.452
5.790	"	6.003	"	96.452
2.895	"	3.001	"	96.468

Mean, 96.4573, ± .0036

Hence Ba = 137.199.

Essentially the same method was adopted by Marignac[4] 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, as given in the third column:

	Ag.	BaCl₂.	Ratio.	
A	3.4445	3.3190	96.356	
	3.7480	3.6110	96.345	Mean, 96.354
	6.3446	6.1140	96.362	
B	4.3660	4.1780	96.356	
	4.8390	4.6625	96.352	Mean, 96.354
C	6.9200	6.6680	96.358	
	5.6230	5.4185	96.363	Mean, 96.360
D	5.8435	5.6300	96.346	
	8.5750	8.2650	96.384	
	4.8225	4.6470	96.361	Mean, 96.367
	6.8460	6.5980	96.377	

Hence Ba = 136.989.   Mean, 96.360, ± .0024

---

[1] Chemical Gazette, October, 1852.
[2] Compt. Rend., 17, 318.
[3] Compt. Rend., 20, 1047. Journ. prakt. Chem., 35, 73.
[4] Arch. Sci. Phys. Nat., 8, 271. Oeuvres Complètes, 1, 219.

Dumas [1] 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:

	$Ag.$	$BaCl_2.$	Ratio.	
A	1.8260	1.7585	96.303	
	3.9980	3.8420	96.339	Mean, 96.333
	2.2405	2.1585	96.340	
	4.1680	4.0162	96.358	
B	1.7270	1.6625	96.265	
	2.5946	2.4987	96.304	
	3.5790	3.4468	96.306	
	4.2395	4.0822	96.290	Mean, 96.290
	4.3683	4.2062	96.289	
	4.6290	4.4564	96.271	
	9.0310	8.6975	96.307	
C	2.3835	2.2957	96.316	
	4.2930	4.1372	96.371	
	4.4300	4.2662	96.303	Mean, 96.338
	4.6470	4.4764	96.329	
	5.8520	5.6397	96.372	

Mean, 96.316, ± .0055

Hence Ba = 136.894.

The work done by Richards [2] was of a much more elaborate kind, for it involved some collateral investigations as to the effect of heat upon barium chloride, etc. Every precaution was taken to secure the spectroscopic purity of the material, which was prepared from several sources, and similar care was taken with regard to the silver. For details upon these points the original paper must be consulted. As for the titrations, three methods were adopted, and a special study was made with reference to the accurate determination of the end point; in which particular the investigations of Pelouze, Marignac and Dumas were at fault. In the first series of determinations, silver was added in excess, and the latter was measured with a standard solution of hydrochloric acid. The end point was ascertained by titrating backward and forward with silver solution and acid, and was taken as the mean between the two apparent end points thus observed. The results of this series, with weights reduced to a vacuum standard, were as follows:

---

[1] Ann. Chem. Pharm., 113, 22. 1860. Ann. Chim. Phys. (3), 55, 129.
[2] Proc. Amer. Acad., 29, 55. 1893.

13

Ag.	BaCl₂.	Ratio.
6.1872	5.9717	96.517
5.6580	5.4597	96.495
3.5988	3.4728	96.499
9.4010	9.0726	96.507
.7199	.6950	96.541

Mean, 96.512, ± .0055

In the second series of experiments a small excess of silver was added as before, and the precipitate of silver chloride was removed by filtration. The filtrate and wash waters were concentrated to small bulk, whereupon a trace of silver chloride was obtained and taken into account. The excess of silver remaining was then thrown down as silver bromide, and from the weight of the latter the silver was calculated, and subtracted from the original amount.

Ag.	BaCl₂.	Ratio.
6.59993	6.36974	96.512
5.55229	5.36010	96.539
4.06380	3.92244	96.522

Mean, 96.524, ± .0054

The third series involved mixing solutions of barium chloride and silver in as nearly as possible equivalent amounts, and then determining the actual quantities of silver and chlorine left unprecipitated. The filtrate and wash waters were divided into two portions, one-half being evaporated with hydrobromic acid and the other with silver nitrate. The small amounts of silver bromide and chloride thus obtained were determined by reduction and the use of Volhard's method:

Ag.	BaCl₂.	Ratio.
4.4355	4.2815	96.528
2.7440	2.6488	96.531
6.1865	5.9712	96.520
3.4023	3.2841	96.526

Mean, 96.526, ± .0016

Two final experiments were carried out by Stas' method, somewhat as in the first series, with variations and greater refinement in the observation of the end point. The results were as follows:

Ag.	BaCl₂.	Ratio.
6.7342	6.50022	96.525
10.6023	10.23365	96.523

Mean, 96.524, ± .0007

A careful study of Richards' paper will show that, although the last two experiments are probably the best, they are not entitled to such preponderance of weight as the " probable error " here computed would give them. If all of the determinations are assigned equal weight, and treated as one series, the mean becomes 96.520, ±.0025, but this figure is not satisfactory. The four series are unequal in merit, and that fact may be fairly recognized by combining the first and second series into one, and the third and fourth series similarly. On this basis the combination of all the data assumes the following form:

$$
\begin{array}{ll}
\text{Pelouze} \dotfill & 96.457, \ \pm .0036 \\
\text{Marignac} \dotfill & 96.360, \ \pm .0024 \\
\text{Dumas} \dotfill & 96.316, \ \pm .0055 \\
\text{Richards, Series 1, 2} \dotfill & 96.5165, \pm .0040 \\
\text{Richards, Series 3, 4} \dotfill & 96.5255, \pm .0010 \\
\hline
\text{General mean} \dotfill & 96.4947, \pm .00086
\end{array}
$$

Richards' determinations alone give $Ba = 137.345$.

The ratio between silver and crystallized barium chloride has been fixed by Marignac.[1] The usual method was employed, and two series of experiments were made, in the second of which the water of crystallization was also determined. Five grammes of chloride were taken in each determination, to which the subjoined weights of silver correspond. The ratio to 100 parts of silver is given in the second column:

	Weight Ag.	Ratio.
	4.4205	113.109
B	4.4195	113.135
	4.4210	113.097
	4.4195	113.135
A	4.4200	113.122
	4.4215	113.060

Mean, 113.110, ± .0079

Hence $Ba = 137.098$.

The direct ratio between the chlorides of silver and barium has been measured by Berzelius, Turner, Richards and Thorpe. Berzelius[2] found of barium chloride proportional to 100 parts of silver chloride—

72.432
72.422

Mean, 72.427

Hence $Ba = 136.714$.

---

[1] Arch. Sci. Phys. Nat., 1, 209. 1858. Journ. prakt. Chem., 74, 212. Oeuvres Complètes, 1, 550.
[2] Poggend. Annalen, 8, 177.

Turner [1] made five experiments, with the following results:

$$72.754$$
$$72.406$$
$$72.622$$
$$72.664$$
$$72.653$$

Mean, 72.680, $\pm$ .0154

Hence Ba $= 137.439$.

Of these, Turner regards the fourth and fifth as the best; but for present purposes it is not desirable to so discriminate.

Richards' determinations [2] fall into three series, and all are characterized by their taking into account chloride of silver recovered from the wash waters. In the first series the barium chloride was ignited at low redness in air or nitrogen; in the second series it was fused in a stream of pure hydrochloric acid; and in the third series it was not ignited at all. In the last series it was weighed in the crystallized state, and the amount of anhydrous chloride was computed from the data so obtained. The data, corrected to vacuum standards, are as follows:

	AgCl.	BaCl$_2$.	Ratio.	
A	8.7673	6.3697	72.653	
	5.1979	3.7765	72.654	
	4.9342	3.5846	72.648	Mean, 72.649
	2.0765	1.5085	72.646	
	4.4271	3.2163	72.650	
B	2.09750	1.52384	72.650	
	7.37610	5.36010	72.669	Mean, 72.6563
	5.39906	3.92244	72.650	
C	8.2189	5.97123	72.6524	
	4.5199	3.28410	72.6587	Mean, 72.6555

Mean, 72.653, $\pm$ .0014

Hence Ba $= 137.362$.

If we combine this with Richards' silver series, which, in mean, may be written $2Ag : BaCl_2 :: 100 : 96.525$, the cross ratio between silver and chlorine becomes $Ag : Cl :: 100 : 32.858$.

Thorpe's [3] measurements of this ratio are not important, for they were merely intended as a check upon the method he used in determining the atomic weight of radium, which involved the manipulation of very small quantities of material. His data are given here for the sake of completeness:

[1] Phil. Trans., 1829, 291.
[2] Proc. Amer. Acad., 29, 55, 1893.
[3] Proc. Roy. Soc., 80A, 298. 1908.

$AgCl.$	$BaCl_2.$	$Ratio.$
.1578	.1147	72.687
.2368	.1721	72.677
.0788	.0571	72.462
.0861	.0626	72.706
.0937	.0681	72.679
.1914	.1395	72.884
.1083	.0788	72.761

Mean, 72.694, $\pm$ .0320

Hence $Ba = 137.48$.

Assigning to Berzelius' work equal weight with that of Turner, the four series representing the ratio $2AgCl : BaCl_2$ combine as follows:

Berzelius .... 72.427, $\pm$ .0154
Turner .... 72.680, $\pm$ .0154
Richards .... 72.653, $\pm$ .0014
Thorpe .... 72.694, $\pm$ .0320

General mean .... 72.650, $\pm$ .0014

The ratio between barium nitrate and barium sulphate has been determined only by Turner.[1] According to his experiments 100 parts of sulphate correspond to the following quantities of nitrate:

112.060
111.990
112.035

Mean, 112.028, $\pm$ .014

Hence $Ba = 136.338, \pm .2706$.

For the similar ratio between barium chloride and barium sulphate, there are determinations by Turner, Berzelius, Struve, Marignac and Richards.

Turner[2] 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 observation bears directly upon many other atomic weight determinations.

---

[1]-Phil. Trans., 1833, 538.
[2] Phil. Trans., 1829, 291.

Berzelius,[1] treating barium chloride with sulphuric acid, obtained the following results in $BaSO_4$ for 100 parts of $BaCl_2$:

<div align="center">

112.17
112.18

Mean, 112.175

</div>

Hence $Ba = 135.653$.

Struve,[2] in two experiments, found:

<div align="center">

112.0912
112.0964

Mean, 112.0938

</div>

Hence $Ba = 137.037$.

Marignac's[3] 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

<div align="right">

Mean, 112.011, $\pm$ .0071

</div>

Hence $Ba = 138.473$.

Richards, in his work on this ratio, regards the results as of slight value, because of the occlusion of the chloride by the sulphate. This source of error he was never able to avoid entirely. Another error in the opposite direction is found in the retention of sulphuric acid by the precipitated sulphate. Eight experiments were made in two series, one set by adding sulphuric acid to a strong solution of barium chloride in a platinum crucible, the other by precipitation in the usual way. Richards gives in his published paper only the end results and the mean of his determinations; the details cited below I owe to his personal kindness. The weights are reduced to a vacuum standard:

	$BaCl_2$.	$BaSO_4$.	Ratio.
First	1.78934	2.0056	112.086
	2.07670	2.3274	112.072
	1.58311	1.7741	112.064
	3.27563	3.6712	112.076
	3.02489	3.3903	112.080
	3.87091	4.3385	112.080
Second	3.02489	3.9726	112.076
	3.87091	3.4880	112.085

<div align="right">

Mean, 112.077, $\pm$ .0017

</div>

Hence $Ba = 137.398$.

---

[1] Poggend. Annalen, 8, 177.

[2] Ann. Chem. Pharm., 80, 204. 1851.

[3] Arch. Sci. Phys. Nat., 1, 209. 1858. Journ. prakt. Chem., 74, 212. Oeuvres Complètes, 1, 559.

This mean is subject to a small correction due to loss of chlorine on drying the chloride, which reduces it to 112.073. Omitting Turner's single determination as unimportant, and assigning to the work of Berzelius and of Struve equal weight with that of Marignac, the measurements of this ratio combine thus:

Berzelius	112.175, ± .0071
Struve	112.094, ± .0071
Marignac	112.011, ± .0071
Richards	112.073, ± .0017
General mean	112.075, ± .0016

In an earlier paper than the one previously cited, Richards [1] studied with great care the ratios connecting barium bromide with silver and silver bromide. The barium bromide was prepared by several distinct processes, its behavior upon dehydration and even upon fusion was studied, and its specific gravity was determined. The ratio with silver was measured by titration, a solution of hydrobromic acid being used for titrating back. The data are subjoined, with the $BaBr_2$ equivalent to 100 parts of silver stated:

$BaBr_2$.	Ag.	Ratio.
2.28760	1.66074	137.746
3.47120	2.52019	137.736
2.19940	1.59687	137.732
2.35971	1.71323	137.735
2.94207	2.13584	137.748
1.61191	1.17020	137.747
2.10633	1.52921	137.740
2.19682	2.11740	137.755
2.37290	1.72276	137.738
1.84822	1.34175	137.747
5.66647	4.11360	137.750
3.52670	2.56010	137.756
4.31690	3.13430	137.731
3.36635	2.44385	137.748
3.46347	2.51415	137.759

Mean, 137.745, ± .0015

Hence Ba = 137.360.

The silver bromide in most of these determinations, and in some others, was collected and weighed in a Gooch crucible with all necessary pre-

---

[1] Proc. Amer. Acad., 28, 1. 1893.

cautions. Vacuum standards were used throughout for both ratios. I give in a third column the $BaBr_2$ equivalent to 100 parts of AgBr:

$BaBr_2$.	$AgBr$.	Ratio.
2.28760	2.89026	79.149
3.47120	4.38635	79.136
3.81086	4.81688	79.133
2.35971	2.98230	79.124
2.94207	3.71809	79.129
2.10633	2.66191	79.128
2.91682	3.68615	79.129
2.37290	2.99868	79.131
1.84822	2.33530	79.143
1.90460	2.40733	79.116
5.66647	7.16120	79.127
3.52670	4.45670	79.133
2.87743	3.63644	79.127
3.46347	4.37669	79.135

Mean, 79.132, ± .0015

Hence $Ba = 137.380$. From the two bromide ratios combined, Ag: Br:: 100: 74.070.

The last ratio was also determined by Thorpe,[1] incidentally to his work on the atomic weight of radium:

$BaBr_2$.	$AgBr$.	Ratio.
.0899	.1136	79.137
.0960	.1214	79.077
.1110	.1403	79.116
.0910	.1149	79.199
.0808	.1021	79.138

Mean, 79.133, ± .0134

Hence $Ba = 137.384$, in confirmation of Richards' series. On combination with the latter no noteworthy change is produced.

The ratios for barium are now as follows:

(1). $2Ag: BaCl_2:: 100: 96.4947$, ± .00086
(2). $2AgCl: BaCl_2:: 100: 72.650$, ± .0014
(3). $2Ag: BaCl_2.2H_2O:: 100: 113.110$, ± .0079
(4). $BaSO_4: BaN_2O_6:: 100: 112.028$, ± .014
(5). $BaCl_2: BaSO_4:: 100: 112.075$, ± .0016
(6). $2Ag: BaBr_2:: 100: 137.745$, ± .0015
(7). $2AgBr: BaBr_2:: 100: 79.132$, ± .0015

[1] Proc. Roy. Soc., 80A, 298. 1908.

Reducing these ratios with

Ag $= 107.880, \pm .00029$	N $= 14.0101, \pm .0001$
Cl $= 35.4584, \pm .0002$	S $= 32.0667, \pm .00075$
Br $= 79.9197, \pm .0003$	H $= 1.0078$

we have—

From ratio 4	....	Ba $= 136.338, \pm .2706$
"	" 3	.........................137.098, $\pm .0171$
"	" 1	.........................137.280, $\pm .0015$
"	" 2	.........................137.354, $\pm .0046$
"	" 6	.........................137.360, $\pm .0034$
"	" 5	.........................137.364, $\pm .0285$
"	" 7	.........................137.380, $\pm .0057$

General mean, Ba $= 137.302, \pm .0013$

This mean is probably too low, for the value from ratio 1 is affected by the doubtful determinations of several early investigators. That ratio, however, has the highest weight in the combination. Rejecting the first three values, the last four give a general mean of

$$Ba = 137.363, \pm .0025$$

which will be adopted in subsequent computations.

A few experiments are on record with reference to determining the atomic weight of barium from the percentage of water in the hydrated chloride. This method has been carefully investigated by Guye and Tsakalotos,[1] who conclude that the chloride in question is not suited to the purpose. Their data give Ba $= 139.5$ approximately; while similar data by Marignac give 136.5. The subject needs no further consideration here.

---

[1] Journ. Chim. Phys., 7, 215. 1909. Marignac's figures are discussed in the second edition of this work.

RADIUM.

The early, preliminary attempts to determine the atomic weight of radium may be ignored, for they were made with confessedly impure material. In 1902 Madame Curie [1] published the first determinations of any value, basing them upon the following analyses of radium chloride. The ratio $2AgCl : RaCl_2$ is given in the third column:

$RaCl_2$.	$AgCl$.	Ratio.
.09192	.08890	103.397
.02936	.08627	103.582
.08839	.08589	102.911

Mean, 103.297, $\pm$ .1349

Hence $Ra = 225.21$.

In the foregoing determinations the radium chloride still contained appreciable amounts of barium chloride. In a later series of determinations Madame Curie [2] used purer material, and in much larger quantities. The results obtained were as follows:

$RaCl_2$.	$AgCl$.[3]	Ratio.
.4052	.39054	103.768
.4020	.38784	103.651
.39335	.37944	103.666

Mean, 103.695, $\pm$ .0236

Hence $Ra = 226.35$.

Still more recent are the determinations by Thorpe,[4] on small quantities of material:

$RaCl_2$.	$AgCl$.	Ratio.
.0627	.0604	103.808
.0639	.0618	103.398
.0784	.0753	104.117

Mean, 103.774, $\pm$ .1399

Hence $Ra = 226.58$.

Thorpe regards his figures, however, as merely corroborative of Madame Curie's. A combination of the two series gives 103.700 for the general mean, and $Ra = 226.37$.

---

[1] Ann. Chim. Phys. (7), 30, 140. 1903. Preliminary data in Compt. Rend., 135, 80. 1902.
[2] Compt. Rend., 145, 422. 1907.
[3] Corrected for the weight of filter ash.
[4] Proc. Roy. Soc., 80, A, 298. 1908.

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[1] and by Longchamp[2] 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."[3] 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

Hence Pb = 207.062.

For the synthesis of lead sulphate we have data by Berzelius, Turner and Stas. Berzelius,[4] whose experiments 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 $PbSO_4$:

[1] Schweig. Journ., 17, 241. 1816.
[2] Ann. Chim. Phys., 34, 105. 1827.
[3] Bd. 3, s. 1218.
[4] Lehrbuch, 5th ed., 3, 1187.

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

Mean, 146.419, $\pm$ .012

Hence Pb = 206.96.

Turner,[1] in three similar experiments, found as follows:

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

Mean, 146.401, $\pm$ .011

Hence Pb = 207.04.

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

The results of Stas' syntheses,[2] effected after the same general method, but with variations in details, are as follows. Corrections for weighing in air were applied:

Weight Pb.	Weight PbSO₄.	Ratio.
141.9925	207.9388	146.443
148.016	217.6141	146.427
100.000	146.419	146.419
200.000	292.864	146.432
250.000	366.0525	146.421
250.000	366.0575	146.423

Mean, 146.4275, $\pm$ .0024

Hence Pb = 206.92.

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 of from the metal. One hundred parts of PbO, upon conversion into PbSO₄, gained weight as follows:

---

[1] Phil. Trans., 1833, 527-538.
[2] Oeuvres Complètes, 1, 390.

35.84
35.71
35.84
35.75
35.79
35.78
35.92

Mean, 35.804, $\pm$ .018

Hence Pb $= 207.625$.

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, $\pm$ .002

Hence Pb $= 204.75$.

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

In 1846 Marignac[1] published two sets of determinations of only moderate value. First, chlorine was conducted over weighed lead, and the amount of chloride so formed was determined. The lead chloride was fused before weighing. The ratio to 100 Pb is given in the last column:

20.506 grm. Pb gave 27.517 $PbCl_2$.	134.190
16.281 " 21.858 "	134.225
25.454 " 34.149 "	134.159

Mean, 134.191, $\pm$ .013

Hence Pb $= 207.41$.

Secondly, lead chloride was precipitated by silver nitrate and the ratio between $PbCl_2$ and $2AgCl$ determined. The third column gives the $PbCl_2$ equivalent to 100 parts of $AgCl$:

---

[1] Ann. Chem. Pharm., 59, 289 and 290. 1846. Oeuvres Complètes, 1, 186.

12.534 grm.	PbCl$_2$ gave	12.911 AgCl.		97.080
14.052	"	14.506	"	96.870
25.533	"	26.399	"	96.720

Mean, 96.890, ± .0704

Hence Pb = 206.84.

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,[1] 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. 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, ± .016

Hence Pb = 206.79.

Dumas,[2] 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, ±.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,[3] gives better 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. The data are as follows, together with the ratio of nitrate to 100 parts of lead:

[1] Journ. prakt. Chem., 74, 218. 1858. Oeuvres Complètes, 1, 574.

[2] Ann. Chem. Pharm., 113, 35. 1860.

[3] Oeuvres Complètes, 1, 386.

Series A.

Weight Pb.	Weight PbN_2O_6.	Ratio.
103.000	164.773	159.973
140.6887	225.0674	159.975
110.2672	176.408	159.982
141.9927	227.1527	159.975
148.616	237.702	159.968
123.348	198.924	159.973

Mean, 159.9743, $\pm$ .0012

Series B.

Weight Pb.	Weight PbN_2O_6.	Ratio.
100.000	159.970	159.970
200.000	319.928	159.964
250.000	399.8975	159.959
250.000	399.914	159.965

Mean, 159.9645, $\pm$ .0015

Mean from both series, 159.9704, $\pm$ .0010

Hence Pb = 206.80.

There is still another set of experiments upon lead nitrate, originally intended to fix the atomic weight of nitrogen, which may properly be included here. It was carried out by Anderson[1] in Svanberg's laboratory, and has also appeared under Svanberg's name. Lead nitrate was carefully ignited, and the residual oxide weighed, with the following results:

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, $\pm$ .0016

Hence Pb = 207.34.

The direct ratio between lead and silver has been roughly measured by the electrochemical experiments of Betts and Kern.[2] Lead silicofluoride was dissolved in hydrofluosilicic acid, and from the solution the lead was thrown down electrolytically, silver being simultaneously precipitated by the same current. Two series of experiments gave the following data. The ratio 2Ag : Pb :: 100 : x is stated in the third column:

---

[1] Ann. Chim. Phys. (3), 9, 254. 1843.
[2] Trans. Amer. Electrochem. Soc., 6, 67.

First Series.

Weight Ag.	Weight Pb.	Ratio.
5.8958	5.6221	95.476
"	5.6396	95.654
5.7863	5.5246	95.477
"	5.5450	95.830
7.8408	7.5108	95.791
"	7.5168	95.868
7.6253	7.3191	95.984
"	7.3221	96.025
6.2287	5.9600	95.676
"	5.9605	95.694
16.6804	15.9996	95.919
"	16.0014	95.923
6.8652	6.5815	95.868
"	6.5812	95.863
9.3253	8.9390	95.858
"	8.9419	95.889
6.8566	6.5695	95.813
6.8754	6.5877	95.816

Mean, 95.801, ± .0243

Second Series.

Weight Ag.	Weight Pb.	Ratio.
9.0470	8.6678	95.809
"	8.6663	95.792
13.4113	12.8607	95.895
"	12.8558	95.858
7.2780	6.9716	95.790
"	6.9755	95.844
7.2738	6.9605	95.693
"	6.9698	95.821
6.5278	6.2550	95.821
6.4864	6.2168	95.844

Mean, 95.817, ± .0109

General mean of both series, 95.814, ± .0097

Hence Pb = 206.73.

Baxter and Wilson [1] determined the atomic weight of lead by analyses of lead chloride, which had been previously fused in an atmosphere of gaseous hydrochloric acid. The ratio to Ag and to AgCl were both determined, and the figures obtained, with vacuum weights, are as follows:

---

[1] Proc. Amer. Acad., 43, 365. 1907. Journ. Amer. Chem. Soc., 30, 187.

$PbCl_2$.	Ag.	$AgCl$.	Ag ratio.	$AgCl$ ratio.
4.67691	3.62987	4.82273	128.845	96.976
3.67705	2.85375	. . . . .	128.850	. . . . .
4.14110	3.21408	4.27016	128.842	96.978
4.56988	3.54672	. . . . .	128.848	. . . . .
5.12287	3.97568	5.28272	128.855	96.974
3.85844	2.99456	3.97949	128.848	96.958
4.67244	3.62628	. . . . .	128.849	. . . . .
3.10317	2.40837	3.19909	128.849	97.002
4.29613	3.33407	4.42982	128.856	96.982

Mean. 128.849,   96.978,
$\pm$ .0010 $\pm$ .0039

From Ag ratio, Pb = 207.088.
From AgCl ratio, Pb = 207.096.
And Ag: Cl:: 100: 32.864.

These ratios combine with others thus:

Ratio $2Ag:PbCl_2$.

Marignac with Dumas........ 128.727, $\pm$ .0130
Baxter and Wilson.......... 128.849, $\pm$ .0010

General mean .... 128.848, $\pm$ .0010

Ratio $2AgCl:PbCl_2$.

Marignac .... 96.890, $\pm$ .0704
Baxter and Wilson........... 96.978, $\pm$ .0039

General mean .... 96.977, $\pm$ .0039

The older determinations practically reject themselves, leaving Baxter and Wilson's figures alone.

The work done upon the atomic weight of lead by Meaglia[1] is confessedly an approximation, and nothing more. Metallic lead was used to precipitate silver from a nitrate solution, and in that way the ratio Ag: Pb was determined. Two series of observations were made, with different preparations of lead. Calculated with Ag = 107.93, the following values for Pb were obtained:

1.	2.
206.872	206.866
206.907	206.897
206.903	206.927
206.909	206.933
206.930	206.935
206.903	
206.929	

[1] Thesis, University of Grenoble, 1907.

14

Treating both series as one, and reducing the figures to the form of ratio adopted in this work, the mean becomes

$$2Ag:Pb::100:95.853, \pm .0020$$

Combined with the series by Betts and Kern, $95.814, \pm .0097$, the general mean becomes $95.850, \pm .0019$.

The following ratios are now available from which to compute the atomic weight of lead:

(1). $PbO:Pb::100:92.8271, \pm .0013$
(2). $PbN_2O_6:PbO::100:67.4027, \pm .0016$
(3). $Pb:PbSO_4::100:146.4262, \pm .0023$
(4). $PbO:PbSO_4::100:135.804, \pm .0180$
(5). $PbSO_4:PbN_2O_6::100:109.307, \pm .0020$
(6). $Pb:PbN_2O_6::100:159.9704, \pm .0010$
(7). $Pb:PbCl_2::100:134.191, \pm .0130$
(8). $2Ag:PbCl_2::100:128.843, \pm .0010$
(9). $2AgCl:PbCl_2::100:96.977, \pm .0039$
(10). $2Ag:Pb::100:95.850, \pm .0019$

Computing with

Ag $= 107.880, \pm .00029$ N $= 14.0101, \pm .0001$
Cl $= 35.4584, \pm .0002$ S $= 32.0667, \pm .00075$

we have—

From ratio 5 ....Pb $= 204.749, \pm .0475$
  "   "   6 ....206.802, $\pm$ .0035
  "   " 10 ....206.806, $\pm$ .0041
  "   "   3 ....206.923, $\pm$ .0104
  "   "   1 ....207.062, $\pm$ .0376
  "   "   8 ....207.075, $\pm$ .0023
  "   "   9 ....207.094, $\pm$ .0112
  "   "   2 ....207.337, $\pm$ .0118
  "   "   7 ....207.414, $\pm$ .0789
  "   "   4 ....207.625, $\pm$ .1125

General mean, Pb $= 206.970, \pm .0017$

The rejection of the first and last two values in this series only raises the general mean to 207.972, and it is therefore immaterial whether they are retained or cast aside. On chemical grounds the values from ratios 8 and 9 are probably the best, but they need additional confirmation. The final result is presumably, but not certainly, too low.

GLUCINUM.

Our knowledge of the atomic weight of glucinum is derived from experiments made upon the sulphate and three organic salts. Leaving out of account the single determination by Berzelius,[1] we have to consider the data furnished by Awdejew, Weeren, Klatzo, Debray, Nilson and Pettersson, Krüss and Moraht, and Parsons.

Awdejew,[2] 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

Hence $Gl = 9.337$.

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[3] gives the following weights of GlO and $BaSO_4$. The ratio is given in a third column, just as with the figures by Awdejew:

GlO.	$BaSO_4$.	Ratio
.3163	2.9332	927.348
.2872	2.6377	918.419
.2954	2.7342	925.592
.5284	4.8823	923.978

Mean, 923.834, $\pm$ 1.303

Hence $Gl = 9.267$.

[1] Poggend. Annal., 8, 1.
[2] Poggend. Annal., 56, 106. 1842.
[3] Poggend. Annal., 92, 124. 1854.

Klatzo's [1] figures are as follows, with the third column added by the writer:

GlO.	BaSO₄.	Ratio.
.2339	2.1520	920.052
.1910	1.7556	919.162
.2673	2.4872	930.490
.3585	3.3115	923.710
.2800	2.5842	922.929

Mean, 923.268, ± 1.346

Hence Gl = 9.283.

Combining these series into a general mean, we have—

Awdejew .... 921.316, ± 1.577
Weeren .... 923.834, ± 1.303
Klatzo .... 923.268, ± 1.346

General mean .... 922.977, ± 0.805

Debray [2] 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:

Salt.	CO₂.	Per Cent. CO₂.
.600	.477	79.500
.603	.478	79.270
.600	.477	79.500

Mean, 79.423, ± .052

Hence, from the ratio between $4CO_2$ and GlO, Gl = 9.3375.

In 1880 the careful determinations of Nilson and Pettersson appeared.[3] These chemists first attempted to work with the sublimed chloride of glucinum, but abandoned the method upon finding the compound to

[1] Zeitsch. anal. Chem., 8, 523. 1869.
[2] Ann. Chim. Phys. (3), 44, 37. 1855.
[3] Ber. Deutsch. chem. Ges., 13, 1451. 1880.

be contaminated with traces of lime derived from a glass tube. They finally resorted to the crystallized sulphate as the most available salt for their purposes. This compound, upon strong ignition, yields pure glucina. The data are as follows:

$GlSO_4.4H_2O.$	$GlO.$	Per cent. $GlO.$
3.8014	.5387	14.171
2.6092	.3697	14.169
4.3072	.6099	14.160
3.0091	.4266	14.176

Mean, 14.169, ± .0023

Hence $Gl = 9.113$.

Krüss and Moraht [1] in their work followed the general method adopted by Nilson and Pettersson, but with various added precautions and greater elaboration of detail. Their glucina was derived from three sources, namely, leucophane, beryl and gadolinite, and the sulphate was repeatedly recrystallized. The results are subjoined:

$GlSO_4.4H_2O.$	$GlO.$	Per cent. $GlO.$
21.1928	3.0008	14.160
16.2038	2.29455	14.161
15.49345	2.1902	14.136
20.1036	2.8433	14.143
22.0465	3.1167	14.137
4.9619	.7019	14.146
18.3249	2.5921	14.145
24.3907	3.0253	14.143
20.18045	2.85255	14.135
20.0253	2.8328	14.146
18.9840	2.6832	14.134
17.0072	2.4073	14.155
22.5044	3.1805	14.133
20.88675	2.95645	14.154
19.0591	2.69305	14.130
17.8227	2.5226	14.153

Mean, 14.144, ± .0017

Hence $Gl = 9.062$.

The first two determinations, which give the highest percentage, were made upon sulphate thrice crystallized. The others were made upon a salt four times crystallized, except in one instance, when there were five crystallizations. To the data derived from the four times crystallized compound Krüss and Moraht give preference, and so find a slightly lower

[1] Liebig's Annalen, 262, 38. 1891.

value for the atomic weight of glucinum. Combining, we have for the mean percentage:

By Nilson and Pettersson...... 14.169, ± .0023
By Krüss and Moraht......... 14.144, ± .0017

General mean .... 14.153, ± .0014

The determinations, by Parsons,[1] of this atomic weight, were based upon analyses of two organic salts, namely, the acetylacetonate, $Gl(C_5H_7O_2)_2$, and the basic acetate, $Gl_4O(C_2H_3O_2)_6$. These compounds are volatile at moderately high temperatures, and can therefore be purified by sublimation; an advantage which the sulphate does not possess. Parsons attempted to make determinations with the sulphate, also but obtained unsatisfactory results.

Weighed quantities of the two organic compounds were first decomposed, in platinum crucibles, with nitric acid. The nitrate solutions so formed were then evaporated to dryness, and the residual salt was converted into oxide by prolonged ignition. The oxide was examined for occluded gases, and its weight was given the necessary correction for them. The data obtained, with vacuum weights, were as follows:

Acetylacetonate.	Oxide.	Per cent. GlO.
2.62245	.31798	12.125
3.28037	.39757	12.119
2.08993	.25286	12.099
2.41401	.29233	12.109
1.61353	.19554	12.118
1.39714	.16905	12.100
1.85023	.22419	12.117

Mean, 12.1124, ± .0025

Hence Gl = 9.103.

Acetate.	Oxide.	Per cent. GlO.
2.61484	.64630	24.716
2.67721	.66109	24.693
3.11534	.76930	24.693
1.89291	.46788	24.717
1.47931	.36534	24.703
1.09012	.26911	24.686
1.35642	.33493	24.692
1.56787	.38715	24.693
1.34465	.33204	24.693

Mean, 24.698, ± .0025

Hence Gl = 9.106.

---

[1] Journ. Amer. Chem. Soc., 26, 721. 1904.

In a later note,[1] Parsons combined the two series of determinations, and deduced simultaneous values for Gl and C. If $O=16$, and $H=1.008$, then $Gl=9.112$, and $C=12.007$. These figures furnish a good check upon the general accuracy of the manipulations.

The atomic weight of glucinum is now fixed by the following ratios:

(1). $GlO:BaSO_4::100:922.977, \pm .805$
(2). $4CO_2:GlO::79.423, \pm .0052:11.433, \pm .081$
(3). $GlSO_4.4H_2O:GlO::100:14.153, \pm .0014$
(4). $Gl(C_5H_7O_2)_2:GlO::100:12.1124, \pm .0025$
(5). $Gl_4O(C_2H_3O_2)_6:4GlO::100:24.698, \pm .0025$

Reducing these ratios with

$C = 12.0038, \pm .0002$ $\quad\quad$ $S = 32.0667, \pm .00075$
$H = 1.00779, \pm .00001$ $\quad\quad$ $Ba = 137.363, \pm .0025$

we have—

From ratio 3 ....$Gl = 9.0805, \pm .0025$
" " 4 ....9.1032, $\pm .0052$
" " 5 ....9.1061, $\pm .0027$
" " 1 ....9.2912, $\pm .0221$
" " 2 ....9.3375, $\pm .1775$

General mean, $Gl = 9.0945, \pm .0017$

The last two values are evidently worthless, but they carry practically no weight in the combination. For all practical purposes the atomic weight of glucinum may be taken as 9.1, which must be very near the true value.

---

[1] Journ. Amer. Chem. Soc., 27, 1204. 1905.

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.

The early determinations made by Berzelius, Longchamp and Gay-Lussac need not be considered here, as they have only antiquarian value. The investigations which demand attention are those of Scheerer, Svanberg and Nordenfeldt, Jacquelain, Macdonnell, Bahr, Marchand and Scheerer, Dumas, Marignac, Burton and Vorce, and Richards and Parker.

Scheerer's method of investigation, was exceedingly simple.[1] 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 $BaSO_4$:

	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 $Mg = 24.467$.

In a later note[2] Scheerer shows that the barium sulphate of these experiments carries down with it magnesium salts in such quantity as to make the atomic weight of magnesium 0.039 too low.

The work of Bahr, Jacquelain, Macdonnell, and Marignac, and in part that of Svanberg and Nordenfeldt, also relates to the composition of magnesium sulphate.

Jacquelain's experiments were as follows:[3] Dry magnesium sulphate was prepared by mixing the ordinary hydrous salt to a paste with sul-

[1] Poggend. Annal., 69, 535, 1846.
[2] Poggend. Annal., 70, 407.
[3] Ann. Chim. Phys. (3), 32, 202.

phuric 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

Hence Mg=24.444.

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, gives 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, and combined with the latter, the mean will be 193.700,±.0331. This again is subject to the correction pointed out by Scheerer for magnesium salts retained by the barium sulphate, but such a correction determined by Scheerer for a single experiment is only a rough approximation, and hardly worth applying.

The determinations published by Macdonnell[1] are of slight importance, and all depend upon magnesium sulphate. First, the crystallized salt, $MgSO_4.7H_2O$, was dried in vacuo over sulphuric acid and then dehydrated at a low red heat. The following percentages of water were found:

$$51.17$$
$$51.13$$
$$51.14$$
$$51.26$$
$$51.28$$
$$51.29$$

Mean, 51.21, ± .020

Secondly, anhydrous magnesium sulphate was precipitated with barium chloride. From the weight of the barium sulphate, with SO_3=80 and Ba=137, Macdonnell computes the percentages of SO_3 given below. I calculate them back to the observed ratio in uniformity with Scheerer's work:

[1] Proc. Royal Irish Acad., 5, 303. British Assoc. Report, 1852, part 2, p. 36.

Per cent. SO₃.	Ratio, MgSO₄:BaSO₄.
66.67	194.177
66.73	194.351
66.64	194.089
66.65	194.118
66.69	194.239

In another experiment 60.05 grains $MgSO_4$ gave 116.65 grains $BaSO_4$, a ratio of 100 : 194.254. Including this with the preceding figures, they give a mean of 194.205, ±.027. This, combined with the work of Scheerer and Jacquelain, 193.700, ±.033, gives a general mean of—

$$MgSO_4 : BaSO_4 :: 100 : 194.003, \pm .021$$

In one final experiment Macdonnell found that 41.44 grains of pure magnesia gave 124.40 grains of $MgSO_4$, or 300.193 per cent.

From Macdonnell's data the atomic weight of magnesium ranges between 24.00 and 24.43.

Bahr's [1] 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. MgSO₄.	296.122
2.0459 " 6.0648 "	296.437
1.0784 " 3.1925 "	296.040

Mean, 296.200, ± .0815

Hence Mg = 24.812.

About four years previous to the investigations of Bahr the paper of Svanberg and Nordenfeldt [2] 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 was 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

Hence Mg = 24.706.

[1] Journ. prakt. Chem., 56, 310. 1852.
[2] Journ. prakt. Chem., 45, 473. 1848.

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:

1.9872 grm. MgO gave	5.8995 grm. $MgSO_4$.	296.875
1.7464 "	5.1783 "	296.513
1.7418 "	5.1666 "	296.624

Mean, 296.671, $\pm$ .072

Hence $Mg = 24.711$.

In 1850 the elaborate investigations of Marchand and Scheerer [1] 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 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, $\pm$ .0037

[1] Journ. prakt. Chem., 50, 385.

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. As for 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, ± .0077

In a supplementary paper [1] by Scheerer, it was shown that an important correction to the foregoing data had been overlooked. Scheerer, re-

---

[1] Ann. Chem. Pharm., 110, 240.

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	52.238
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. ± .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:

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

Result, ± .0020, probable error of the general mean.

We may now combine the results obtained from both magnesites:

Snarum mineral . . . . Per cent. MgO, 47.624, ± .0037
Frankenstein mineral . . . .   "   47.628, ± .0020

General mean . . . . Per cent. MgO, 47.627, ± .0018

Hence Mg = 24.016.

The next investigation upon the atomic weight of magnesium which we have to consider is that of Dumas.[1] 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 poportional to 100 parts of silver, the quantities of $MgCl_2$ stated in the third column:

---

[1] Ann. Chem. Pharm., 113, 33. 1860.

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 "	5.902	"		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

Hence Mg = 24.581.

This determination gives a very high value to the atomic weight of magnesium, which is unquestionably wrong. The error, probably, is due to the presence of oxychloride in the magnesium chloride taken, an impurity tending to raise the apparent atomic weight of the metal. Richards' and Parker's revision of this ratio is more satisfactory.

Marignac,[1] in 1883, resorted to the old method of determination, depending upon the direct ratio between MgO and SO$_3$. This ratio he measured both synthetically and analytically. First, magnesia from various sources was converted into sulphate. The MgSO$_4$ from 100 parts of MgO is given in the third column:

	MgO.	*MgSO$_4$.*	*Ratio.*
1..............	1.5635	4.6620	298.17
2..............	1.4087	4.2025	298.32
3..............	1.5917	4.7480	298.30
4..............	1.4705	4.3855	298.23
5..............	1.4778	4.4060	298.15
6..............	1.6267	4.8530	298.33
7..............	1.3657	4.0740	298.37
8..............	1.9575	5.8390	298.29
9..............	1.6965	5.0600	298.26
10..............	1.8680	5.5715	298.26

Mean, 298.27, $\pm$ .0149

Hence Mg = 40.383.

The magnesia for experiments 1 to 5 was prepared by calcination of the nitrate, that of 6 to 8 from the sulphate, and the remaining two from the carbonate. But Richards and Rogers [2] have shown that magnesia derived from the nitrate always contains occluded gaseous impurity, so that the experiments depending upon its use are somewhat questionable. The results tend to give an atomic weight for magnesium which is possibly too high. Whether the other samples of magnesia are subject to similar objections I cannot say.

---

[1] Arch. Sci. Phys. Nat. (3), 10, 206. Oeuvres Complètes, 2, 742.
[2] Amer. Chem. Journ., 15, 567. 1893.

Marignac's second series was obtained by the calcination of the sulphate, with results as follows:

$MgSO_4$.	MgO.	Ratio.
3.7705	1.2642	298.25
4.7396	1.5884	298.39
3.3830	1.1345	298.19
4.7154	1.5806	298.33
4.5662	1.5302	298.43
4.5640	1.5300	298.30
3.2733	1.0979	298.14
4.8856	1.6378	298.30
5.0092	1.6792	298.31
5.3396	1.7898	298.33
5.1775	1.7352	298.38
5.0126	1.6807	298.24
5.0398	1.6894	298.32

Mean, 298.30, ± .0150

Hence $Mg = 40.377$.

These data may now be combined with the work of previous investigators, giving Macdonnell's one result and Jacquelain's two, each equal weight with a single experiment in Bahr's series:

Macdonnell	300.193, ± .1413
Jacquelain	297.968, ± .0999
Bahr	296.200, ± .0815
Svanberg and Nordenfeldt....	296.671, ± .0720
Marignac, synthetic	298.27, ± .0149
Marignac, calcination	298.30, ± .0150
General mean	298.210, ± .0103

Burton and Vorce,[1] who published their work on magnesium in 1890, began with the metal itself, which had been purified by distillation in a Sprengel vacuum. This metal was dissolved in pure nitric acid, and the resulting nitrate was converted into oxide by calcination at a white heat. The oxide was carefully tested for oxides of nitrogen, which were proved to be absent, but occluded gases, the impurity pointed out by Richards and Rogers, were not suspected. This impurity must have been present, and it would tend to lower the apparent atomic weight of magnesium as calculated from the data obtained. The results were as follows, together with the percentage of Mg in MgO:

---

[1] Amer. Chem. Journ., 12, 219. 1890.

Mg taken.	MgO formed.	Per cent. Mg.
.33009	.54766	60.273
.34512	.57252	60.281
.26058	.43221	60.290
.28600	.47432	60.297
.30917	.51273	60.299
.27636	.45853	60.271
.36457	.60475	60.284
.32411	.53746	60.304
.32108	.53263	60.282
.28323	.46988	60.262

Mean, 60.2845, $\pm$ .0027

Hence $Mg = 24.287$.

The best determinations of all are those of Richards and Parker,[1] who studied magnesium chloride with all the precautions suggested by the most recent researches. The salt itself was not only free from oxychloride, but also spectroscopically pure as regards alkaline contaminations, and all weighings were reduced to a vacuum standard. The first series of experiments gives the ratio between silver chloride and magnesium chloride, and I have reduced the data to the form $2AgCl : MgCl_2 :: 100 : x$. The weighings and values for x are subjoined:

$MgCl_2$.	AgCl.	Ratio.
1.33550	4.01952	33.225
1.51601	4.56369	33.219
1.32413	3.98528	33.226
1.40664	4.23297	33.231
1.25487	3.77670	33.227

Mean, 33.226, $\pm$ .0013

Hence $Mg = 24.335$.

The remaining series of experiments, three in number, relate to the ratio $2Ag : MgCl_2$, which was earlier investigated by Dumas. For the elaborate details of manipulation the original memoir must be consulted. I can give little more than the weights found, and their reduction to the usual form of ratio, $2Ag : MgCl_2 :: 100 : x$:

Second Series.

$MgCl_2$.	Ag.	Ratio.
2.78284	6.30284	44.152
2.29360	5.19560	44.145
2.36579	5.35989	44.130

Mean, 44.142, $\pm$ .0043

Hence $Mg = 24.324$.

[1] Zeitsch. anorg. Chem., 13, 81. 1896.

This series gives slightly higher results than the others, and the authors, for reasons which they assign, discard it:

Third Series.

$MgCl_2$.	Ag.	Ratio.
1.99276	4.51554	44.131
1.78870	4.05256	44.138
2.12832	4.82174	44.140
2.51483	5.69714	44.141
2.40672	5.45294	44.136
1.95005	4.41747	44.144

Mean, 44.138, $\pm$ .0013

Hence $Mg = 24.315$.

The fourth series, because of the experience gained in the conduct of the preceding determinations, is best of all, and the authors adopt its results in preference to the others:

Fourth Series.

$MgCl_2$.	Ag.	Ratio.
2.03402	4.60855	44.136
1.91048	4.32841	44.138
2.09932	4.75635	44.137
1.82041	4.12447	44.137
1.92065	4.35151	44.138
1.11172	2.51876	44.138

Mean, 44.137, $\pm$ .0003

Hence $Mg = 24.313$.

These series combine with that of Dumas as follows:

Dumas	44.261, $\pm$ .0200
Richards and Parker, second series....	44.142, $\pm$ .0043
Richards and Parker, third series......	44.138, $\pm$ .0013
Richards and Parker, fourth series.....	44.137, $\pm$ .0003
General mean	44.138, $\pm$ .0003

Here the first two values practically vanish, and the third and fourth series of Richards and Parker appear alone. Combining this figure with their value for the AgCl ratio, the subjoined cross ratio appears: $Ag : Cl :: 100 : 32.842$.

To sum up, we now have the following ratios, bearing upon the atomic weight of magnesium:

(1). $MgSO_4 : BaSO_4 :: 100 : 194.003$, $\pm$ .021
(2). $MgO : MgSO_4 :: 100 : 298.210$, $\pm$ .0103
(3). Per cent. of water in $MgSO_4$, $7H_2O$, 51.21, $\pm$ .020
(4). Per cent. of MgO in oxalate, 27.3665, $\pm$ .0023
(5). Per cent. of MgO in carbonate, 47.627, $\pm$ .0018
(6). Per cent. of Mg in MgO, 60.2845, $\pm$ .0027
(7). $2Ag : MgCl_2 :: 100 : 44.138$, $\pm$ .0003
(8). $2AgCl : MgCl_2 :: 100 : 33.226$, $\pm$ .0013

The antecedent values for reducing these ratios are:

Ag = 107.880, ± .00029	S = 32.0667, ± .00075
Cl = 35.4584, ± .0002	C = 12.0038, ± .0002
Ba = 137.363, ± .0025	H = 1.00779, ± .00001

Hence, for magnesium, we have

From ratio 5 ....Mg = 24.0162, ± .0020
    "   " 3 ....24.0803, ± .0680
    "   " 1 ....24.2561, ± .0333
    "   " 6 ....24.2865, ± .0020
    "   " 7 ....24.3154, ± .0007
    "   " 8 ....24.3344, ± .0033
    "   " 2 ....24.394, = .0021
    "   " 4 ....24.7063, ± .0037

General mean, Mg = 24.3039, ± .0006

This final value is possibly a little too low, as compared with the individual values which are presumably the best. The figures are, however, peculiarly instructive. Ratios 2, 7 and 8, representing essentially the work of Marignac and Richards and Parker, were originally reduced with the Stas values for sulphur, silver and chlorine. These values are Ag = 107.93, Cl = 35.457 and S = 32.074. With these figures, and using only Marignac's data for ratio 2, the following values for magnesium are obtained:

From $MgSO_4:MgO$,   Mg = 24.383
    " $2Ag:MgCl_2$,   Mg = 24.382
    " $2AgCl:MgCl_2$,   Mg = 24.371

From the general mean represented by ratio 2, Mg = 24.398, a slightly higher value.

The concordance here is much greater than in the reduction with modern values, and may be interpreted in either of two ways. Either the Stas values are more exact than the new values for Ag, Cl and S, or the earlier concordance is deceptive. In short, an agreement between determinations of atomic weight made by diverse methods, is dependent in great part upon the antecedent values used in the computations. Concordance and discordance may be equally deceptive. Illustrations of this statement are not uncommon.

ZINC.

The several determinations of the atomic weight of zinc are by no means closely concordant. The results obtained by Gay-Lussac[1] and Berzelius[2] were undoubtedly too low, and may be disregarded here. We need consider only the work done by later investigators.

In 1842 Jacquelain published the results of his investigations upon this important constant.[3] 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:

Nitric Series.

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

Sulphuric Series.

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

Mean of all four, 80.541, ± .007

Hence Zn = 66.224.

The method adopted by Axel Erdmann[4] 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 subsequent 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, ± .0037

Hence Zn = 65.054.

[1] Mémoire d'Arcueil, 2, 174.
[2] Gilb. Annal., 37, 460.
[3] Compt. Rend., 14, 636.
[4] Poggend. Annal., 62, 611. Berz. Lehrb., 3, 1219.

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.

Favre[1] 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 = 65.995.

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 = 65.996.

Both of these determinations are open to objections. In the 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. Indeed, a fourth

[1] Ann. Chim. Phys. (3), 10, 163. 1844.

combustion is omitted from the series as given, having been rejected by Favre himself. In this case the oxide formed was contaminated by traces of sulphide.

Baubigny,[1] in 1883, resorted to the well-known sulphate method. Zinc sulphate, elaborately purified, was dried at 440° to constant weight, and then calcined at a temperature equal to the fusing point of gold. These data were obtained:

$ZnSO_4$.	ZnO.	Per cent. ZnO.
6.699	3.377	50.410
8.776	4.4245	50.416

Mean, 50.413, ± .0020

Hence $Zn = 65.400$.

In Marignac's determinations of the atomic weight of zinc, published also in 1883,[2] there is a peculiar complication. After testing and criticising some other methods, he finally decided to study the double salt K_2ZnCl_4, which, however, is difficult to obtain in absolutely definite condition. Although the compound was purified by repeated crystallizations, it was found to deliquesce readily, and thereby to undergo partial dissociation, losing chloride of zinc, and leaving the porous layer on the crystalline surfaces richer in potassium. In order to evade this difficulty, Marignac placed a large quantity of the salt in a funnel, and collected the liquid product of deliquescence as it ran down. In this product he determined chlorine by volumetric titration with a standard solution of silver, and also estimated zinc by precipitation with sodium carbonate, and weighing as oxide. From the data thus obtained equations were formed, giving for each analysis an atomic weight of zinc which is independent of the proportion between $ZnCl_2$ and KCl in the substance analyzed. The data unfortunately are too bulky for reproduction here and the calculations are complex; but the results found for zinc, when $Ag = 107.93$, $Cl = 35.457$, and $K = 39.137$, are as follows:

1. One titration .... $Zn = 65.22$
2. Two titrations 65.37
3. Two titrations 65.31
4. Two titrations 65.28
5. One titration 65.26

Each of these values represents a distinct sample of the deliquesced material, and the number of chlorine determinations is indicated.

[1] Compt. Rend., 97, 906. 1883.
[2] Arch. Sci. Phys. Nat. (3), 10, 194. Oeuvres Complètes, 2, 731.

A second set of determinations was made by the same analytical method directly upon the recrystallized and carefully dried K_2ZnCl_4. The values for Zn are as follows:

6. Two titrations .... Zn = 65.28
7. Two titrations 65.39
8. One titration 65.32

In order to adapt these data to the uniform scheme of calculation employed in this work, taking into account their probable error and the probable errors of the antecedent values for K, Cl and Ag, it seems to be best to calculate them back with the atomic weights used by Marignac into the form of the ratio $4Ag : K_2ZnCl_4 :: 100 : x$. Doing this, and taking each value as many times as there are titrations represented in it—that is, giving the results of a double determination twice the weight of a single one—we have the following series of data for the ratio in question:

From 1.............................. 66.090
From 2.............................. { 66.124
                                      { 66.124
From 3.............................. { 66.110
                                      { 66.110
From 4.............................. { 66.104
                                      { 66.104
From 5.............................. 66.099
From 6.............................. { 66.104
                                      { 66.104
From 7.............................. { 66.129
                                      { 66.129
From 8.............................. 66.113

Mean, 66.111, ± .0023

Hence, from Marignac's work, $4Ag : K_2ZnCl_4 :: 100 : 66.111, \pm .0023$, a ratio which can be discussed along with others at the close of this chapter. It corresponds to Zn = 65.249.

During the years between 1883 and 1889, a number of determinations were made of the direct ratio between zinc and hydrogen—that is, weighed quantities of zinc were dissolved in acid, the hydrogen evolved was measured, and from its volume, with Regnault's data, the weight of H was computed. First in order are Van der Plaats' determinations,[1] whose results, as given by himself, are subjoined. The weights are reduced to a vacuum. Sulphuric acid was the solvent:

Zn, grm.	H, litres.	Zn =
6.6725	1.1424	65.21
9.1271	1.5643	65.14
13.8758	2.3767	65.18

Mean, 65.177, ± .0137

[1] Compt. Rend., 100, 52. 1885.

With the new value for the weight of hydrogen, 0.89872 gramme per litre, this becomes $Zn = 64.980, \pm .0137$, when $H = 1$.

Reynolds and Ramsay made 29 determinations of this ratio,[1] rejecting, however, all but 5. The weighings were reduced to vacuum, and in each experiment the volume of hydrogen was fixed by the mean of seven or eight readings. The values for Zn are as follows:

$$65.5060$$
$$65.4766$$
$$65.4450$$
$$65.5522$$
$$65.4141$$

Mean, $65.4787, \pm .0161$

These values were computed with Regnault's data for the weight of H. Corrected by the new value the mean becomes $Zn = 65.280, \pm .0161$.

A few determinations by Mallet were made incidentally to his work on the atomic weight of gold, and appear in the same paper.[2] According to these experiments, one gramme of zinc gives—

341.85 cc. H., and Zn =	65.158
341.91 " "	65.146
341.93 " "	65.143
342.04 " . "	65.122

Mean, $65.142, \pm .0039$

In this case the Crafts-Regnault weight of H was taken, one litre = .08979 gramme. Corrected, the mean gives $Zn = 65.082, \pm .0039$.

Two other series of determinations of questionable value remain to be noticed before leaving the consideration of the direct H : Zn ratio. They represent really the practice work of students, and are interesting as an illustration of the closeness with which such work can be done. The first series was made in the laboratory of the Johns Hopkins University, under the direction of Morse and Keiser,[3] and contains 51 determinations, as follows:

$Zn =$		
64.68	65.74	65.40
65.26	64.72	64.80
65.32	65.26	65.20
65.20	64.74	64.40
65.60	64.72	65.00
64.60	65.10	64.40
65.00	64.76	65.24

[1] Journ. Chem. Soc., 51, 854. 1887.
[2] Amer. Chem. Journ., 12, 205. 1890.
[3] Amer. Chem. Journ., 6, 347. 1884.

65.68	64.90	64.60
65.38	64.92	64.80
65.06	64.64	65.14
64.84	65.24	64.84
64.88	64.72	64.82
65.00	65.20	64.80
65.08	65.12	64.40
65.06	66.40	64.60
64.74	64.60	64.80
65.12	65.60	64.74

Mean of all, Zn = 64.997, ± .0328

Corrected for the difference between Regnault's value for H and the new value, this becomes Zn = 64.800, ± .0328.

The second student series was published by Torrey,[1] who gives 15 determinations, as follows:

$$Zn =$$

65.36	64.96
65.30	64.70
64.92	65.00
64.72	64.78
65.04	64.44
64.80	65.24
65.20	64.92
64.90	

Mean, 64.952, ± .0436

Corrected as in the other series, this gives Zn = 64.755, ± .0436.

The five corrected means for the ratio H : Zn may now be combined, thus:

	$H = 1.$	$O = 16.$
Van der Plaats	64.980, ± .0137	65.487
Reynolds and Ramsay...	65.280, ± .0161	65.789
Mallet	65.082, ± .0039	65.590
Morse and Keiser........	64.800, ± .0328	65.305
Torrey	64.755, ± .0036	65.260
General mean	65.079, ± .0036	65.587, ± .0036

Morse and Burton,[2] in their determinations of the atomic weight of zinc, returned essentially to the old method adopted by Erdmann and by Jacquelain. Their zinc was obtained spectroscopically pure by distillation in a vacuum, and was oxidized by nitric acid which left absolutely no residue upon evaporation. The conversion to oxide was effected in a porcelain crucible, which was enclosed in a larger one, and the ignition of the nitrate was carried out in a muffle. In weighing, the crucible was tared by one of nearly equal weight. Results as follows:

[1] Amer. Chem. Journ., 10, 74. 1888.
[2] Amer. Chem. Journ., 10, 311. 1888.

Wt. Zn.	Wt ZnO.	Per cent. Zn in ZnO.
1.11616	1.38972	80.320
1.03423	1.28782	80.308
1.11628	1.38987	80.315
1.05760	1.31681	80.316
1.04801	1.30492	80.313
1.02957	1.28193	80.318
1.09181	1.35944	80.315
1.16413	1.44955	80.305
1.07814	1.34248	80.305
1.12754	1.40400	80.306
.91112	1.13446	80.310
1.10011	1.36981	80.311
1.17038	1.45726	80.313
1.03148	1.28436	80.310
1.05505	1.31365	80.308

Mean, 80.3115, ± .00084

Hence Zn = 65.266.

Morse and Burton verified by experiment the stability of oxide of zinc
at the temperatures of ignition, and found that it did not dissociate.
They also proved the absence of oxides of nitrogen from the zinc oxide.
The investigations of Richards and Rogers,[1] however, have shown that
zinc oxide prepared by ignition of the nitrate always carries gaseous
occlusions, so that the atomic weight of zinc computed from the data of
Morse and Burton is certainly too low. This consideration led Morse and
Arbuckle[2] to reinvestigate zinc oxide, with the purpose of avoiding the
indicated error. The zinc used was a portion of the sample employed by
Morse and Burton, and the process was essentially the same, except that
the oxide, after weighing, was dissolved in sulphuric acid, and the gases
which were evolved were collected, measured and analyzed. All weights
were corrected for displacement of air. The crude data are as follows:

Wt. Zn.	Wt. ZnO.	Gases, cc.	Per cent. Zn, uncorrected.
1.19573	1.48860	.468	80.326
1.03381	1.28707	.402	80.323
1.06519	1.32599	.342	80.332
1.05802	1.31711	.312	80.329
1.26618	1.57619	.521	80.332
1.03783	1.29198	.408	80.329
1.08655	1.35276	.412	80.321
1.11364	1.38647	.456	80.322

Mean, 80.327, ± .0011

[1] Proc. Amer. Acad., 1893, 200.
[2] Am. Chem. Journ., 20, 195. 1898. Also published as a doctoral dissertation, Johns Hopkins
University, by Arbuckle.

The gases evolved contained only nitrogen and oxygen, in varying proportions, which were determined in each case. Uncorrected, $Zn = 65.328$; corrected, the value ranged between 65.437 and 65.489, in mean, 65.456. The last figure corresponds to 80.358 per cent. of zinc in the oxide, an increase of 0.031. If we assume that the same proportional error existed in all the other experiments upon zinc oxide, the several series may be corrected and combined as follows:

Jacquelain	80.572, ± .0070
Erdmann	80.291, ± .0037
Morse and Burton	80.343, ± .00084
Morse and Arbuckle	80.358, ± .0011
General mean	80.349, ± .00065

Here the two earlier series practically disappear, and the modern determinations alone are retained.

The determinations made by Gladstone and Hibbard[1] represent still another process for measuring the atomic weight of zinc. Zinc was dissolved in a voltameter, and the same current was used to precipitate metallic silver or copper in equivalent amount. The weight of zinc dissolved, compared with the weight of the other metal thrown down, gives the atomic weight sought for. Two voltameters were used in the experiments, giving duplicate estimates for zinc with reference to each weighing of silver or copper. The silver series is as follows, with the ratio $2Ag : Zn :: 100 : x$ in the third column:

Zn.	Ag.	Ratio.
.7767	2.5589	30.353
.7758	2.5589	30.318
.5927	1.9551	30.316
.5924	1.9551	30.300
.2277	.7517	30.291
.2281	.7517	30.345
.7452	2.4588	30.307
.7475	2.4588	30.401
.8770	2.9000	30.241
.8784	2.9000	30.290
.9341	3.0809	30.319
.9347	3.0809	30.339

Mean, 30.318, ± .0077

Hence $Zn = 65.414$.

---

[1] Journ. Chem. Soc., 55, 443. 1889.

To the copper series I add the ratio $Cu : Zn :: 100 : x$:

Zn.	Cu.	Ratio.
.7767	.7526	103.13
.7758	.7526	103.08
.5927	.5737	103.31
.5924	.5737	103.26
.2277	.2209	103.08
.2281	.2209	103.26
.8770	.8510	103.05
.8784	.8510	103.22
.9341	.9038	103.36
.9347	.9038	103.42

Mean, 103.22, $\pm$ .0261

Hence $Zn = 65.601$.

Richards and Rogers,[1] in their investigation of the atomic weight of zinc, studied the anhydrous bromide. This was prepared by solution of zinc oxide in hydrobromic acid, evaporation to dryness, and subsequent distillation in an atmosphere of carbon dioxide. In some experiments, however, the bromide was heated in an atmosphere of nitrogen, mingled with gaseous hydrobromic acid. All water can thus be removed, without formation of oxybromides.

The zinc bromide so obtained was dissolved in water and precipitated with a solution containing a known amount of silver in the form of nitrate. The silver bromide was weighed on a Gooch crucible, and the ratio $2AgBr : ZnBr_2$ thus found. An excess of silver was always used, and in one series of experiments it was estimated by precipitation with hydrobromic acid. Deducting the excess thus found from the original quantity of silver, the amount of the latter proportional to the zinc bromide was found; hence the ratio $Ag_2 : ZnBr_2$. The results, with vacuum weights, are as follows:

Series A.

ZnBr$_2$.	AgBr.	Ratio.
1.69616	2.82805	59.976
1.98198	3.30450	59.978
1.70920	2.84949	59.984
2.35079	3.91941	59.978
2.66078	4.43751	59.961

Mean, 59.975, $\pm$ .0034

---

[1] Zeitsch. anorg. Chem., 10, 1. 1895.

Series B.

$ZnBr_2$.	Ag.	$AgBr$.	Ag Ratio.	$AgBr$ Ratio.
2.33882	2.24063	3.90067	104.382	59.959
1.97142	1.88837	3.28742	104.398	59.969
2.14985	2.05971	3.58539	104.376	59.961
2.00966	1.92476	3.35074	104.411	59.977

Mean, 104.392, Mean, 59.967,
$\pm$ .0054 $\pm$ .0027

At the end of the same paper, Richards alone gives two more series of determinations made upon zinc bromide prepared by the action of pure bromine upon pure electrolytic zinc. The bromide so obtained was further refined by sublimation or distillation, and dried by heating in a stream of carbon dioxide and gaseous hydrobromic acid. Thus was ensured the absence of basic salts and water. The weights and results found in the two series were as follows:

Series C.

$ZnBr_2$.	Ag.	Ratio.
6.23833	5.09766	104.379
5.26449	5.0436	104.380
9.36283	8.9702	104.377

Mean, 104.379, $\pm$ .0007

Series D.

$ZnBr_2$.	$AgBr$.	Ratio.
2.65847	4.43358	59.962
2.30939	3.85149	59.961
5.26449	8.77992	59.961

Mean, 59.961, $\pm$ .0004

In some details of manipulation these series differ from those given by Richards and Rogers jointly, but their minutiæ are not essential to the present discussion.

Combining these several series, we have—

For $2Ag:ZnBr_2::100:x$.

Series B .... 104.392, $\pm$ .0054
Series C .... 104.379, $\pm$ .0007

General mean .... 104.380, $\pm$ .0007

For $2AgBr:ZnBr_2::100:x$.

Series A .... 59.975, ± .0034
Series B .... 59.967, ± .0027
Series D .... 59.961, ± .0004

General mean .... 59.962, ± .0004

From the Ag ratio, Zn = 65.371.
From the AgBr ratio, Zn = 65.378.
And Ag : Br :: 100 : 74.077.
In order to determine the atomic weight of zinc, Meaglia [1] measured the direct ratios between that metal and silver or gold. The silver was precipitated from a sulphate solution by zinc, and the gold from a solution of sodium chloraurate. From the weights obtained the following values for zinc were computed, when Ag = 107.93 and Au = 197.2.

Silver Series.	*Gold Series.*
65.58	65.509
65.45	65.424
65.50	65.440
65.41	65.470
Mean, 65.485, ± .0247	Mean, 65.436, ± .0087

From the silver ratio, with Ag = 107.88, Zn = 65.455.
From the gold ratio, with Au = 197.269, Zn = 65.459.
For the ratio 2Ag : Zn, Gladstone and Hibbert's data give the value 30.318, ±.0077. Meaglia's figures, reduced to the same basis, give 30.337, ±.0115. The two series combined give

$$2Ag:Zn::100:30.324, ± .0064$$

For computing the atomic weight of zinc we now have the subjoined ratios :

(1). $ZnO:Zn::100:80.349$, ± .00065
(2). $ZnSO_4:ZnO::100:50.413$, ± .0020
(3). $H_2O:Zn::100:366.319$, ± .088
(4). $2CO_2:ZnO::100:93.169$, ± .012
(5). $H:Zn::1:65.079$, ± .0036
(6). $4Ag:K_2ZnCl_4::100:66.111$, ± .0023
(7). $2Ag:Zn::100:30.324$, ± .0060
(8). $Cu:Zn::100:103.22$, ± .0261
(9). $2Ag:ZnBr_2::100:104.38$, ± .0007
(10). $2AgBr:ZnBr_2::100:59.962$, ± .0004
(11). $Au:Zn::197.2:65.436$, ± .0087

[1] Thesis, University of Grenoble, 1907.

The values used in reducing these ratios are:

Ag = 107.880, ± .00029   C = 12.0038, ± .0002
Cl = 35.4584, ± .0002   K = 39.0999, ± .0002
Br = 79.9197, ± .0003   Cu = 63.5550, ± .00063
S = 32.0667, ± .00075   Au = 197.269, ± .0030
                    H = 1.00779, ± .00001

Hence,

From ratio 6 ....Zn = 65.2488, ± .0100
      "   "   9 ....65.3709, ± .0018
      "   " 10 ....65.3775, ± .0017
      "   "   2 ....65.4004, ± .0047
      "   "   1 ....65.4208, ± .00053
      "   "   7 ....65.4271, ± .0129
      "   " 11 ....65.4589, ± .0088
      "   "   5 ....65.5870, ± .0036
      "   "   8 ....65.6015, ± .0166
      "   "   3 ....65.9946, ± .0159
      "   "   4 ....65.9958, ± .0106

General mean, Zn = 65.4182, ± .00048

This mean is almost identical with one of the values determined by Gladstone and Hibbert, Zn = 65.414. It is distinctly higher than the figure derived from the work of Richards and Rogers. The work of Morse and his colleagues upon zinc oxide evidently dominates the entire combination and, mathematically, at least, outweighs all else. The five highest values in the mean count for very little, in fact their rejection only lowers the atomic weight found for zinc to 65.4137.

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.[1] Hence $Cd = 111.483$. This result has now only a historical interest.

The more modern estimates of the atomic weight of cadmium begin with the work of v. Hauer.[2] He heated pure anhydrous cadmium sulphate in a stream of dry hydrogen sulphide, and weighed the cadmium sulphide thus obtained. His results were as follows, with the percentage of CdS in $CdSO_4$ therefrom deduced:

7.7650 grm. $CdSO_4$ 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, $\pm$ .0042

Hence $Cd = 111.935$.

Lenssen[3] 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, $\pm$ .014

Hence $Cd = 112.07$.

Dumas[4] 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 $CdCl_2$ and 100 parts of silver:

---

[1] See Berz. Lehrbuch, 5th Aufl., 3, 1219.
[2] Journ. prakt. Chem., 72, 350. 1857.
[3] Journ. prakt. Chem., 79, 281. 1860.
[4] Ann. Chem. Pharm., 113, 27. 1860.

2.369 grm.	CdCl$_2$ =	2.791 grm.	Ag.			84.880
4.540	"	5.348	"			84.892
6.177	"	7.260	"			85.083
2.404	"	2.841	"			84.618
3.5325	"	4.166	"			84.794
4.042	"	4.767	"			84.791

Mean, 126.076, ± .0052

Hence Cd = 112.14.

Next in order comes Huntington's[1] work, carried out in the laboratory of J. P. Cooke. Bromide of cadmium 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.	CdBr$_2$ 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
3.4773	"	4.7593	"	"	72.433

Mean, 72.4216, ± .0028

Hence Cd = 112.18.

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.	CdBr$_2$ =	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, 84.843, ± .026

Hence Cd = 112.19.

---

[1] Proc. Amer. Acad., 17, 28. 1881.

According to Huntington's own calculations, these experiments fix the ratio between silver, bromine and cadmium as $Ag : Br : Cd :: 108 : 80 : 112.31$.

In 1890, Partridge[1] published determinations of the atomic weight of cadmium, made by three methods, the weighings being reduced to a vacuum standard throughout. First, Lenssen's method was followed, viz., the ignition of the oxalate, with the subjoined results:

$CdC_2O_4.$	$CdO.$	Per cent. $CdO.$
1.09898	.70299	63.966
1.21548	.77746	63.962
1.10711	.70807	63.957
1.17948	.75440	63.959
1.16066	.74327	63.959
1.17995	.75471	63.964
1.34227	.85864	63.968
1.43154	.91573	63.970
1.53510	.98197	63.968
1.41311	.90397	63.971

Mean, 63.964, $\pm$ .0010

Hence $Cd = 111.80$.

Secondly, v. Hauer's experiments were repeated, cadmium sulphate being reduced to sulphide by heating in a stream of H_2S. The following data were obtained:

$CdSO_4.$	$CdS.$	Per cent. $CdS.$
1.60514	1.11076	69.204
1.55831	1.07834	69.197
1.67190	1.15669	69.185
1.66976	1.15554	69.200
1.40821	.97450	69.202
1.56290	1.08156	69.205
1.63278	1.12985	69.194
1.58270	1.09524	69.198
1.53873	1.06481	69.201
1.70462	1.17962	69.201

Mean, 69.199, $\pm$ .0012

v. Hauer found, 69.231, $\pm$ .0042

General mean, 69.202, $\pm$ .0012

The Partridge series alone gives $Cd = 111.718$.

---

[1] Amer. Journ. Sci. (3), 40, 377. 1890.

In the third set of determinations cadmium oxalate was transformed to sulphide by heating in H_2S, giving the ratio $CdC_2O_4 : CdS :: 100 : x$:

CdC_2O_4.	CdS.	Per cent. CdS.
1.57092	1.13065	71.972
1.73654	1.24979	71 973
2.19276	1.57825	71.974
1.24337	.89492	71.974
1.18743	.85463	71.975
1.54038	1.10858	71.968
1.38905	.99974	71.976
2.03562	1.46517	71.979
2.03781	1.46658	71.970
1.91840	1.38075	71.971

Hence Cd $=111.61$.   Mean, $71.973, \pm .0007$

This work of Partridge was presently discussed by Clarke,[1] with reference to the concordance of the data, and it was shown that the three ratios determined could be discussed algebraically, giving values for the atomic weights of Cd, S and C when $O = 16$. These values are—

$$Cd = 111.7850$$
$$C = 11.9958$$
$$S = 32.0002$$

and are independent of all antecedent values except that assumed for the standard, oxygen.

Morse and Jones,[2] starting with cadmium purified by fractional distillation in vacuo, adopted two methods for their determinations. First, they effected the synthesis of the oxide from known weights of metal by dissolving the latter in nitric acid, evaporating to dryness, and subsequent ignition of the product. The oxide thus obtained was thought to be completely free from oxides of nitrogen. The weighings, which are given below, were made in tared crucibles. The third column gives the percentage of Cd in CdO:

Cd taken.	CdO found.	Per cent. Cd.
1.77891	2.03288	87.507
1.82492	2.08544	87.508
1.74688	1.99626	87.507
1.57000	1.79418	87.505
1.98481	2.26820	87.506
2.27297	2.59751	87.504
1.75695	2.00775	87.508
1.70028	1.94305	87.505
1.92237	2.19679	87.508
1.92081	2.19502	87.508

Hence Cd $=112.068$.   Mean, $87.5066, \pm .00032$

[1] Amer. Chem. Journ., 13, 34. 1891.
[2] Amer. Chem. Journ., 14, 261. 1892.

The second method employed by Morse and Jones was that of Lenssen with cadmium oxalate. This salt they found to be somewhat hygroscopic, a property against which the operator must be on his guard. The data found are as follows:

CdC_2O_4.	CdO.	Per cent. CdO.
1.53937	.98526	64.004
1.77483	1.13582	63.996
1.70211	1.08949	64.008
1.70238	1.08967	64.004
1.74447	1.11651	64.003

Mean, 64.003, ± .0042

Hence Cd = 112.03.

Lorimer and Smith,[1] like Morse and Jones, determined the atomic weight of cadmium by means of the oxide, but by analysis instead of synthesis. Weighed quantities of oxide were dissolved in potassium cyanide solution, from which metallic cadmium was thrown down electrolytically. The weights are reduced to a vacuum standard:

CdO taken.	Cd found.	Per cent. Cd.
.34767	.30418	87.491
.41538	.36352	87.515
1.04698	.91618	87.507
1.04066	.91500	87.493
1.26447	1.10649	87.506
.78493	.68675	87.492
.86707	.75884	87.518
.67175	.58785	87.510
1.44362	1.26329	87.508

Mean, 87.5044, ± .0023

Hence Cd = 112.042.

Mr. Bucher's dissertation[2] upon the atomic weight of cadmium does not claim to give any final measurements, but rather to discuss the various methods by which that constant has been determined. Nevertheless, it gives many data which seem to have positive value, and which are certainly fit for discussion along with those which have preceded this paragraph. Bucher began with cadmium purified by distillation nine times in vacuo, and from this his various compounds were prepared. His first series of determinations was made by reducing cadmium oxalate to oxide, the oxalate having been dried fifty hours at 150°. The reduction was effected by heating in jacketed porcelain crucibles, with various precautions, and the results obtained, reduced to a vacuum standard, are as follows:

---

[1] Zeitsch. anorg. Chem., 1, 361. 1892.

[2] "An examination of some methods employed in determining the atomic weight of cadmium." Johns Hopkins University doctoral dissertation. By John E. Bucher. Baltimore, 1895.

Oxalate.	Oxide.	Per cent. oxide.
1.97674	1.26414	63.951
1.94912	1.24682	63.968
1.96786	1.25886	63.971
1.87099	1.19675	63.958
1.37550	.87994	63.972
1.33313	.85308	63.991
1.94450	1.24452	64.002
2.01846	1.29210	64.014

Mean, 63.978, ± .0052

Hence Cd = 111.89.

Combining this with the means found by previous experimenters, we have for the percentage of oxide in oxalate—

Lenssen .... 64.010, ± .0140
Partridge .... 63.964, ± .0010
Morse and Jones.............. 64.003, ± .0042
Bucher .... 63.978, ± .0052

General mean .... 63.966, ± .0010

Bucher's next series of determinations was by Partridge's method—the conversion of cadmium oxalate into cadmium sulphide by heating in a stream of sulphuretted hydrogen. The sulphide was finally cooled in a current of dry nitrogen. The vacuum weights and ratios are subjoined:

Oxalate.	Sulphide.	Percentage.
2.56319	1.84716	72.065
2.18364	1.57341	72.055
2.11643	1.52462	72.037
3.13105	2.25582	72.047

Mean, 72.051, ± .0127
Partridge found, 71.973, ± .0007

General mean, 71.974, ± .0007

Here Bucher's mean practically vanishes. Taken alone, it gives Cd = 112.15.

The third method employed by Bucher was that of weighing cadmium chloride, dissolving in water, precipitating with silver nitrate, and weighing the silver chloride found. The cadmium chloride was prepared, partly by solution of cadmium in hydrochloric acid, evaporation to dryness, and sublimation in vacuo; and partly by the direct union of the metal with chlorine. The silver chloride was weighed in a Gooch-crucible, with platinum sponge in place of the asbestos. To the vacuum weights I append the ratio $2AgCl : CdCl_2 :: 100 : x$.

$CdCl_2$.	$AgCl$.	Ratio.
3.09183	4.83856	63.900
2.26100	3.53854	63.896
1.35729	2.12431	63.893
2.05582	3.21727	63.899
1.89774	2.97041	63.886
3.50367	5.48473	63.880
2.70292	4.23087	63.886
4.24276	6.63598	63.936
3.40200	5.32314	63.910
4.60659	7.20386	63.946
2.40832	3.76715	63.930
2.19144	3.42724	63.942
2.84628	4.45477	63.893
2.56748	4.01651	63.923
2.31003	3.61370	63.924
1.25008	1.95652	63.893
1.96015	3.06541	63.944
2.29787	3.59391	63.938
1.94227	3.03811	63.915
1.10976	1.73547	63.946
1.63080	2.55016	63.949

Mean, 63.916, $\pm$ .0032

Hence Cd $= 112.315$.

Bucher gives a rather full discussion of the presumable errors in this method, which, however, he regards as somewhat compensatory. The series is followed by a similar one with cadmium bromide, the latter having been sublimed in vacuo. Results as follows:

$CdBr_2$.	$AgBr$.	Ratio.
4.39941	6.07204	72.454
3.18030	4.38831	72.472
3.60336	4.97150	72.480
4.04240	5.58062	72.453
3.60505	4.97519	72.461

Mean, 72.464, $\pm$ .0035

Hence Cd $= 112.34$.

In order to fix a minimum value for the atomic weight of cadmium, Bucher effected the synthesis of the sulphate from the metal. 1.15781 grammes of cadmium gave 2.14776 of sulphate.

Hence Cd $= 112.36$.

The sulphate produced was dried at 400°, and afterwards examined for free sulphuric acid, giving a correction which was applied to the weighings. The corrected weight is given above. Any impurity in the sulphate would tend to lower the apparent atomic weight of cadmium, and therefore the result is believed by the author to be a minimum.

Finally, Bucher examined the oxide method followed by Morse and Jones. The syntheses of oxide were effected in double crucibles, first with both crucibles porcelain, and afterwards with the small inner crucible of platinum. Two experiments were made by the first method, three by the last. Weights and percentages (Cd in CdO) as follows:

Cd.	CdO.	Percentage.
1.26142	1.44144	87.511
.99785	1.14035	87.504

Mean, 87.5075, ± .0024

Cd.	CdO.	Percentage.
1.11321	1.27247	87.484
1.02412	1.17054	87.491
2.80966	3.21152	87.487

Mean, 87.4873, ± .0016

The two means given above, representing work done with porcelain and with platinum crucibles, correspond to a difference of about 0.2 in the atomic weight of cadmium. Experiments were made with pure oxide of cadmium by converting it into nitrate and then back to oxide, exactly as in the foregoing syntheses. In each case the oxide obtained at the end of the operation represented an increase in weight, but the increase was greater in platinum than in porcelain. Hence the weighings of cadmium oxide in the foregoing determinations are subject to constant errors, and cannot be trusted to fix the atomic weight of cadmium.

A different class of determinations relative to the atomic weight of cadmium are those of Hardin,[1] who effected the electrolysis of the chloride and bromide, and also made a direct comparison between cadmium and silver. The aqueous solutions of the salts, mixed with potassium cyanide, were electrolyzed in platinum dishes. The cadmium which served as the starting point for the investigation was purified by distillation in hydrogen. All weights are reduced to a vacuum. The data for the chloride series are as follows, with a column added for the percentage of Cd in $CdCl_2$:

[1] Journ. Amer. Chem. Soc., 18, 1016. 1896.

Weight CdCl₂.	Weight Cd.	Percentage Cd.
.43140	.26422	61.247
.49165	.30112	61.247
.71752	.43942	61.241
.72188	.44208	61.241
.77264	.47319	61.245
.81224	.49742	61.240
.90022	.55135	61.246
1.02072	.62505	61.236
1.26322	.77365	61.244
1.52344	.93314	61.252

Mean, 61.244, ± .0010

Hence Cd = 112.07.

The results for the bromide, similarly stated, are these:

Weight CdBr₂.	Weight Cd.	Percentage Cd.
.57745	.23790	41.198
.76412	.31484	41.203
.91835	.37842	41.207
1.01460	.41808	41.206
1.15074	.47414	41.203
1.24751	.51392	41.196
1.25951	.51905	41.210
1.51805	.62556	41.208
1.63543	.67378	41.199
2.15342	.88722	41.200

Mean, 41.203, ± .0010

Hence Cd = 112.01.

The direct comparison of cadmium and silver was effected by the simultaneous electrolysis, in the same current, of double cyanide solutions. Silver was thrown down in one platinum dish and cadmium in another. The process was not altogether satisfactory, and gave divergent results, those which are cited below having been selected by Hardin from the mass of data obtained. I have added in a third column the cadmium proportional to 100 parts of silver:

Weight Cd.	Weight Ag.	Ratio.
.12624	.24335	51.876
.11032	.21262	51.886
.12720	.24515	51.887
.12616	.24331	51.852
.22058	.42520	51.877

Mean, 51.876, ± .0041

Hence Cd = 111.93.

The work of Morse and Arbuckle [1] upon the atomic weight of cadmium was similar in character and purpose to their work upon zinc. The presence of occluded gases in the oxide was recognized, and in the new determinations they were extracted, measured and analyzed. Cadmium was converted into oxide, and corrections for the gaseous impurities were applied. The vacuum weights of metal and oxide are given below, together with the volume of extracted gas, and the crude, *uncorrected* percentage of Cd in CdO :

Weight Cd.	Weight CdO.	Gas cc.	Per cent.
1.931882	2.207639	.574	87.509
1.679348	1.919096	.480	87.507
1.484296	1.696195	.441	87.507
1.364861	1.559717	.402	87.507
1.502948	1.717441	.419	87.511
1.438035	1.643297	.431	87.509
1.440410	1.646037	.406	87.508
1.459384	1.667714	.421	87.508
1.403791	1.604196	.390	87.507

Mean, 87.508, ± .0003

This gives Cd = 112.082. Corrected for occluded gases, Cd = 112.377 in mean, ranging from 112.359 to 112.395. The correction adds 0.029 to the percentage of metal; and if we assume the same correction to the older determinations of this ratio, the several series combine as follows :

Morse and Jones............	87.5356, ± .0003
Lorimer and Smith.........	87.5334, ± .0023
Bucher, 1	87.5365, ± .0024
Bucher, 2	87.5163, ± .0016
Morse and Arbuckle.........	87.5370, ± .0003
General mean	87.5360, ± .0002

This combination is equivalent to a rejection of all the data except those of Morse and his colleagues.

Baxter and Hines,[2] in order to determine the atomic weight of cadmium, resorted to the analysis of the chloride, with all the precautions characteristic of the Harvard laboratory. First, the gravimetric ratio $2AgCl : CdCl_2$ was determined, with the subjoined results. Vacuum weights are given throughout :

Weight CdCl₂.	Weight AgCl.	Ratio.
5.53421	8.65356	63.953
7.77758	12.16166	63.952
8.87917	13.88344	63.955

---

[1] Amer. Chem. Journ., 20, 536. 1898. See also Arbuckle, Thesis, Johns Hopkins University, 1898.
[2] Journ. Amer. Chem. Soc., 27, 222. 1905.

Secondly, the ratio $2Ag : CdCl_2$ was measured by adding to the solution of the cadmium salt as nearly as possible its exact equivalent of a standard silver solution, and then determining the slight excess of silver or chlorine by titration. The results are as follows:

Weight $CdCl_2$.	Weight Ag.	Ratio.
4.92861	5.80063	84.967
3.86487	4.54891	84.963
5.08551	5.98569	84.961
5.84335	6.87704	84.969
5.99952	7.06084	84.969
3.73092	4.39095	84.968

A year later, the same ratios were remeasured by Baxter, Hines and Frevert.[1] I subjoin their data:

Weight $CdCl_2$.	Weight Ag.	Weight AgCl.	Ag ratio.	AgCl ratio.
5.62500	6.61993	. . . .	84.972	. . . . . .
6.81031	8.01496	10.64918	84.970	63.9515
5.50089	6.47393	8.60174	84.970	63.9509
6.11750	. . . . . .	9.56590	. . . . .	63.9511

These series are so nearly identical and so short that it seems well to treat both investigations as one. On this basis, $2Ag : CdCl_2 :: 100 : 84.9677, \pm.0008$, and $2AgCl : CdCl_2 :: 100 : 63.9523, \pm.0004$.

Hence, from the Ag ratio, $Cd = 112.41$.

From the AgCl ratio, $Cd = 112.42$.

And $Ag : Cl :: 100 : 32.861$.

Combined with the values found by former investigators, the ratios assume the following form:

Silver Ratio.

Dumas . . . . 84.843, $\pm$ .0260

Baxter, etc. . . . . 84.9677, $\pm$ .0008

General mean . . . . 84.9676, $\pm$ .0008

Silver Chloride Ratio.

Bucher . . . . 63.916, $\pm$ .0032

Baxter, etc. . . . . 63.9523, $\pm$ .0004

General mean . . . . 63.9518, $\pm$ .0004

Baxter, Hines and Frevert also made analyses of cadmium bromide by the usual Harvard methods. Their data follow:

---

[1] Journ. Amer. Chem. Soc., 28, 770. 1906.

Weight $CdBr_2$.	Weight Ag.	Weight AgBr.	Ag ratio.	AgBr ratio.
11.46216	9.08379	15.81319	126.182	72.485
6.82282	5.40724	9.41267	126.182	72.486
6.75420	5.35277	9.31830	126.181	72.483
[1] 7.08588	[1] 5.61597	[1] 9.77649	126.174	72.479
5.13859	4.07226	7.08933	126.183	72.483
5.84324	4.63072	8.06130	126.183	72.485
5.99704	4.75259	8.27360	126.183	72.484
5.90796	4.68200	8.15070	126.183	72.484
		Mean,	126.181.	72.4836,
			± .0009	± .0005

From the Ag ratio, Cd = 112.42.
From the AgBr ratio, Cd = 112.41.
And Ag: Br:: 100 : 74.082.

These ratios combine with former series as follows:

Silver Ratio.

Huntington .... 126.076, ± .0052
Baxter, etc. .... 126.181, ± .0009

General mean .... 126.178, ± .0009

Silver Bromide Ratio.

Huntington .... 72.4216, ± .0028
Bucher .... 72.464, ± .0035
Baxter, etc. .... 72.4836, ± .0005

General mean .... 72.4813, ± .0005

The determinations of the atomic weight of cadmium by Meaglia[2] were based upon the quantitative precipitation by that metal of silver from a sulphate solution, and gold from a solution of sodium chloraurate. With Ag = 107.93 and Au = 197.2 the following values for cadmium were obtained:

Silver series.	Gold series.
112.37	112.41
112.56	112.45
112.45	112.65
112.38	112.47
	112.48
Mean, 112.44, ± .0295	112.40
	112.42
	112.41
	Mean, 112.461, ± .0196

From the silver series, with Ag = 107.88, Cd = 112.39.
From the gold series, with Au = 197.269, Cd = 112.50.

---

[1] This analysis is rejected by the authors.
[2] Thesis, University of Grenoble, 1907.

For the ratio 2Ag: Cd Hardin found the value 51.876, ±.0041. Meaglia's series gives 52.090, ±.0136. The general mean of both series combined is

$$2Ag:Cd::100:51.893, \pm .0039$$

The determinations made by Blum [1] depended upon the conversion of CdO into CdS by heating in a stream of hydrogen sulphide. His figures, with vacuum weights, are given below, together with the ratio CdO: CdS :: 100 : x:

CdO.	CdS.	Ratio.
1.80552	2.03108	112.493
.66349	.74617	112.461
1.82460	2.05256	112.494
1.88424	2.11974	112.498
3.59206	4.04081	112.493
4.38093	4.92695	112.464

Mean, 112.484, ± .0046

Hence Cd = 112.69. This ratio is not of much value.
For cadmium the subjoined ratios are now available.

Bucher's single experiment upon the synthesis of the sulphate, although important and interesting, cannot carry weight enough to warrant its consideration in connection with the other ratios, and is therefore not included.

(1). $CdO:Cd::100:87.536, \pm .0002$
(2). $CdC_2O_4:CdO::100:63.966, \pm .0010$
(3). $CdC_2O_4:CdS::100:71.974, \pm .0007$
(4). $CdSO_4:CdS::100:69.202, \pm .0012$
(5). $2Ag:CdCl_2::100:84.9676, \pm .0008$
(6). $2AgCl:CdCl_2::100:63.9518, \pm .0004$
(7). $2Ag:CdBr_2::100:126.178, \pm .0009$
(8). $2AgBr:CdBr_2::100:72.4813, \pm .0005$
(9). $CdCl_2:Cd::100:61.244, \pm .0010$
(10). $CdBr_2:Cd::100:41.203, \pm .0010$
(11). $2Ag:Cd::100:51.893, \pm .0039$
(12). $Au:Cd::197.2:112.461, \pm .0196$
(13). $CdO:CdS::100:112.484, \pm .0046$

Reducing these ratios with

Ag = 107.880, ± .00029	S = 32.0667, ± .00075
Cl = 35.4584, ± .0002	C = 12.0038, ± .0002
Br = 79.9197, ± .0003	Au = 197.269, ± .0030

---

[1] Thesis, University of Pennsylvania, 1908.

we have—

From ratio 3	....	Cd = 111.607,	± .0050
"	" 4	....	111.739, ± .0062
"	" 2	....	111.822, ± .0041
"	" 11	....	111.964, ± .0071
"	" 10	....	112.010, ± .0033
"	" 9	....	112.066, ± .0035
"	" 1	....	112.370, ± .0018
"	" 8	....	112.400, ± .0021
"	" 7	....	112.403, ± .0022
"	" 5	....	112.410, ± .0018
"	" 6	....	112.416, ± .0013
"	" 12	....	112.500, ± .0197
"	" 13	....	112.689, ± .0478

General mean, Cd = 112.323, ± .0007

This mean value is almost certainly too low. If the six lowest values in the foregoing series are omitted, the general mean of the seven higher values is

$$Cd = 112.402, \pm .0008$$

which agrees well with the determinations by Baxter and his colleagues, and yet takes into account the work of Morse and Arbuckle. In short, Cd = 112.4, within the limits of experimental uncertainty.

MERCURY.

In dealing with the atomic weight of mercury we may reject the early determinations by Sefström [1] and a large part of the work done by Turner. [2] The latter chemist, in addition to the data which will be cited below, gives figures to represent the percentage composition of both the chlorides of mercury; but these results are neither trustworthy 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, $\pm$ .0050

Hence Hg = 200.626.

In the experiments of Erdmann and Marchand [3] 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, $\pm$ .0015

Hence Hg = 200.205.

Hardin's determination of the same ratio, being different in character, will be considered later.

[1] Sefström. Berz. Lehrb., 5th ed., 3, 1215. Work done in 1812.

[2] Phil. Trans., 1833, 531-535.

[3] Journ. 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 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. ± .0027

Hence Hg = 200.520.

For the percentage of mercury in mercuric chloride we have data by Turner, Millon, Svanberg and Hardin. Turner,[1] 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, ± .005

Hence Hg = 199.665.

Millon[2] 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, ± .010

Hence Hg = 200.224.

Svanberg,[3] following the general method of Erdmann and Marchand, made three distillations of mercuric chloride with lime, and got the following results:

[1] Phil. Trans., 1833, 531-535.
[2] Ann. Chim. Phys. (3), 18, 345. 1846.
[3] Journ. prakt. Chem., 45, 472. 1848.

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

Hence Hg = 199.706.

Much more recent determinations of the atomic weight of mercury are
due to Hardin,[1] whose methods were entirely electrolytic. First, pure
mercuric oxide was dissolved in dilute, aqueous potassium cyanide, and
electrolyzed in a platinum dish. Six determinations are published, out
of a larger number, but without reduction of the weights to a vacuum.
The data, with a percentage column added, are as follows:

Weight HgO.	Weight Hg.	Per cent. Hg.
.26223	.24281	92.594
.23830	.22065	92.593
.23200	.21482	92.595
.14148	.13100	92.593
.29799	.27592	92.594
.19631	.18177	92.593

Mean, 92.594, ± .0003

Hence Hg = 200.041.

Various sources of error were detected in these experiments, and the
series is therefore rejected by Hardin. It combines with previous series
as follows:

Turner .... 92.614, ± .0050

Erdmann and Marchand...... 92.5996, ± .0015

Hardin .... 92.594, ± .0003

General mean .... 92.595, ± .0003

Hardin also studied mercuric chloride, bromide and cyanide, and the
direct ratio between mercury and silver, with reduction of weights to a
vacuum. Electrolysis was conducted in a platinum dish, as usual. With
the chloride and bromide, the solutions were mixed with dilute potassium
cyanide. The data for the chloride are as follows, the percentage column
being added by myself:

---

[1] Journ. Amer. Chem. Soc., 18, 1003. 1896.

Weight $HgCl_2$.	Weight Hg.	Per cent. Hg.
.45932	.33912	73.831
.54735	.40415	73.838
.56002	.41348	73.833
.63586	.46941	73.823
.64365	.47521	73.831
.73281	.54101	73.827
.86467	.63840	73.832
1.06776	.78825	73.823
1.07915	.79685	73.820
1.51402	1.11780	73.830

Mean, 73.829, $\pm$ .0012

Hence Hg = 200.058.

For the bromide Hardin's data are—

Weight $HgBr_2$.	Weight Hg.	Per cent Hg.
.70002	.38892	55.558
.56430	.31350	55.555
.57142	.31750	55.563
.77285	.42932	55.550
.80930	.44955	55.548
.85342	.47416	55.560
1.11076	.61708	55.555
1.17270	.65145	55.551
1.26186	.70107	55.559
1.40142	.77870	55.565

Mean, 55.556, $\pm$ .0012

Hence Hg = 199.803.

And for the cyanide—

Weight HgC_2N_2.	Weight Hg.	Per cent. Hg.
.55776	.44252	79.337
.63290	.50215	79.341
.70652	.56053	79.337
.80241	.63663	79.340
.65706	.52130	79.338
.81678	.64805	79.342
1.07628	.85392	79.340
1.22615	.97282	79.339
1.66225	1.31880	79.338
2.11170	1.67541	79.339

Mean, 79.339, $\pm$ .0004

Hence Hg = 199.835.

In the last series cited no potassium cyanide was used, but the solution of mercuric cyanide, with the addition of one drop of sulphuric acid, was electrolyzed directly.

The direct ratio between silver and mercury was determined by throwing down the two metals, simultaneously, in the same electric current. Both metals were taken in double cyanide solution. With Hardin's equivalent weights I give a third column, showing the quantity of mercury corresponding to 100 parts of silver. Many experiments were rejected, and only the following seven are published by the author:

Weight Hg.	Weight Ag.	Ratio.
.06126	.06610	92.678
.06190	.06680	92.665
.07814	.08432	92.671
.10361	.11181	92.666
.15201	.16402	92.678
.26806	.28940	92.626
.82808	.89388	92.639

Mean, 92.660, ± .0051

Hence $Hg = 199.923$.

The determinations by Easley[1] are quite unlike those made by his predecessors. First, mercuric chloride in solution was reduced to metal by means of hydrogen dioxide, and was precipitated partly as a globule and partly in finely divided form. The globule was washed with water and acetone and weighed. The finely divided mercury was again dissolved, and with a little mercury remaining in solution, was deposited electrolytically upon a gold cathode. Its weight was then added to that of the globule. The following results, with vacuum weights, were obtained:

$HgCl_2$.	Hg.	Per cent. Hg.
23.43239	17.30826	73.865
12.59751	9.30608	73.873
10.94042	8.08154	73.869
11.73734	8.67044	73.871

Mean, 73.8695, ± .0012

Hence $Hg = 200.478$.

Combining this with the earlier determinations we have—

Turner	73.791,	± .0050
Millon	73.845,	± .0100
Svanberg	73.795,	± .0060
Hardin	73.829,	± .0012
Easley	73.8695,	± .0012
General mean	73.8459,	± .0008

[1] Journ. Amer. Chem. Soc., 31, 1207. 1909.

17

In the filtrate from the mercury the chlorine was precipitated as silver chloride and so weighed. The results were as follows, with vacuum weights:

$HgCl_2$.	$AgCl$.	Ratio.
10.50276	11.08744	94.7257
9.03634	9.54027	94.7179
23.43239	24.73606	94.7297
10.94042	11.55158	94.7093
11.11409	11.73470	94.7113
16.63910	17.56808	94.7121

Mean, 94.7177, $\pm$ .0023

Hence $Hg = 200.617$.

We now have seven ratios involving the atomic weight of mercury, as follows:

(1). Per cent. of Hg in HgO, 92.595, $\pm$ .0003
(2). Per cent. of Hg in HgS, 86.2127, $\pm$ .0027
(3). Per cent. of Hg in $HgCl_2$, 73.8459, $\pm$ .0008
(4). Per cent. of Hg in $HgBr_2$, 55.556, $\pm$ .0012
(5). Per cent. of Hg in HgC_2N_2, 79.339, $\pm$ .0004
(6). $2Ag:Hg::100:92.660$, $\pm$ .0051
(7). $2AgCl:HgCl_2::100:94.7177$, $\pm$ .0023

The antecedent atomic weights are—

Ag = 107.880, $\pm$ .00029	S = 32.0667, $\pm$ .00075
Cl = 35.4584, $\pm$ .0002	N = 14.0101, $\pm$ .0001
Br = 79.9197, $\pm$ .0003	C = 12.0038, $\pm$ .0002

Hence,

From ratio 4	$Hg =$ 199.803, $\pm$ .0069
" " 5	199.835, $\pm$ .0045
" " 6	199.923, $\pm$ .0110
" " 1	200.070, $\pm$ .0081
" " 3	200.233, $\pm$ .0066
" " 2	200.520, $\pm$ .0394
" " 7	200.617, $\pm$ .0067

General mean, $Hg = 200.054$, $\pm$ .0027

Mathematically, Hardin's determinations seem to outweigh the others. They are, moreover, comparatively concordant and by four methods. But it is quite possible that Easley's much higher figures may prove to be more correct. His work is to be continued; but, until it is finished, it would be unwise to adopt his results exclusively. The atomic weight of mercury is still much in doubt.

BORON.

In the first edition of this book the data relative to boron were few and unimportant. There was a little work on record by Berzelius and by Laurent, and this was eked out by a discussion of Deville's analyses of boron chloride and bromide. As the latter were not intended for atomic weight determinations they will be omitted from the present recalculation, which includes a number of later researches.

Berzelius [1] based his determination upon three concordant estimations of the percentage of water in borax. Laurent [2] 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 = 11.019.

In 1869 Dobrovolsky [3] published a dissertation, in Russian, on the atomic weight of boron. The original I have not seen, and I am therefore compelled to use the data as cited by Brauner.[4] According to Dobrovolsky, borax is completely dehydrated by ignition when small quantities of it are taken. With large quantities, some water is retained. Two series of experiments are given to illustrate this assertion:

First Series.

Borax.	Water.	Per cent. water.
.138	.0651	47.174
.283	.1338	47.279
.312	.1472	47.179

Mean, 47.211, ± .023

Hence B = 10.855.

Second Series.

Borax.	Water.	Per cent. water.
2.701	1.268	46.946
1.793	.843	47.016
3.004	1.402	46.671

Mean, 46.878, ± .072

Hence B = 11.532.

---

[1] Poggend. Annal., 8, 1. 1826.
[2] Journ. prakt. Chem., 47, 415. 1849.
[3] Doctoral Dissertation, Kiev, 1869.
[4] In Abegg's Handbuch der anorganischen Chemie, Bd. 3, Abth. 1, p. 6.

These figures are of no present importance, for the supposed difficulty of dehydration, in the light of more recent investigations, seems to be imaginary.

In 1892 the posthumous notes of the late Hoskyns-Abrahall were edited and published by Ewan and Hartog.[1] This chemist especially studied the ratio between boron bromide and silver, and also redetermined the percentage of water in crystallized borax. The latter work, which was purely preliminary, although carried out with great care, gave the following results, reduced to a vacuum standard:

$Na_2B_4O_7.10H_2O.$	$Na_2B_4O_7.$	Per cent. $H_2O.$
7.00667	3.69587	47.2069
12.95936	6.82560	47.3308
4.65812	2.45248	47.3504
4.47208	3.93956	47.2763
4.94504	2.60759	47.2686
		Mean, 47.2866, ± .0171

Hence B = 10.702.

Two sets of determinations were made with the bromide, which was prepared from boron and bromine directly, freed from excess of the latter by standing over mercury, and finally collected, after distillation, in small, weighed, glass bulbs. It was titrated with a solution of silver after all the usual precautions. The first series of experiments was as follows, with BBr_3 proportional to 100 parts of silver stated as the ratio:

$BBr_3.$	$Ag.$	Ratio.
1.31203	1.69406	77.449
4.39944	5.67829	77.478
5.04022	6.50820	77.444
6.51597	8.38919	77.433
7.75343	10.01235	77.439
		Mean, 77.449, ± .0053

This series of data is regarded by the editors as preliminary, and not entitled to much consideration. The second series, which follows, was the final one; both represent vacuum standards:

$BBr_3.$	$Ag.$	Ratio.
4.467835	5.771268	77.415
8.423151	10.880648	77.414
1.655111	2.137593	77.429
8.032352	10.374201	77.426
4.092743	5.285949	77.427
2.389993	3.086842	77.425
7.721944	9.974054	77.420
		Mean, 77.422, ± .0018
		First series, 77.449, ± .0053

Hence B = 10.819.   General mean, 77.425, ± .0017

---

[1] Journ. Chem. Soc., 61, 650. 1892.

Ramsay and Aston,[1] in their paper upon the atomic weight of boron, suggest that Abrahall's bromide may have contained hydrobromic acid, which would fully account for the low result obtained. They themselves adopt two distinct methods, the first one being the time-honored determination of water in crystallized borax. The latter was prepared from pure boric acid and pure sodium hydroxide. Results as follows, reduced to a vacuum:

$Na_2B_4O_7.10H_2O.$	$Na_2B_4O_7.$	Per cent. $H_2O.$
10.3581602	5.4784357	47.1099
5.3440080	2.8246677	47.1433
4.9962580	2.6378934	47.2026
5.7000256	3.0101127	47.1912
5.3142725	2.8065646	47.1882
4.9971924	2.6392016	47.1865
5.2366921	2.7674672	47.1524

Mean, 47.1677, ± .0086

Hence B = 10.942.

The second method adopted by Ramsay and Aston was to distill anhydrous borax with hydrochloric acid and methyl alcohol, both scrupulously pure, thereby converting it into sodium chloride. The operation was conducted in a glass flask, and in the first series of determinations ordinary soft glass was used. This, however, was somewhat attacked, so that the sodium chloride contained silica; hence oxygen in the material of the flask had been replaced by chlorine, thereby increasing its weight and lowering the apparent atomic weight of boron. In a second series flasks of hard combustion tubing were taken, and the error, though not absolutely avoided, was reduced to a very small amount. Both series are subjoined, together with the percentage of chloride formed; but the weights, given by the authors to seven decimal places, are only quoted to the nearest tenth milligramme. They are reduced to a vacuum standard:

First Series.

$Na_2B_4O_7.$	$NaCl.$	Per cent. $NaCl.$
4.7684	2.7598	57.877
5.2740	3.0578	57.978
3.2344	1.8727	57.899
4.0862	2.3713	58.032
3.4970	2.0266	57.953

Mean, 57.948, ± .0187

---

[1] Journ. Chem. Soc., 63, 211. 1893.

Second Series.

$Na_2B_4O_7$.	$NaCl$.	Per cent. $NaCl$.
5.3118	3.0761	57.911
4.7806	2.7700	57.943
4.9907	2.8930	57.968
4.7231	2.7360	57.928
3.3138	1.9187	57.900

Mean, 57.930, ± .0081
First series, 57.948, ± .0187

General mean of both, 57.933, ± .0074

Hence $B = 10.957$.

As a check upon the last series of results, the sodium chloride was dissolved in water, and precipitated with silver nitrate. The silver chloride was collected and weighed in a Gooch crucible, and its weight gives a new ratio with anhydrous borax. The cross ratio between the two chlorides, silver and sodium, has already been used in the discussion upon sodium. The new ratio I give in terms of $Na_2B_4O_7$ equivalent to 100 parts of AgCl.

$Na_2B_4O_7$.	$AgCl$.	Ratio.
5.3118	7.5259	70.580
4.7806	6.7794	70.517
4.9907	7.0801	70.489
4.7231	6.6960	70.536
3.3138	4.6931	70.610

Mean, 70.546, ± .0146

Hence $B = 11.054$.

Rimbach [1] based his determination of the atomic weight of boron upon the fact that boric acid is neutral to methyl orange, and that therefore it is possible to titrate a solution of borax directly with hydrochloric acid. His borax was prepared from carefully purified boric acid and sodium carbonate, and his hydrochloric acid was standardized by a series of precipitations and weighings as silver chloride. It contained 1.84983 per cent. of actual HCl. The borax, dissolved in water, was titrated by means of a weight-burette. I give the weights found in the first and second columns of the following table, and in the third column, calculated by myself, the HCl proportional to 100 parts of crystallized borax. Rimbach himself computes the percentage of Na_2O and thence the atomic weight of boron, but the ratio $Na_2B_4O_7.10H_2O : 2HCl$ is the ratio actually determined.

---

[1] Ber. Deutsch. chem. Ges., 26, 164. 1893.

$Na_2B_4O_7.10H_2O.$	HCl Solution.	Ratio.
10.00214	103.1951	19.0853
15.32772	158.1503	19.0864
15.08870	155.7271	19.0917
10.12930	104.5448	19.0922
5.25732	54.2571	19.0908
15.04324	155.2307	19.0883
15.04761	155.2959	19.0908
10.43409	107.6602	19.0868
5.04713	52.0897	19.0915

Mean, 19.0893, $\pm$ .0006

Hence B = 10.970.

Obviously, this error should be increased by the probable errors involved in standardizing the acid, but they are too small to be worth considering.

The work of Armitage on the atomic weight of boron was published only in abstract.[1] The data, however, were fortunately given to Brauner,[2] who has stated them in partially available form. First, six determinations were made of the proportion of water in borax giving in mean, 47.1475 per cent., with a minimum of 47.1224 and a maximum of 47.1637. Hence B = 10.983. If these figures alone are considered, the probable error of the mean is $\pm$ .0091. Secondly, anhydrous borax was titrated with standard sulphuric acid, with the subjoined results:

$Na_2B_4O_7.$	$SO_4.$	Ratio.
1.94033	.924615	209.053
1.56303	.743413	210.251

Mean, 210.052, $\pm$ .133

Hence B = 10.943. The determination is evidently of small significance.

Combining the data relative to the percentage of water in borax, we have—

Berzelius with Laurent	47.130,	$\pm$ .0130
Dobrovolsky, 1	47.211,	$\pm$ .0230
Dobrovolsky, 2	46.878,	$\pm$ .0720
Hoskyns-Abrahall	47.2866,	$\pm$ .0171
Ramsay and Aston	47.1677,	$\pm$ .0086
Armitage	47.1475,	$\pm$ .0091

General mean 47.1654, $\pm$ .0052

This mean is very close to that of Ramsay and Aston. Dobrovolsky's figures count for practically nothing.

---

[1] Proc. Chem. Soc., 14, 22. 1898. The communication was followed by several adverse criticisms. See also Leonard, Chem. News, 77, 104.

[2] Op. cit.

Gautier's determinations[1] were based upon analyses of four boron compounds. First, boron sulphide was decomposed by caustic soda; the solution was then oxidized with bromine water, and the sulphur was precipitated and weighed as barium sulphate. I give the ratio $3BaSO_4 : B_2S_3 :: 100 : x$ in the third column below. The weights are all reduced to a vacuum standard:

B_2S_3.	$BaSO_4$.	Ratio.
.2754	1.6312	16.883
.3380	2.0004	16.897
.3088	1.8300	16.874
.2637	1.5614	16.888

Mean, 16.8855, ± .0033

Hence B = 11.024.

Secondly, boron carbide was heated in chlorine to expel the boron as BCl_3. The residual carbon was then burned in oxygen, and the dioxide so produced was weighed. I subjoin the weights, and also the ratio $CO_2 : B_6C :: 100 : x:$

B_6C.	CO_2.	Ratio.
.2686	.1515	177.293
.3268	.1844	177.224

Mean, 177.258, ± .024

Hence B = 10.999.

Third, boron tribromide was decomposed by water, and its bromine content was then determined as silver bromide. The following data relate to two samples of the boron compound, with five analyses of the first lot and four of the second:

BBr_3.	$AgBr$.	Ratio.
3.1130	6.994	44.510
3.3334	7.490	44.505
3.7456	8.414	44.516
3.2780	7.364	44.514
4.2074	9.452	44.513
3.3956	7.628	44.515
4.0295	9.052	44.514
3.7886	8.512	44.509
3.1711	7.124	44.513

Mean, 44.512, ± .0009

Hence B = 11.021.

Finally, the analysis of boron chloride was effected in the same way with the following results:

---

[1] Ann. Chim. Phys. (7), 18, 352. 1899.

BCl_3.	$AgCl$.	Ratio.
2.6412	9.682	27.279
2.7920	10.234	27.282
2.4634	9.026	27.292
2.4489	12.640	27.285
2.2015	8.070	27.280
2.6957	9.878	27.289

Mean, 27.2845, $\pm$ .0014

Hence B = 10.952.

The ratios from which to compute the atomic weight of boron are now as follows:

(1). $Na_2B_4O_7.10H_2O:10H_2O::100:47.1654, \pm .0052$
(2). $Na_2B_4O_7.10H_2O:2HCl::100:19.0893, \pm .0006$
(3). $Na_2B_4O_7:2NaCl::100:57.933, \pm .0074$
(4). $2AgCl:Na_2B_4O_7::100:70.546, \pm .0146$
(5). $SO_4:Na_2B_4O_7::100:210.052, \pm .133$
(6). $3AgCl:BCl_3::100:27.2845, \pm .0014$
(7). $3Ag:BBr_3::100:77.425, \pm .0017$
(8). $3AgBr:BBr_3::100:44.512, \pm .0009$
(9). $3BaSO_4:B_2S_3::100:16.8855, \pm .0033$
(10). $CO_2:B_6C::100:177.258, \pm .024$

The values used in reducing these ratios are—

$Ag = 107.880, \pm .00029$		$S = 32.0667, \pm .00075$
$Cl = 35.4584, \pm .0002$		$C = 12.0038, \pm .0002$
$Br = 79.9197, \pm .0003$		$Ba = 137.363, \pm .0025$
$Na = 23.0108, \pm .00024$		$H = 1.00779, \pm .00001$

Hence,

From ratio 7 ....B = 10.8191, $\pm$ .0056
"   "   5 ....10.9431, $\pm$ .0319
"   "   1 ....10.9472, $\pm$ .0068
"   "   6 ....10.9523, $\pm$ .0061
"   "   3 ....10.9572, $\pm$ .0065
"   "   2 ....10.9700, $\pm$ .0031
"   " 10 ....10.9994, $\pm$ .0018
"   "   8 ....11.0211, $\pm$ .0051
"   "   9 ....11.0236, $\pm$ .0122
"   "   4 ....11.0544, $\pm$ .0105

General mean, B = 10.9805, $\pm$ .0013

In this combination, ratio 10 is enormously overvalued. It receives weight out of all proportion to its merits. The uncertainties, however, are so great that the final mean may be allowed to stand until better evidence as to the true atomic weight of boron is obtained. The round number 11.0 is enough for common use.

ALUMINUM.

The atomic weight of aluminum has been determined by Berzelius, Mather, Tissier, Dumas, Isnard, Terreil, Mallet, Baubigny, Thomsen and Kohn-Abrest. The early calculations of Davy and of Thomson we may properly disregard.

Berzelius'[1] 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 $Al = 27.31$.

In 1835 Mather[2] published a single analysis of aluminum chloride, from which he sought to fix the atomic weight of the metal. 0.646 grm. of $AlCl_3$ 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 $AlCl_3$, $Al = 28.737$.

Tissier's[3] 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 $Al = 27.185$.

Essentially the same method of determination was adopted by Isnard,[4] who, although not next in chronological order, may fittingly be mentioned here. He found that 9 grm. of aluminum gave 17 grm. of Al_2O_3. Hence $Al = 27$.

In 1858 Dumas,[5] in his celebrated revision of the atomic weights, made seven experiments with aluminum chloride. The material was prepared in quantity, 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 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 $AlCl_3$ stated in the third column, as proportional to 100 parts of silver:

[1] Poggend. Annal., 8, 177.
[2] Amer. Journ. Sci., 27, 241.
[3] Compt. Rend., 46, 1105.
[4] Compt. Rend., 66, 508. 1868.
[5] Ann. Chim. Phys. (3), 55, 151. Ann. Chem. Pharm., 113, 26.

$AlCl_3$.	Ag.	$Ratio$.
1.8786	4.543	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 $AlCl_3$ contained traces of iron. Rejecting this experiment, the remaining six give a mean of $41.344, \pm .007$. These data give a value for Al approximating to 27.4, and were for many years regarded as satisfactory. It now seems probable that the chloride contained traces of an oxy-compound, which would tend to raise the atomic weight.

In 1879 Terreil[1] 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 was found equivalent to 508.2 cc., or .045671 grm. of hydrogen. Hence $Al = 27.142$.

About a year after Terreil's determination appeared, the lower value for aluminum was thoroughly confirmed by J. W. Mallet.[2] After giving a full résumé of the work done by others, exclusive of Isnard, the author describes his own experiments, which may be summarized as follows:

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

[1] Bull. Soc. Chim., 31, 153.
[2] Phil. Trans., 1880, p. 1003.

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

Series B.

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, ± .0011

Combined, these series give a general mean of 11.2793, ±.0008. Hence Al = 27.153.

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 $AlBr_3$; series B from the second portion, and series C from the third portion:

Series A.

$AlBr_3$.	Ag.	$Ratio$.
6.0024	7.2793	82.458
8.6492	10.4897	82.454
3.1808	3.8573	82.462

Series B.

$AlBr_3$.	Ag.	$Ratio$.
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.

$AlBr_3$.	Ag.	$Ratio$.
9.3515	11.3424	82.447
4.4426	5.3877	82.458
5.2750	6.3975	82.454

Mean, 82.455, ± .001

Hence $Al = 27.098$.

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, reckoned at .089872 gramme per litre.

Wt. Al.	Vol. H.	Wt. H.	At. Wt. (H = 1).
.3697	458.8	.041234	26.898
.3769	467.9	.042051	26.889
.3620	449.1	.040362	26.907
.7579	941.5	.084614	26.872
.7314	907.9	.081595	26.891
.7541	936.4	.084156	26.882

Mean, 26.890, ± .0034

Hence Al = 27.099, when O = 16.

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, ± .0017

Hence Al = 27.073.

From the last two series of experiments an independent value for the atomic weight of oxygen may be calculated. They give O = 15.895, when H = 1. The closeness of this figure to some of the best determinations affords a good indication of the accuracy of Mallet's work.

In connection with Mallet's work it is worth noting that Torrey[1] published a series of measurements of the H : Al ratio, representing determinations made under his direction by elementary students. These measurements are thirteen in number, and calculated with Regnault's old value for the weight of hydrogen, range from 26.661 to 27.360, or in mean, 27.049. ± .323. Corrected by the latest value for the weight of H, this mean becomes 26.967, when H = 1. This figure, of course, has only confirmatory significance.

---

[1] Amer. Chem. Journ., 10, 74. 1888.

By Baubigny [1] we have only two determinations, based upon the calcination of anhydrous aluminum sulphate, $Al_2(SO_4)_3$.

3.6745 grm. salt gave 1.0965 Al_2O_3.	29.841 per cent.
2.539　　　"　　　.7572　"	29.823　　"

Mean, 29.832, $\pm$ .0061

Hence Al = 27.061.

Thomsen's [2] value for the atomic weight of aluminum was derived from his earlier work on the hydrogen-oxygen ratio. In that investigation one part of aluminum was found equivalent to 0.11190, $\pm$.000015 of hydrogen, and 0.88787, $\pm$.000018 of oxygen. The aluminum, however, was impure, and the first step in the new research was to determine its impurities. These were, in one gramme of metal, 0.00819 gramme of silicon and .00322 of iron. Correcting for these, and also for the change of volume in the soda solution following the solution of the metal, the equivalent values become 0.99897 grm. Al, 0.11195 grm. H, and 0.88824 grm. O. From the oxygen ratio Al = 26.992, $\pm$.0011. From the hydrogen, the ratio H : Al :: 1 : 26.765, $\pm$.0036 is derived. For the same ratio Mallet found 26.890, $\pm$.0034. The two series, combined, give a general mean of 26.860, $\pm$.0025.

The determinations by Kohn-Abrest [3] are of very slender value. Impure aluminum was dissolved in hydrochloric acid, the hydrogen evolved was burned over hot copper oxide, and the water formed was weighed. The weights of metal taken and the percentages of water produced are given below:

Weight Al.	Per cent. H_2O.
.7909	98.08
.7428	98.20
.5477	97.86
.5132	98.10
.6571	98.44
.4993	98.03
.5384	97.98

Mean, 98.10, $\pm$ .0473

Corrected for the known impurities of the aluminum, this mean becomes 99.151. Hence Al = 27.255.

Mallet's value for this ratio, reduced to the same standard, is 99.818. $\pm$.0170. Combining, the general mean is 99.742, $\pm$.0160.

---

[1] Compt. Rend., 97, 1369. 1883.
[2] Zeitsch. anorg. Chem., 15, 447. 1897. See also *ante*, p. 25.
[3] Bull. Soc. Chim. (3), 33, 121. 1905. Preliminary in Compt. Rend., 139, 669.

Kohn-Abrest also made two determinations of atomic weight by converting metallic aluminum into oxide. as follows:

.3429 grm. Al gave .6444 Al_2O_3.   53.212 per cent.
.4168   "   .7850   "   53.095   "

Mean, 53.153, $\pm$ .0387

Hence $Al = 27.230$. This can be combined with Thomsen's figure for the $Al : O$ ratio, but its probable error is so high that it exerts no appreciable influence.

It is clear that the single determinations of Berzelius, Mather, Tissier, Isnard and Terreil may now be safely left out of account, for the reason that none of them could affect appreciably the final value for Al. The ratios to consider are as follows:

(1). $3Ag : AlCl_3 :: 100 : 41.344$, $\pm$ .0070
(2). Percentage Al_2O_3 in ammonium alum, 11.2793, $\pm$ .0008
(3). $3Ag : AlBr_3 :: 100 : 82.455$, $\pm$ .0010
(4). $H : Al :: 1 : 26.860$, $\pm$ .0025
(5). $2Al : 3H_2O :: 100 : 99.742$, $\pm$ .0160
(6). $Al_2(SO_4)_3 : Al_2O_3 :: 100 : 29.832$, $\pm$ .0061
(7). $O : Al :: 16 : 26.992$, $\pm$ .0011

The antecedent atomic weights are

$Ag = 107.880$, $\pm$ .00029 $S = 32.0667$, $\pm$ .00075
$Cl = 35.4584$, $\pm$ .0002 $N = 14.0101$, $\pm$ .0001
$Br = 79.9197$, $\pm$ .0003 $H = 1.00779$, $\pm$ .00001

Hence,

From ratio 7 ....$Al = 26.9920$, $\pm$ .0011
  "   " 6 ....27.0607, $\pm$ .0115
  "   " 4 ....27.0695, $\pm$ .0025
  "   " 5 ....27.0933, $\pm$ .0087
  "   " 3 ....27.0983, $\pm$ .0015
  "   " 2 ....27.1533, $\pm$ .0041
  "   " 1 ....27.4305, $\pm$ .0227

General mean, $Al = 27.0400$, $\pm$ .0008

The last value. from ratio 1. is worthless, but is of no influence in the general combination. No one of the other values is entitled to exclusive confidence. The atomic weight of aluminum needs reinvestigation.

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:[1]

3.1044 grammes gallium ammonium alum, upon ignition, left .5885 grm. Ga_2O_3.

Hence $Ga = 70.12$.

.4481 gramme gallium, converted into nitrate and ignited, gave .6024 grm. Ga_2O_3.

Hence $Ga = 69.70$.

These values, assigned equal weight, give in mean $Ga = 69.91$, with an uncertainty of perhaps half a unit.

INDIUM.

Reich and Richter, the discoverers of indium, were also the first to determine its atomic weight.[2] 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, $In = 110.61$; 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 $BaSO_4 = 233.43$, $In = 111.99$; also too low.

Soon after the publication of Reich and Richter's paper the subject was taken up by Winkler.[3] He dissolved indium in nitric acid, evaporated to dryness, ignited the residue, and weighed the oxide thus obtained.

---

[1] Journ. Chem. Soc., 1878, p. 646.
[2] Journ. prakt. Chem., 92, 484.
[3] Journ. prakt. Chem., 94, 8.

.5574 grm. In gave .6817 grm. In_2O_3.
.6661   "   .8144   "
.5011   "   .6126   "

Hence, in mean, In = 107.76; a result even lower than the values already cited.

In a later paper by Winkler[1] 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

Hence, if Au = 197.269, In = 114.06.

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_2O_3:

1.124 grm. In gave 1.3616 grm. In_2O_3.   82.550 per cent.
1.015   "   1.2291   "   82.581   "
 .6370   "   .7725   "   82.537   "

These figures were confirmed by a single experiment of Bunsen's,[2] published simultaneously with the specific heat determinations which showed that the oxide of indium was In_2O_3, and not InO, as had been previously supposed:

1.0592 grm. In gave 1.2825 grm. In_2O_3.   82.589 per cent.

For convenience we may add this figure in with Winkler's series, which gives a mean percentage of In in In_2O_3 of 82.564. Hence In = 113.646.

Recent investigations have shown that all of the foregoing determinations are untrustworthy, and that they give values for the atomic weight of indium which are too low. Thiel[3] carefully investigated the properties of indium oxide, and found it to be quite unsuited to atomic

[1] Journ. prakt. Chem., 102, 282.
[2] Poggend. Annal., 141, 28.
[3] Zeitsch. anorg. Chem., 40, 280. 1904. Preliminary in Vol. 39, 119, and Ber., 37, 175.

weight determinations. Calcined at low temperatures it tends to retain gaseous occlusions; at high temperatures it is distinctly volatile. Syntheses of the indium halides also gave unsatisfactory results. Thiel finally made analyses of indium trichloride and tribromide, purified by sublimation, and obtained the following ratios with the corresponding silver salts. First, the ratio $3AgCl : InCl_3 : 100 : x$, with weights corrected to a vacuum:

Weight InCl₃.	Weight AgCl.	Ratio.
5.0194	9.7526	51.467
4.7049	9.1401	51.475
5.7067	11.0862	51.476
5.4075	10.5055	51.473

Mean, 51.473, ± .0015

Hence In = 114.98.

In the bromide series the weights were not reduced to a vacuum standard.

Weight InBr₃.	Weight AgBr.	Ratio.
8.9040	14.1531	62.912
8.2140	13.0512	62.937
9.4016	14.9422	62.920

Mean, 62.923, ± .0070

Hence In = 114.75.

Thiel regards the chloride series as the better of the two, and attaches little importance to the bromide determinations.

Mathers,[1] like Thiel, derived the atomic of indium from analyses of the two trihalides. His weights and ratios are as follows:

Weight InCl₃.	Weight AgCl.	Ratio.
2.1156	4.11421	51.422
4.95920	9.64176	51.435
1.98175	3.85125	51.457
5.54540	10.77904	51.446
1.46361	2.84557	51.435
4.08602	7.94054	51.458

Mean, 51.442, ± .0038

Hence In = 114.83.

[1] Journ. Amer. Chem. Soc., 29, 485. 1907.

Combined with Thiel's series, the general mean for the ratio is 51.469, $\pm .0014$.

Weight InBr₃.	Weight AgBr.	Ratio.
2.73494	4.34550	62.937
7.69880	12.23341	62.933
6.27450	9.96917	62.939
5.36642	8.52741	62.931
5.16112	8.20128	62.931
4.98336	7.92009	62.921

Mean, 62.932, $\pm$ .0011

Hence $In = 114.80$.

On combination of this series with Thiel's the general mean becomes 62.931, $\pm .0011$.

Neglecting the older work there are now two ratios from which to deduce the atomic weight of indium:

(1). $3AgCl:InCl_3::100:51.469, \pm .0014$

(2). $3AgBr:InBr_3::100:62.932, \pm .0011$

Computing with $Ag = 107.880, \pm .00029$; $Cl = 35.4584, \pm .0002$, and $Br = 79.9197, \pm .0003$ we have—

From ratio 2 .... $In = 114.799, \pm .0053$

"   "   1 .... $114.949, \pm .0061$

General mean, $In = 114.864, \pm .0040$

This mean is, of course, not conclusive. Other indium ratios need to be determined before the atomic weight can be more than approximately known. The true value probably lies between 114.8 and 115.0. For the present the mean value 114.9 may be accepted.

THALLIUM.

The atomic weight of this interesting metal has been fixed by the researches of Lamy, Werther, Hebberling, Crookes and Lepierre.

Lamy and Hebberling investigated the chloride and sulphate; Werther studied the iodide; Crookes' experiments involved the synthesis of the nitrate. Lepierre's work is still more recent, and is based upon several compounds.

Lamy [1] gives the results of one analysis of thallium sulphate and three of thallium chloride. 3.423 grammes of Tl_2SO_4 gave 1.578 grm. $BaSO_4$; whence 100 parts of the latter are equivalent to 216.920 of the former. Hence $Tl = 205.14$.

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, $\pm$ .1905

Hence $Tl = 203.79$.

Hebberling's [2] 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:

1.4195 grm. Tl_2SO_4 gave	.6534 grm. $BaSO_4$.		217.248
1.1924 "	.5507 "		216.524
.8560 "	.3957 "		216.325

Mean, 216.699

Hence $Tl = 204.89$.

Including Lamy's single result as of equal weight, we get a mean of 216.754, $\pm$ .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, $\pm$ .097

Hence $Tl = 203.15$.

[1] Zeit. Anal. Chem., 2, 211. 1863.
[2] Ann. Chem. Pharm., 134, 11. 1865.

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

Werther's [1] 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. Hence Tl=203.32.

In 1873 Crookes,[2] 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 of 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.

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

---

[1] Journ. prakt. Chem., 92, 128. 1864.
[2] Phil. Trans., 1873, p. 277.

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, $130.3910, \pm .00034$

Hence $Tl = 204.041$.

Lepierre's [1] determinations were published in 1893, and represented several distinct methods. First, thallous sulphate was subjected to electrolysis in presence of an excess of ammonium oxalate, the reduced metal being dried and weighed in an atmosphere of hydrogen. The corrected weights, etc., are as follows:

1.8935 grm. Tl₂SO₄ gave 1.5327 Tl.   80.945 per cent.
2.7243   "   2.2055 "   80.957   "
2.8112   "   2.2759 "   80.958   "

Mean, $80.953, \pm .0030$

Hence $Tl = 204.150$.

Secondly, weighed quantities of crystallized thallic oxide were converted into thallous sulphate by means of sulphurous acid, and the solution was then subjected to electrolysis, as in the preceding series.

3.2216 grm. Tl₂O₃ gave 2.8829 Tl.   89.487 per cent.
2.5417   "   2.2742 "   89.475   "

Mean, $89.481, \pm .0040$

Hence $Tl = 204.158$.

In the third set of experiments a definite amount of thallous sulphate or nitrate was fused in a polished silver crucible with ten times its weight of absolutely pure caustic potash. Thallic oxide was thus formed, which, with various precautions, was washed with water and alcohol, and finally weighed in the original crucible. One experiment with the nitrate gave—

2.7591 grm. TlNO₃ yields 2.3649 Tl₂O₃.   85.713 per cent.

Hence $Tl = 204.037$.

---

[1] Bull. Soc. Chim. (3), 9, 166.

Two experiments were made with the sulphate, as follows:

3.1012 grm. Tl$_2$SO$_4$ gave 2.8056 Tl$_2$O$_3$.   90.468 per cent.
2.3478   "   2.1239   "   90.463   "

Mean, 90.465, ± .0020

Hence Tl = 204.021.

Finally, crystallized thallic oxide was reduced by heat in a stream of hydrogen, and the water so formed was collected and weighed.

2.7873 grm. Tl$_2$O$_3$ gave .3301 H$_2$O.   11.843 per cent.
3.9871   "   .4716   "   11.828   "
4.0213   "   .4761   "   11.839   "

Mean, 11.837, ± .0029

Hence Tl = 204.300.

In a supplementary note [1] Lepierre states that his weights were all reduced to a vacuum standard.

Some work by Wells and Penfield,[2] incidentally involving a determination of atomic weight, but primarily intended for another purpose, may also be taken into account. Their question was as to the constancy of thallium itself. The nitrate was repeatedly crystallized, and the last crystallization, with the mother liquor representing the opposite end of the series, were both converted into chloride. In the latter the chlorine was estimated as silver chloride, which was weighed on a Gooch filter, with the results given below, which are sensibly identical. The TlCl equivalent to 100 parts of AgCl is stated in the last column.

	TlCl.	AgCl.	Ratio.
Crystals	3.9146	2.3393	167.341
Mother liquor	3.3415	1.9968	167.343

Mean, 167.342

Hence Tl = 204.41.

The general mean of Lamy's and Hebberling's determinations of this ratio gave 166.555, ± .0865. If we arbitrarily assign Wells and Penfield's mean equal weight with that, we get a new general mean of 166.948, ± .0610.

---

[1] Bull. Soc. Chim. (3), 11, 423. 1894.
[2] Amer. Journ. Sci. (3), 47, 466. 1894.

The ratios to be considered are now as follows:

(1). $BaSO_4:Tl_2SO_4::100:216.754, \pm .1387$
(2). $AgCl:TlCl::100:166.948, \pm .0610$
(3). $AgI:TlI::100:140.648, \pm .016$
(4). $Tl:TlNO_3::100:130.391, \pm .00034$
(5). $Tl_2SO_4:2Tl::100:80.953, \pm .0030$
(6). $Tl_2O_3:2Tl::100:89.481, \pm .0040$
(7). $2TlNO_3:Tl_2O_3::100:85.713$
(8). $Tl_2SO_4:Tl_2O_3::100:90.465, \pm .0020$
(9). $Tl_2O_3:3H_2O::100:11.837, \pm .0029$

The antecedent atomic weights are as follows:

$Ag = 107.880, \pm .00029$ $N = 14.0101, \pm .0001$
$Cl = 35.4584, \pm .0002$ $S = 32.0667, \pm .00075$
$I = 126.9204, \pm .00033$ $H = 1.00779, \pm .00001$

Ratio 7 rests upon a single experiment, and the atomic weight derived from it must therefore be arbitrarily weighted. To do this its probable error is assumed to be the same as that given by ratio 8. Taking so much for granted, the nine values for thallium are

From ratio 3 ....$Tl = 203.322, \pm .0376$
"   "   2 ....$203.842, \pm .0875$
"   "   8 ....$204.021, \pm .0695$
"   "   7 ....$204.037, \pm .0695$
"   "   4 ....$204.041, \pm .0023$
"   "   5 ....$204.150, \pm .0330$
"   "   6 ....$204.158, \pm .0780$
"   "   9 ....$204.300, \pm .0593$
"   "   1 ....$204.950, \pm .1619$

A glance at the "probable errors" in this series of values will show that Crookes' ratio, No. 4, carries overwhelming weight. It is therefore unnecessary to compute the general mean, for it could not vary much from that. The value $Tl = 204.04$ is to be accepted as the best.

SILICON.

Although Berzelius [1] 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 consider only the work of Pelouze, Schiel, Dumas, Thorpe and Young, and Becker and Meyer.

Pelouze,[2] 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, $39.4447, \pm .0083$

Hence $Si = 28.373$.

Essentially the same method was adopted by Dumas.[3] 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, $39.377, \pm .014$

Hence $Si = 28.080$.

Dumas' and Pelouze's series combine as follows:

Pelouze	$39.4447, \pm .0083$
Dumas	$39.377, \pm .014$
General mean	$39.4265, \pm .0071$

Schiel,[4] 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:

---

[1] Lehrbuch, 5 Aufl., 3, 1200.
[2] Compt. Rend., 20, 1047. 1845.
[3] Ann. Chem. Pharm., 113, 31. 1860.
[4] Ann. Chem. Pharm., 120, 94.

.6738 grm. $SiCl_4$ gave 2.277 grm. AgCl. 29.592
1.3092 " 4.418 " 29.633

Mean, 29.6125 ± .0138

Hence $Si = 27.952$.

Thorpe and Young,[1] working with silicon bromide, obtained better results. The bromide was perfectly clear and colorless, and boiled constantly at 153°. It was weighed, decomposed with water and evaporated to dryness, the crucible containing it being finally ignited. The crucible was tared by one precisely similar, in which an equal volume of water was also evaporated. Results as follows, with vacuum weights:

9.63007 grm. $SiBr_4$ gave 1.67070 SiO_2. 17.349 per cent.
12.36099 " 2.14318 " 17.338 "
12.98336 " 2.25244 " 17.349 "
9.02269 " 1.56542 " 17.350 "
15.38426 " 2.66518 " 17.324 "
9.74550 " 1.69020 " 17.343 "
6.19159 " 1.07536 " 17.368 "
9.51204 " 1.65065 " 17.353 "
10.69317 " 1.85555 " 17.353 "

Mean, 17.347, ± 0027

Hence $Si = 28.379$.

The determinations by Becker and Meyer[2] resemble the foregoing series, except that silicon tetrachloride was used instead of the bromide. The carefully purified substance was decomposed by water, the solution was evaporated to dryness, and the silica produced was weighed. In a second communication Meyer[3] discusses the possible retention of chlorine by the silica, and shows that that error was avoided. The data obtained by Becker and Meyer follow, with vacuum weights, and a percentage column computed by myself:

4.16733 grm. $SiCl_4$ gave 1.47597 SiO_2. 35.417 per cent.
4.69585 " 1.66304 " 35.415 "
4.91918 " 1.74204 " 35.413 "
5.37434 " 1.90349 " 35.418 "
5.93985 " 2.10364 " 35.416 "
6.73605 " 2.38570 " 35.417 "
7.16361 " 2.53606 " 35.402 "
7.82779 " 2.77242 " 35.418 "

Mean, 35.4145, ± .0017

Hence $Si = 28.226$.

[1] Journ. Chem. Soc., 51, 576. 1887.
[2] Zeitsch. anorg. Chem., 43, 251. 1905.
[3] Zeitsch. anorg. Chem., 46, 45. 1905. In Vol. 43, p. 242, Meyer discusses the problem of the calculation of atomic weights.

The ratios for silicon are now—

    (1). $4Ag:SiCl_4::100:39.4265, \pm .0071$
    (2). $4AgCl:SiCl_4::100:29.6125, \pm .0138$
    (3). $SiCl_4:SiO_2::100:35.4145, \pm .0017$
    (4). $SiBr_4:SiO_2::100:17.347, \pm .0027$

Reducing these ratios with $Ag = 107.880, \pm .00029$, $Cl = 35.4584, \pm .0002$, and $Br = 79.9197, \pm .0003$, we have—

From ratio 2 .... $Si = 27.9516, \pm .0792$
   "   " 3 .... $28.2257, \pm .0045$
   "   " 1 .... $28.2996, \pm .0307$
   "   " 4 .... $28.3785, \pm .0115$

General mean, $Si = 28.2462, \pm .0041$

The rounded-off mean, $Si = 28.25$, is probably as near the truth as any of the individual values.

TITANIUM.

The earliest determinations of the atomic weight of titanium are due to Heinrich Rose.[1] 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.[2] 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, $\pm$ .121	33.156, $\pm$.019

Hence $Ti = 48.262$, from column 5.

[1] Gilbert's Annalen, 1823, 67 and 129.
[2] Poggend. Annalen, 15, 145. Berz. Lehrbuch, 3, 1210.

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, $\pm$ .036

Hence Ti = 49.617.

Shortly after the appearance of Rose's paper, Mosander[1] published some figures giving the percentage 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 46.38 to 48.34; or, in mean, Ti = 47.15. They are not, however, sufficiently explicit to deserve any farther consideration.

In 1847 Isidor Pierre made public a series of important determinations.[2] 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 of Pelouze. I subjoin Pierre's weighings, and add, in a third column, the ratio of $TiCl_4$ to 100 parts of silver:

---

[1] Berz. Jahresbericht, 10, 108. 1831.
[2] Ann. Chim. Phys. (3), 20, 257.

TiCl₄.	Ag.	Ratio.
.8215	1.84523	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, ± .0173

Hence Ti = 49.894.

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. These give Ti = 50.265.

The memoir of Pierre upon the atomic weight of titanium was soon followed by a paper from Demoly,[1] who obtained much higher results. He also began with 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 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

[1] Ann. Chem. Pharm., 72, 214. 1849.

filtrate as silver chloride. Three analyses were performed, yielding the following results. I give the actual weighings :

1.470 grm. TiCl₄ gave 4.241 grm. AgCl and .565 grm. TiO₂
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. TiO₂ from TiCl₄.	TiCl₄ : 100AgCl.	TiO₂ : 100AgCl.
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, ranging from about 36 to more than 56, the latter figure being derived from the ratio between AgCl and TiCl₄. This value, 56, is assumed by Demoly to be the best, the others being practically ignored.

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 1883 [1] Thorpe published a series of experiments upon titanium tetrachloride, determining three distinct ratios and getting sharply concordant results. The first ratio, which was essentially like Pierre's, by decomposition with water and titration with silver, was in detail as follows :

---

[1] Ber. Deutsch. chem. Gesell., 16, 3014. 1883.

$TiCl_4$.	Ag.	$TiCl_4 : 100 Ag$.
2.43275	5.52797	44.008
5.42332	12.32260	44.015
3.59601	8.17461	44.000
3.31222	7.52721	44.003
4.20093	9.54679	44.004
5.68888	12.92686	44.008
5.65346	12.85490	43.979
4.08247	9.28305	43.978

Mean, 43.999, ± .0032

Pierre found, 44.432, ± .0073

General mean, 44.017, ± .0031

Thorpe's figures alone give Ti = 48.025.

The second ratio, which involved the weights of $TiCl_4$ taken in the last five determinations of the preceding series, included the weighing of the silver chloride formed. The $TiCl_4$ proportional to 100 parts of AgCl is given in a third column:

$TiCl_4$.	$AgCl$.	$Ratio$.
3.31222	10.00235	33.114
4.20093	12.68762	33.111
5.68888	17.17842	33.117
5.65346	17.06703	33.125
4.08247	12.32442	33.125

Mean, 33.118, ± .0019

Rose found, 33.156, ± .019

Demoly found, 34.581, ± .030

General mean, 33.123, ± .0019

Hence Ti = 48.044 (Thorpe).

In the third series the chloride was decomposed by water, and after evaporation to dryness the resulting TiO_2 was strongly ignited:

$TiCl_4$.	TiO_2.	Per cent. TiO_2.
6.23398	2.62825	42.160
8.96938	3.78335	42.181
10.19853	4.30128	42.176
6.56894	2.77011	42.170
8.99981	3.79575	42.176
8.32885	3.51158	42.162

Mean, 42.171, ± .0022

Rose found, 42.933, ± .121

Demoly found, 38.294, ± .180

General mean, 42.171, ± .0022

Hence Ti = 48.095.

In short, the work of Rose, Pierre and Demoly practically vanishes. Furthermore, as will be seen later, the three ratios now give closely agreeing values for the atomic weight of titanium. The cross ratio, $4AgCl : TiO_2$ is not directly given by either of Thorpe's series; but the data furnished by Rose and Demoly combine into a general mean of $4AgCl : TiO_2 :: 100 : 13.980, \pm .0303$.

Some two years later Thorpe published his work more in detail,[1] and added a set of determinations, like those made upon the chloride, in which titanium tetrabromide was studied. Three ratios were measured, as was the case with the chloride. In the first, the bromide was decomposed by water and titrated with a silver solution.

$TiBr_4.$	$Ag.$	$TiBr_4 : 100Ag.$
2.854735	3.34927	85.235
3.120848	3.66122	85.241
4.731118	5.55097	85.230
6.969075	8.17645	85.234
6.678099	7.83493	85.234

Mean, 85.235, $\pm$ .0027

Hence Ti=48.127.

In the four last experiments of the preceding series, the silver bromide formed was weighed. The third column gives the $TiBr_4$ proportional to 100 parts of AgBr.

$TiBr_4.$	$AgBr.$	$Ratio.$
3.120848	6.375391	48.951
4.731118	9.663901	48.957
6.969075	14.227716	48.982
6.678099	13.639956	48.959

Mean, 48.962, $\pm$ .0049

Hence Ti=48.123.

For the third ratio the bromide was decomposed by water; and after evaporation with ammonia the residual titanic oxide was ignited and weighed :

$TiBr_4.$	$TiO_2.$	$Per cent. TiO_2.$
6.969730	1.518722	21.790
8.836783	1.923609	21.768
9.096309	1.979513	21.762

Mean, 21.773, $\pm$ .0062

Hence Ti=48.070.

---

[1] Journ. Chem. Soc., 47, 108 and 129. 1885.

19

Ignoring Mosander's work as unavailable, we have the following ratios to consider:

(1). $4Ag:TiCl_4::100:44.017, \pm .0031$

(2). $4AgCl:TiCl_4::100:33.123, \pm .0019$

(3). $4AgCl:TiO_2::100:13.980, \pm .0303$

(4). $TiCl_4:TiO_2::100:42.171, \pm .0022$

(5). $4Ag:TiBr_4::100:85.235, \pm .0027$

(6). $4AgBr:TiBr_4::100:48.962, \pm .0049$

(7). $TiBr_4:TiO_2::100:21.773, \pm .0062$

Computing with $Ag = 107.880, \pm .00029$, $Cl = 35.4584, \pm .0002$, and $Br = 79.9197, \pm .0003$, we have—

From ratio 7	....	$Ti = 48.0699, \pm .0292$
"	" 2	$48.0794, \pm .0135$
"	" 4	$48.0947, \pm .0072$
"	" 1	$48.1085, \pm .0135$
"	" 6	$48.1232, \pm .0369$
"	" 5	$48.1273, \pm .0117$
"	" 3	$48.1553, \pm .1742$

General mean, $Ti = 48.0991, \pm .0049$

This may be rounded off to 48.1.

GERMANIUM.

The data relative to the atomic weight of germanium are imperfect, and due entirely to the discoverer of the element, Winkler.[1] The pure tetrachloride was decomposed by sodium carbonate, mixed with a known excess of standard silver solution, and then titrated back with ammonium sulphocyanate. The data given are as follows:

$GeCl_4$.	Cl found.	Per cent. Cl.
.1067	.076112	66.177
.1258	.083212	66.146
.2223	.147136	66.188
.2904	.192190	66.182
		Mean, 66.173

Hence $Ge = 72.504$.

[1] Journ. prakt. Chem. (2), 34, 177. 1886.

ZIRCONIUM.

The atomic weight of zirconium has been determined by Berzelius, Hermann, Marignac, Weibull, Bailey and Venable. Berzelius[1] 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
———
Mean, 75.853, ± .023

</div>

This gives 43.134, ± .0142 as the percentage of zirconia in the sulphate. Hence $Zr = 89.46$.

Hermann's[2] estimate of the atomic weight of zirconium was based upon analyses of the chloride, concerning which he gives no details nor 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, $Zr = 89.56$.

Marignac's results[3] were obtained by analyzing the double fluoride of zirconium and potassium. His weights are as follows:

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 "

These figures give us three ratios. A, the ZrO_2 from 100 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, ± .043	Mean, 61.365, ± .094	Mean, 70.396, ± .079
Hence $Zr = 90.03$	91.54	90.68

---

[1] Poggend. Annal., 4, 126. 1825.
[2] Journ. prakt. Chem., 31, 77. Berz. Jahresb., 25, 147.
[3] Ann. Chim. Phys. (3), 60, 270. 1860.

Weibull,[1] following Berzelius, ignited the sulphate, and also made a similar set of experiments with the selenate of zirconium, obtaining results as follows:

Sulphate. $Zr(SO_4)_2$.

1.5499 grm. salt gave	.6684	ZrO_2.	43.126 per cent.	
1.5445	"	.6665	"	43.153 "
2.1683	"	.9360	"	43.168 "
1.0840	"	.4670	"	43.081 "
.7913	"	.3422	"	43.321 "
.6251	"	.2695	"	43.113 "
.4704	"	.2027	"	43.091 "

Mean, 43.150, ± .0207

Hence Zr = 89.54.

Selenate. $Zr(SeO_4)_2$.

1.0212 grm. salt gave	.3323	ZrO_2.	32.540 per cent.	
.8418	"	.2744	"	32.597 "
.6035	"	.1964	"	32.544 "
.8793	"	.2870	"	32.640 "
.3089	"	.1003	"	32.470 "

Mean, 32.558, ± .0192

Hence Zr = 90.79.

Bailey[2] also ignited the sulphate, after careful investigation of his material, and of the conditions needful to ensure success. He found that the salt was perfectly stable at 400°, while every trace of free sulphuric acid was expelled at 350°. The chief difficulty in the process arises from the fact that the zirconia produced by the ignition is very light, and easily carried off mechanically, so that the percentage found is likely to be too low. This difficulty was avoided by the use of a double crucible, the outer one retaining particles of zirconia which otherwise might be lost. The results, corrected for buoyancy of the air, are as follows:

2.02357 salt gave	.87785	ZrO_2.	43.381 per cent.	
2.6185	"	1.1354	"	43.360 "
2.27709	"	.98713	"	43.350 "
2.21645	"	.96152	"	43.385 "
1.75358	"	.76107	"	43.402 "
1.64065	"	.7120	"	43.397 "
2.33255	"	1.01143	"	43.361 "
1.81105	"	.78485	"	43.337 "

Mean, 43.372, ± .0056

Hence Zr = 90.65.

---

[1] Lund. Arsskrift, Vol. 18. 1881-'82.
[2] Proc. Roy. Soc., 46, 74. Chem. News, 60, 32.

This, combined with previous determinations, gives—

Berzelius	43.134, ± .0142
Weibull	43.150, ± .0207
Bailey	43.372, ± .0056
General mean	43.317, ± .0051

Venable [1] determined the atomic weight of zirconium by analysis of the oxychloride, $ZrOCl_2.3H_2O$. This compound was purified by crystallization from hot hydrochloric acid and dried in a stream of hydrochloric acid gas. It was then dissolved in water, and after evaporating the solution to dryness in a platinum crucible the residue was converted into zirconia by prolonged ignition. The data are subjoined:

Weight $ZrOCl_2.3H_2O$.	Weight ZrO_2.	Per cent. ZrO_2.
5.25762	2.78450	52.961
3.53994	1.87550	52.981
3.25036	1.72435	53.051
1.52245	.80708	53.012
2.98802	1.58274	52.969
2.11371	1.11920	52.949
2.38139	1.26161	52.978
1.90285	1.00958	53.055
2.61847	1.38658	52.954
1.07347	.56840	52.951
		Mean, 52.986, ± .0085

Hence $Zr = 90.805$.

For computing the atomic weight of zirconium we now have the subjoined ratios:

(1). Percentage ZrO_2 in $Zr(SO_4)_2$, 43.317, ± .0051
(2). Percentage ZrO_2 in $Zr(SeO_4)_2$, 32.558, ± .0192
(3). Percentage ZrO_2 from K_2ZrF_6, 43.200, ± .043
(4). Percentage K_2SO_4 from K_2ZrF_6, 61.365, ± .094
(5). Percentage ZrO_2 in $ZrOCl_2.3H_2O$, 52.986, ± .0085
(6). $K_2SO_4 : ZrO_2 :: 100 : 70.396$, ± .0079

The antecedent values for reduction are—

Cl = 35.4584, ± .0002		K = 39.0999, ± .0002
S = 32.0667, ± .00075		F = 19.041, ± .00135
Se = 79.176, ± .0029		H = 1.00779, ± .00001

---

[1] Journ. Amer. Chem. Soc., 20, 119. 1898.

Hence,

From ratio 3 ....Zr $=$ 90.030, $\pm$ .2390
"   "   1 ....90.374, $\pm$ .0201
"   "   6 ....90.677, $\pm$ .0138
"   "   2 ....90.790, $\pm$ .0804
"   "   5 ....90.805, $\pm$ .0297
"   "   4 ....91.538, $\pm$ .4350
_____

General mean, Zr $=$ 90.621, $\pm$ .0105

The final combination, in this case, is unsatisfactory because of the wide divergence among the individual values. On chemical grounds, ratios 1 and 5 seem to be the only ones worth considering. Their weighted combination gives Zr$=$90.483. The value adopted in the latest International table is 90.6. The atomic weight of zirconium evidently needs careful revision.

_____ _ _____

TIN.

The atomic weight of tin has been determined by means of the oxide, the chloride, the bromide, the sulphide and the stannichlorides of potassium and ammonium.

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, Dumas, Van der Plaats and Bongartz and Classen.

Berzelius' oxidized 100 parts of tin by nitric acid, and found that 127.2 parts of SnO_2 were formed. Hence Sn $=$ 117.65.

The work done by Mulder and Vlaanderen[2] 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. One hundred parts of tin gave of SnO_2:

127.56—Mulder
127.56—Vlaanderen
127.43—Vlaanderen
_____

Mean, 127.517, $\pm$ .029

Hence Sn$=$116.3.

_____

1 Poggend. Annal., 8, 177.
2 Journ. prakt. Chem., 49, 35. 1849.

Dumas[1] 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

Hence $Sn = 118.06$.

In an investigation later than that previously cited, Vlaanderen[2] 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 become, if reduced to the above common standard,

127.100
127.064

Mean, 127.082, $\pm$ .012

Hence $Sn = 118.16$.

Van der Plaats[3] prepared pure stannic oxide from Banca tin, and upon the material obtained made two series of experiments; one by reduction and one by oxidation. The results, with vacuum weights, are as follows, the ratio between Sn and SnO_2 appearing in the third column:

Oxidation Series.

9.6756 grm. tin gave 12.2967 SnO_2.	127.091
12.7356 " 16.1885 "	127.114
23.4211 " 29.7667 "	127.093

Reduction Series.

5.5015 grm. SnO_2 gave 4.3280 tin.	127.114
4.9760 " 3.9145 "	127.117
3.8225 " 3.0078 "	127.086
2.9935 " 2.3553 "	127.096

Mean of both series as one, 127.102, $\pm$ .0033

Hence $Sn = 118.07$.

The reductions were effected in a porcelain crucible.

Bongartz and Classen[4] purified tin by electrolysis, and oxidized the electrolytic metal by means of nitric acid. The oxide found was dried

[1] Ann. Chem. Pharm., 113, 26.
[2] Jahresbericht, 1858, 183.
[3] Compt. Rend., 100, 52. 1885.
[4] Berichte Deutsch. chem. Gesell., 21, 2900. 1888.

over a water-bath, then heated over a weak flame, and finally ignited for
several hours in a gas-muffle. Some reduction experiments gave values
which were too low. The oxidation series was as follows, with the usual
ratio stated in a third column:

Sn.	SnO_2.	Ratio.
2.5673	3.2570	126.865
3.8414	4.8729	126.852
7.3321	9.2994	126.831
5.4367	6.8962	126.845
7.3321	9.2994	126.831
9.8306	12.4785	126.935
11.2424	14.2665	126.896
5.5719	7.0685	126.860
9.8252	12.4713	126.932
4.3959	5.5795	126.925
6.3400	8.0440	126.877

Mean, 126.877, ± .0080

Hence $Sn = 119.06$.

We now have six series of experiments showing the amount of SnO_2
formed from 100 parts of tin. To Berzelius' single determination may be
assigned the weight of one experiment in Mulder and Vlaanderen's
series:

Berzelius .... 127.200, ± .041
Mulder and Vlaanderen........ 127.517, ± .029
Dumas .... 127.105, ± .024
Vlaanderen .... 127.082, ± .012
Van der Plaats............... 127.102, ± .0033
Bongartz and Classen.......... 126.877, ± .0080

General mean .... 127.076, ± .0026

Dumas, in the paper previously quoted, also gives the results of some
experiments with stannic chloride, $SnCl_4$. This was titrated with a solu-
tion 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, ± .006

Hence $Sn = 117.97$.

Tin tetrabromide and the stannichlorides of potassium and ammonium
were all studied by Bongartz and Classen; who, in each compound, care-
fully purified, determined the tin electrolytically. The data given are
as follows, the percentage columns being added by myself:

Tin Tetrabromide.

$SnBr_4$ taken.	Sn found.	Per cent. Sn.
8.5781	2.3270	27.127
9.5850	2.6000	27.126
9.9889	2.7115	27.145
10.4914	2.8445	27.113
16.8620	4.5735	27.123
16.6752	4.5236	27.119
11.1086	3.0125	27.116
10.6356	2.8840	27.113
11.0871	3.0060	27.123
19.5167	5.2935	27.128

Mean, 27.123, $\pm$ .0020

Hence $Sn = 118.98$.

Potassium Stannichloride.

K_2SnCl_6.	Sn found.	Per cent. Sn.
2.5718	.7472	29.054
2.2464	.6524	29.042
9.3353	2.7100	29.030
12.1525	3.5285	29.035
12.4223	3.6070	29.036
15.0870	4.3812	29.040
10.4465	3.0330	29.034
18.9377	5.5029	29.058
18.4743	5.3630	29.029
17.6432	5.1244	29.045

Mean, 29.040, $\pm$ .0021

Hence $Sn = 119.07$.

Ammonium Stannichloride.

| Am_2SnCl_6.	Sn found.	Per cent. Sn.
1.6448	.5328	32.393
1.8984	.6141	32.347
2.0445	.6620	32.381
2.0654	.6690	32.391
2.0058	.6496	32.386
2.4389	.7895	32.371
4.0970	1.3254	32.351
3.4202	1.1078	32.390
3.6588	1.1836	32.349
1.5784	.5108	32.362
7.3248	2.3710	32.370
13.1460	4.2528	32.351
11.9483	3.8650	32.348
18.4747	5.9788	32.362
18.6635	6.0415	32.371
17.8894	5.7923	32.378

Mean, 32.369, $\pm$ .0088

Hence $Sn = 119.1$.

One other method of determination for the atomic weight of tin was employed by Bongartz and Classen. Electrolytic tin was converted into sulphide, and the sulphur so taken up was oxidized by means of hydrogen peroxide, by Classen's method, and weighed as barium sulphate. The results, as given by the authors, are subjoined:

Sn taken.	Per cent. of S gained.
2.6285	53.91
.7495	53.87
1.4785	53.94
2.5690	53.94
2.1765	53.85
1.3245	53.88
.9897	53.83
2.7160	53.86

Mean, 53.885, $\pm$ .0098

This percentage of sulphur, however, was computed from weighings of barium sulphate. What values were assigned to the atomic weights of barium and sulphur is not stated, but as Meyer and Seubert's figures are used for other elements throughout this paper, we may assume that they apply here also. Putting $O = 15.96$, $S = 31.98$, and $Ba = 136.86$, the 53.885 per cent. of sulphur becomes $392.056, \pm .0713$ of $BaSO_4$, the compound actually weighed. This gives us the ratio—

$$Sn : 2BaSO_4 :: 100 : 392.056, \pm .0713$$
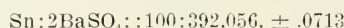
as the real result of the experiments, from which, with the later values for Ba, S and O, the atomic weight of tin may be calculated.

A single determination of the atomic weight of tin, made by Schmidt,[1] ought not to be overlooked, although it was only incidental to his research upon tin sulphide. In one experiment, 0.5243 grm. Sn gave 0.6659 SnO_2. Hence $Sn = 118.49$. This lies about midway between the two sets of values already computed.

We now have, for tin, the following available ratios:

(1). $Sn : SnO_2 :: 100 : 127.076, \pm .0026$
(2). $4Ag : SnCl_4 :: 100 : 60.207, \pm .0060$
(3). Percentage of tin in $SnBr_4$, $27.123, \pm .0020$
(4). Percentage of tin in K_2SnCl_6, $29.040, \pm .0021$
(5). Percentage of tin in Am_2SnCl_6, $32.369, \pm .0088$
(6). $Sn : 2BaSO_4 :: 100 : 392.056, \pm .0713$

The values to use in reduction of these ratios are—

$Ag = 107.880, \pm .00029$	$N = 14.0101, \pm .0001$
$Cl = 35.4584, \pm .0002$	$S = 32.0667, \pm .00075$
$Br = 79.9197, \pm .0003$	$Ba = 137.363, \pm .0025$

$H = 1.00779, \pm .00001$

---

[1] Berichte, 27, 2743. 1894.

Hence the following values for tin:

From ratio 2	....	Sn = 117.971, ± .0258
"	" 1	.......................118.186, ± .0113
"	" 3	.......................118.976, ± .0094
"	" 4	.......................119.070, ± .0082
"	" 6	.......................119.080, ± .0876
"	" 5	.......................119.099, ± .0359

General mean, Sn = 118.648, ± .0052

The discordance between the first two and the last four of these values is glaring, and there seems to be no true compensation of errors. On chemical grounds, the five fairly concordant series of determinations by Bongartz and Classen seem to be better than the earlier measurements. Their arithmetical mean gives Sn = 119.057, which, until further evidence is obtained, should be accepted. New determinations of the atomic weight of tin are much to be desired.

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,[1] 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, gives a mean of 58.026, ± .214, and Th = 238.9.

From the ratio between the K_2SO_4 and the ThO_2 in the double sulphate, Th = 236.88.

[1] Poggend. Annal., 16, 3)8. 1829. Lehrbuch, 3, 1224.

In 1861 new determinations were published by Chydenius,[1] whose memoir is accessible to me only in an abstract[2] 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

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, ± .219	66.54	
		65.85	
Mean, 67.326, ± .201			

Mean, 65.85, ± .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 = 269.18
From acetate	"　= 269.46
From formate	"　= 273.25
From oxalate	"　= 263.42
Average	ThO_2 = 268.83

And Th = 236.83.

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.[3] 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:

---

[1] Kemisk undersökning af Thorjord och Thorsalter. Helsingfors, 1861. An academic dissertation.

[2] Poggend. Annal., 119, 55. 1863.

[3] Arch. Sci. Phys. Nat. (2), 18, 343.

45.08
44.90
45.06
45.21
45.06

Mean, 45.062, $\pm$ .0332

Hence Th = 232.34.

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:

52.83 ⎫
52.52 ⎪ A
52.72 ⎬
52.13 ⎭

52.47 ⎫
52.49 ⎪
52.53 ⎪
52.13 ⎪
52.13 ⎪
52.43 ⎬ B
52.60 ⎪
52.40 ⎪
52.96 ⎪
52.82 ⎭

Mean, 52.511, $\pm$ .047

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 parentheses 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 figures:

106.597
106.704
109.226

Mean, 107.509, $\pm$ .585

Delafontaine was soon followed by Hermann,[1] who published a single analysis of the lower hydrated sulphate, as follows:

ThO_2	52.87
SO_3	32.11
H_2O	15.02
	100.00

Hence, from the ratio between SO_3 and ThO_2, Th $=231.67$. Probably the SO_3 percentage was loss upon calcination.

Both Hermann's results and those of Delafontaine are affected by one serious doubt, namely, as to the true composition of the lower hydrated sulphate. The latest and best evidence seems to establish the fact that it contains four molecules of water instead of four and a half,[2] a fact which tends to change the resulting atomic weight of thorium considerably. In the final discussion of these data, therefore, the formula $Th(SO_4)_2.4H_2O$ will be adopted. As for Hermann's single analysis, his percentage of ThO_2, 52.87, may be included in one series with Delafontaine's, giving a mean of $52.535, \pm .0473$. Hence Th $=229$.

The next determinations to consider are those of Cleve,[3] 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 Th $=234.01$.

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:

[1] Journ. prakt. Chem., 93, 114.
[2] See Hillebrand, Bull. 90, U. S. Geol. Survey, p. 29.
[3] K. Svenska Vet. Akad. Handling., Bd. 2, No. 6, 1874.

Oxalate.	ThO₂.	CO₂.	Ratio.
1.7135	1.0189	.6736	151.262
1.3800	.8210	.5433	151.114
1.1850	.7030	.4650	151.183
1.0755	.6398	.4240	150.896

Mean, 151.114, ± .053

Hence Th = 233.98.

In 1882, Nilson's determinations appeared.[1] This chemist studied both the anhydrous sulphate, and the salt with nine molecules of water, using the usual calcination method, but guarding especially against the hygroscopic character of the dry $Th(SO_4)_2$ and the calcined ThO_2. The hydrated sulphate gave results as follows:

$Th(SO_4)_2.9H_2O$.	ThO₂.	Per cent. ThO₂.
2.0549	.9267	45.097
2.1323	.9615	45.092
3.0017	1.3532	45.081
2.7137	1.2235	45.086
2.6280	1.1849	45.088
1.9479	.8785	45.099

Mean, 45.091, ± .0019

Delafontaine found, 45.062, ± .0332

General mean, 45.090, ± .0019

Hence Th = 232.64.

The anhydrous sulphate gave data as follows:

$Th(SO_4)_2$.	ThO₂.	Per cent. ThO₂.
1.4467	.9013	62.300
1.6970	1.0572	62.298
2.0896	1.3017	62.294
1.5710	.9787	62.298

Mean, 62.297, ± .0009

Hence Th = 232.59.

The last four determinations appear again in a paper published five years later by Krüss and Nilson,[2] who, however, give four more made upon material obtained from a different source. The new data are subjoined:

$Th(SO_4)_2$.	ThO₂.	Per cent. ThO₂.
1.1630	.7245	62.296
.8607	.5362	62.298
1.5417	.9605	62.301
1.5217	.9479	62.292

Mean, 62.297, ± .0013

Hence Th = 232.59.

---

[1] Ber. Deutsch. chem. Gesell., 15, 2519. 1882.
[2] Ber. Deutsch. chem. Gesell., 20, 1665. 1887.

Urbain,[1] who purified his material by crystallizing thorium acetyl-acetonate from solution in chloroform, gives the following analyses of the anhydrous sulphate, effected by calcination:

$Th(SO_4)_2$.	ThO_2.	Per cent. ThO_2.
1.0925	.6815	62.374
.5926	.3699	62.420
1.0230	.6384	62.405

Mean, 62.400, ± .0096

Hence Th = 233.75.

Meyer and Gumperz,[2] in order to determine whether thorium is complex or not, prepared the octohydrated sulphate from material of diverse origin, and analyzed it by dehydration and calcination. Their data, which I give as one series, represent, first, six experiments upon preparations obtained by fractional precipitation as chromate; and, secondly, six analyses of the sulphate prepared from three samples of thorium chloride. I give here only the weights of the anhydrous sulphate and the oxide, for the reason that the hydration of the compound was too irregular to yield good values for the atomic weight of thorium.

$Th(SO_4)_2$.	ThO_2.	Per cent. ThO_2.
.9301	.5793	62.284
.9927	.6184	62.295
1.0344	.6442	62.278
.9349	.5821	62.263
.6680	.4160	62.276
.4296	.2676	62.291
.9199	.5730	62.289
.7647	.4764	62.299
1.0650	.6633	62.300
.7758	.4834	62.310
.8824	.5496	62.285
.5545	.3454	62.290

Mean, 62.288, ± .0024

Hence Th = 232.45. From the uniformity of their results, Meyer and Gumperz conclude that there is no evidence of a separation of thorium into substances of different atomic weights. Their figures combine with those of previous investigations thus:

Cleve	62.423, ± .0140
Nilson	62.297, ± .0009
Krüss and Nilson.............	62.297, ± .0013
Urbain	62.400, ± .0096
Meyer and Gumperz...........	62.288, ± .0024
General mean	62.296, ± .0007

---

[1] Ann. Chim. Phys. (7), 19, 223. 1900.
[2] Ber. Deutsch. chem. Ges., 38, 817. 1905.

Neglecting the work of Chydenius, which has no present value, we have six ratios from which to deduce the atomic weight of thorium, as follows:

(1). $2BaSO_4 : ThO_2 :: 100 : 58.026, \pm .214$

(2). $2BaSO_4 : Th(SO_4)_2.4H_2O :: 100 : 107.509, \pm .585$

(3). $4CO_2 : ThO_2 :: 100 : 151.114, \pm .053$

(4). $Th(SO_4)_2.9H_2O : ThO_2 :: 100 : 45.090, \pm .0019$

(5). $Th(SO_4)_2.4H_2O : ThO_2 :: 100 : 52.535, \pm .0473$

(6). $Th(SO_4)_2 : ThO_2 :: 100 : 62.296, \pm .0007$

To reduce these ratios we have—

$S = 32.0667, \pm .00075$ $\qquad Ba = 137.363, \pm .0025$

$C = 12.0038, \pm .0002$ $\qquad H = 1.00779, \pm .00001$

Hence,

From ratio 2 ....Th $= 226.295, \pm 2.7311$

"   "   5 ....228.998, $\pm$ .3451

"   "   6 ....232.579, $\pm$ .0063

"   "   4 ....232.639, $\pm$ .0145

"   "   3 ....233.983, $\pm$ .0933

"   "   1 ....238.900, $\pm$ .9998

Three of these values, the first two and the last, are absolutely worthless, and can be rejected at once. To include them would not appreciably affect the final combination. The values from ratios 3, 4 and 6, combined, give a general mean Th $= 232.598, \pm .0058$, or 232.6 rounded off.

In this discussion the question of the definite individuality of thorium has not been touched. Recent investigations upon radioactivity have shown that the supposed element may be really complex, or at least that it contains traces of other substances. Baskerville[1] and Brauner[2] have both claimed to have fractionated thoria into different component earths, which differed widely in atomic weight and physical properties. These claims, however, are not as yet fully substantiated. Meyer and Gumperz believe that their atomic weight determinations establish the integrity of thorium; but the question is still open. Much work remains to be done before the controversy can be declared ended. Meanwhile the atomic weight as given above represents that of the thorium which is recognized as an element by all analysts.

---

[1] Journ. Amer. Chem. Soc., 23, 761 and 26, 922.

[2] Proc. Chem. Soc., 17, 67.

20

PHOSPHORUS.

The material from which to calculate the atomic weight of phosphorus is by no means abundant. Berzelius, in his Lehrbuch,[1] 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 have been considered with reference to gold.

Pelouze,[2] in a single titration of phosphorus trichloride with a standard solution of silver, obtained a wholly erroneous result; and Jacquelain,[3] in his similar experiments, did even worse. Schrötter's criticism upon Jacquelain sufficiently disposes of the latter.[4]

Only the determinations made by Schrötter, Dumas, Van der Plaats, Ter Gazarian and Baxter and Jones remain to be considered.

Schrötter[5] 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 $P = 31.027$.

Dumas[6] 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] 5th ed., 1188.
[2] Compt. Rend., 20, 1047.
[3] Compt. Rend., 33, 693.
[4] Journ. prakt. Chem., 57, 315.
[5] Journ. prakt. Chem., 53, 435. 1851.
[6] Ann. Chem. Pharm., 113, 29. 1860.

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, $\pm$ .0036

Hence P = 31.027.

By Van der Plaats [1] three methods of determination were adopted, and all weights were reduced to a vacuum standard. First, silver was precipitated from a solution of the sulphate by means of phosphorus. The latter had been twice distilled in a current of nitrogen. The silver, before weighing, was heated to redness. The phosphorus equivalent to 100 parts of silver is given in the third column:

.9096 grm. P gave 15.8865 Ag.   5.7256
.5832 "   10.1622 "   5.7389

Mean, 5.7322, $\pm$ .0045

Hence P = 30.920.

The second method consisted in the analysis of silver phosphate; but the process is not given. Van der Plaats states that it is difficult to be sure of the purity of this salt.

6.6300 grm. Ag_3PO_4 gave 5.1250 Ag.   77.300 per cent.
12.7170 "   9.8335 "   77.326 "

Mean, 77.313, $\pm$ .0088

Hence P = 30.970.

In the third set of determinations, yellow phosphorus was oxidized by oxygen at reduced pressure, and the resulting P_2O_5 was weighed:

10.8230 grm. P gave 24.7925 P_2O_5.   Ratio, 2.29072
7.7624 "   17.7915 "   " 2.29201

Hence P = 30.975.

As these figures fall within the range of Schrötter's, they may be averaged in with his series, the entire set of twelve determinations giving a mean of 2.28955, $\pm$ .00032.

Ter Gazarian [2] determined the density of gaseous phosphine, from which its molecular weight is deducible. For the weight of the normal litre, in grammes, he found—

1.52955
1.52907
1.52933
1.52944
1.52907
1.52933

Mean, 1.52930, $\pm$ .000054

[1] Compt. Rend., 100, 52. 1885.
[2] Journ. Chim. Phys., 7, 337. 1909.

From these figures, reduced by means of the critical constants, Ter Gazarian finds $PH_3 = 33.931$. The probable error is 0.0012. Hence P = 30.908.

Baxter and Jones [1] based their determinations of the atomic weight of phosphorus upon analyses of silver phosphate. This salt, was dissolved, and the silver precipitated and weighed as bromide, and in one experiment as chloride.

The weights, in vacuo, and the ratios are as follows:

Ag_3PO_4.	$AgBr$.	Ratio.
6.20166	8.34490	134.558
6.35722	8.55419	134.559
5.80244	7.80819	134.567
5.05845	6.80685	134.564
7.15386	9.62694	134.570
7.20085	9.68947	134.560
6.20182	8.34522	134.561
5.20683	7.00605	134.555

Mean, 134.562, ± .0012

Hence P = 31.051.

Ag_3PO_4.	$AgCl$.	Ratio.
3.34498	3.43544	102.704, ± .0034

Hence P = 31.054.

The probable error assigned to the last ratio is that of one experiment in the bromide series.

From the following ratios the atomic weight of phosphorus is now to be computed.

(1). $2P:P_2O_5::1.0:2.28955$, ± .00032
(2). $3Ag:PCl_3::100:42.4553$, ± .0036
(3). $5Ag:P::100:5.7322$, ± .0045
(4). $Ag_3PO_4:3Ag::100:77.313$, ± .0088
(5). $Ag_3PO_4:3AgCl::100:102.704$, ± .0034
(6). $Ag_3PO_4:3AgBr::100:134.562$, ± .0012
(7). $PH_3 = 33.931$, ± .0012

To reduce these we have—

Ag = 107.880, ± .00029		Br = 79.9197, ± .0003
Cl = 35.4584, ± .0002		H = 1.00779, ± .00001

---

[1] Journ. Amer. Chem. Soc., 32, 298. 1910.

Hence,

From ratio	7	....	P = 30.908, ± .0012
"	" 3	....	30.920, ± .0243
"	" 4	....	30.970, ± .0384
"	" 1	....	31.018, ± .0077
"	" 2	....	31.027, ± .0117
"	" 6	....	31.051, ± .0039
"	" 5	....	31.054, ± .0148

General mean, P = 30.925, ± .0011

Ratio 7 is here evidently overweighted to an enormous extent. It outweighs all the others collectively, which is a highly improbable condition. If we reject it altogether, the remaining six ratios give a general mean of P = 31.041, ± .0032, which appears to be more probable than the much lower value given above. The arithmetic average of the seven values is P = 30.993. The true value is probably near 31, as is commonly assumed.

- - - - - -

VANADIUM.

Roscoe's determination of the atomic weight of vanadium was the first to have any scientific value. The results obtained by Berzelius[1] and by Czudnowicz[2] were 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[3] studied two compounds of vanadium, namely, the pentoxide, 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. 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 = 51.381, ± .0220.

[1] Poggend. Annal., 22, 14. 1831.
[2] Poggend. Annal., 120, 17. 1863.
[3] Journ. Chem. Soc., 6, pp. 330 and 344. 1868.

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 grm.	$VOCl_3 =$ 5.2853 grm. Ag.		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 $VOCl_3$ is 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 grm.	$VOCl_3$ gave 5.4039 grm. AgCl.		40.391
2.5054	" 6.2118	"	40.333

Mean, 40.378, ± .028

These two series give us two values for the molecular weight of $VOCl_3$:

From volumetric series...... $VOCl_3 =$ 173.426, ± .1262
From gravimetric series..... " = 173.631, ± .1204
General mean .... $VOCl_3 =$ 173.532, ± .0871

Hence $V = 51.157, ± .0872$, when $Ag = 107.880$ and $Cl = 35.4584$.

From the oxide, $V = 51.381, ± .0220$. The two values combined give $V = 51.367, ± .0214$.

Addendum. Since the manuscript of the volume went to the printer the determinations made by Prandtl and Bleyer[1] have been published. They made two series of analyses of vanadium oxychloride, as was done gravimetrically by Roscoe. The data, with vacuum weights, are as follows:

<div align="center">

I.

</div>

$VOCl_3$.	$AgCl$.	*Ratio.*
5.47218	13.54724	40.393
5.85234	14.50771	40.346
3.23175	8.00636	40.365
5.24732	13.01359	40.322
3.56589	8.83375	40.367

<div align="right">Mean, 40.359, $\pm$ .0080</div>

Hence $V = 51.175$.

<div align="center">

II.

</div>

$VOCl_3$.	$AgCl$.	*Ratio.*
4.91432	12.18494	40.331
3.64470	9.04685	40.286
4.96088	12.30438	40.318
6.46766	16.04232	40.315
4.33158	10.74624	40.308
4.05060	10.04498	40.325

<div align="right">Mean, 40.314, $\pm$ .0043</div>

Hence $V = 50.977$.

These series, combined with Roscoe's similar series, give a general mean of $3AgCl : VOCl_3 :: 100 : 40.3245, \pm .0037$. Hence $V = 51.027, \pm .0160$. Combining this with the value from Roscoe's oxide series, the final, general mean becomes $V = 51.037, \pm .0036$.

---

[1] Zeitsch. anorg. Chem., 65, 152. 1909.

ARSENIC.

For the determination of the atomic weight of arsenic five compounds have been studied—the chloride, the trioxide and three arsenates. 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 [1] heated arsenic trioxide with sulphur 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 $As = 75.02$.

In 1845 Pelouze [2] 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 $AsCl_3$:

$$56.029$$
$$56.009$$
$$56.016$$

Mean, 56.018, ± .004

Hence $As = 74.92$.

Later, the same method was employed by Dumas,[3] 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, ± .008

Hence $As = 74.86$.

The two series of Pelouze and Dumas, combined, give a general mean of 56.014, ± .0035, as the amount of $AsCl_3$ equivalent to 100 parts of silver. Hence $As = 74.91$, a value closely agreeing with that deduced from the single experiment of Berzelius.

The same process of titration with silver was applied by Wallace [4] to the analysis of arsenic tribromide, $AsBr_3$. This compound was repeatedly distilled to ensure purity, and was well crystallized. His weighings

[1] Poggend. Annalen, 8, 1.
[2] Compt. Rend., 20, 1047.
[3] Ann. Chim. Phys. (3), 55, 174. 1859.
[4] Phil. Mag. (4), 18, 270.

show that the quantities of bromide given in the third column are proportional to 100 parts of silver:

8.3246 grm. AsBr₃	= 8.58 grm. Ag.	97.023
4.4368 "	4.573 "	97.022
5.098 "	5.257 "	96.970

Mean, 97.005, $\pm$ .012

Hence As $=74.19$. Why this value should be so much lower than that from the chloride is unexplained.

The volumetric work done by Kessler,[1] for the purpose of establishing the atomic weights of chromium and of arsenic, is 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, $\pm$ .028	41.224
	41.161
	41.193
	41.149
	41.126

Mean, 41.172, $\pm$ .009

Another series with the dichromate gave the following figures:

99.08
99.06
99.10
98.97
98.97

Mean, 99.036, $\pm$ .019
Previous series, 99.045, $\pm$ .028
General mean, 99.039, $\pm$ .016

[1] Poggend. Annal., 95, 204. 1855. Also 113, 134. 1861.

Other defective series are given to illustrate the partial oxidation of the As_2O_3 by the action of the air. From Kessler's data we get two values for the atomic weight of As, thus:

From $KClO_3$ series.............. As = 75.225
From $K_2Cr_2O_7$ series............. " = 75.032

The determinations made by Hibbs[1] are based upon an altogether different process from any of the preceding measurements. Sodium pyroarsenate was heated in gaseous hydrochloric acid, yielding sodium chloride. The latter was perfectly white, completely soluble in water, unfused, and absolutely free from arsenic. The vacuum weights are subjoined, with a column giving the percentage of chloride obtained from the pyroarsenate:

$Na_4As_2O_7$.	$NaCl$.	Percentage.
.02177	.01439	66.100
.04713	.03115	66.094
.05795	.03830	66.091
.40801	.26981	66.128
.50466	.33345	66.092
.77538	.51249	66.098
.82897	.54791	66.095
1.19124	.78731	66.092
1.67545	1.10732	66.091
3.22637	2.13267	66.101

Mean, 66.098, ± .0030

Hence As = 74.895.

The determinations by Ebaugh[2] are analogous to those of Hibbs. First, silver arsenate was converted into silver chloride by heating in gaseous hydrochloric acid, and the chloride was afterwards reduced to metal in a stream of hydrogen. The data obtained are as follows:

Ag_3AsO_4.	$AgCl$.	Ag.	Per cent. $AgCl$.	Per cent. Ag.
.23182	.21547	.162175	92.947	69.957
.47996	.44615	.33583	92.956	69.970
.52521	.48820	.367525	92.953	69.977
.80173	.74517	.56099	92.945	69.972
.94782	.88083	.66318	92.932	69.969
1.02047	.94836	.71400	92.928	69.968
1.03558	.96258	......	92.951	.....
1.05462	.98014	.73771	92.938	69.950

Mean, 92.944, ± .0025   69.966, ± .0024

From Ag series, As = 74.928.
From AgCl series, As = 75.000.

---

[1] Doctoral thesis, University of Pennsylvania, 1896. Work done under the direction of Professor E. F. Smith. In the fifth experiment the weight of NaCl is printed .33045. This is evidently a misprint, which I have corrected by comparison with the other data. The rejection of this experiment would not affect the final result appreciably.

[2] Doctoral thesis, University of Pennsylvania, 1901.

A similar series of experiments with lead arsenate gave the subjoined figures:

$Pb_3(AsO_4)_2$.	$PbCl_2$.	Per cent. $PbCl_2$.
.38152	.35381	92.737
.436197	.40449	92.731
.57218	.53065	92.742
.60085	.55717	92.730
.74123	.68736	92.732
.77107	.71494	92.721
.88282	.81858	92.723
.97779	.90674	92.734

Mean, 92.731, ± .0019

Hence As = 75.05.

Lead arsenate was also transformed into lead bromide, by heating in a stream of hydrobromic acid:

$Pb_3(AsO_4)_2$.	$PbBr_2$.	Per cent. $PbBr_2$.
.59704	.73092	122.424
.61712	.75567	122.451
.65799	.80569	122.447

Mean, 122.441, ± .0076

Hence As = 74.916.

All of Ebaugh's weights are reduced to a vacuum.

Silver arsenate was also chosen by Baxter and Coffin[1] for their determinations of the atomic weight of arsenic. In some experiments Ebaugh's method of heating in gaseous hydrochloric acid was adopted; in others the arsenate was dissolved in nitric acid, and the silver then precipitated as chloride or bromide. Corrections were applied, not only for weighing in air, but also for traces of moisture in the initial substance. Different samples of the arsenate were prepared, which gave slightly varying results for the atomic weight, and the determinations, for that reason, fall into two groups. In series 1 and 2, which may be treated as one here, the first five determinations were made by Ebaugh's method, and the last two by solution and precipitation. The figures thus obtained are as follows:

Ag_3AsO_4.	$AgCl$.	Ratio.
3.17276	2.94922	92.9544
2.65042	2.46367	92.9539
3.51128	3.26396	92.9564
5.83614	5.42503	92.9558
5.72252	5.31947	92.9568
4.59149	4.26796	92.9537
3.38270	3.14436	92.9542

Mean, 92.9550, ± .00036

Hence As = 74.956.

[1] Journ. Amer. Chem. Soc., 31, 297. 1909.

Series 4 and 5, with silver arsenate of different origin from that previously used, gave the subjoined figures. Only the last experiment was conducted by the precipitation method:

Ag_3AsO_4.	$AgCl$.	Ratio.
4.67268	4.34389	92.9636
7.71882	7.17597	92.9672
5.28049	4.90908	92.9664
4.25346	3.95424	92.9652
3.47340	3.22893	92.9616
5.17269	4.80879	92.9650
4.10766	3.81858	92.9624
5.47133	5.08643	92.9646

Mean, 92.9681, $\pm$ .00044

Hence As = 74.901.

These series combine with Ebaugh's thus:

Ebaugh	92.944,	$\pm$ .0025
Baxter and Coffin, 1..........	92.9550,	$\pm$ .00036
Baxter and Coffin, 2..........	92.9681,	$\pm$ .00044
General mean	92.9614,	$\pm$ .00028

Baxter and Coffin also determined the ratio between silver arsenate and silver bromide by the solution and precipitation method. Here again two series of analyses are given, numbered 3 and 6, representing different preparations of the arsenate. The two series are as follows:

Series 3.

Ag_3AsO_4.	$AgBr$.	Ratio.
8.75751	10.66553	121.787
6.76988	8.24545	121.796
5.19424	6.32590	121.787
5.33914	6.50258	121.791
8.24054	10.03552	121.782
7.57962	9.23147	121.793
6.05230	7.37106	121.789

Mean, 121.789, $\pm$ .0016

Series 6.

Ag_3AsO_4.	$AgBr$.	Ratio.
4.96261	6.04440	121.7988
5.31743	6.47658	121.7991
4.46882	5.44300	121.7995
4.16702	5.07539	121.7990

Mean, 121.7991, $\pm$ .00015

In the last mean the probable error is so low as to give it inordinate weight, especially as Baxter and Coffin suspect the presence of basic impurities in the arsenate. It is better, therefore, to treat both series as one, giving in mean $Ag_3AsO_4 : 3AgBr :: 100 : 121.793, \pm .0012$. Hence $As = 74.947$.

There are now the following ratios from which to compute the atomic weight of arsenic. The single determination by Berzelius has been arbitrarily assigned equal weight with that of Wallace's series:

  (1). $2As_2O_3 : 3SO_2 :: 100 : 48.525, \pm .012$
  (2). $3Ag : AsCl_3 :: 100 : 56.014, \pm .0035$
  (3). $3Ag : AsBr_3 :: 100 : 97.005, \pm .012$
  (4). $3As_2O_3 : 2K_2Cr_2O_7 :: 100 : 99.039, \pm .016$
  (5). $3As_2O_3 : 2KClO_3 :: 100 : 41.172, \pm .009$
  (6). $Na_4As_2O_7 : 4NaCl :: 100 : 66.098, \pm .0030$
  (7). $Ag_3AsO_4 : 3Ag :: 100 : 69.966, \pm .0024$
  (8). $Ag_3AsO_4 : 3AgCl :: 100 : 92.9614, \pm .00028$
  (9). $Ag_3AsO_4 : 3AgBr :: 100 : 121.793, \pm .0012$
  (10). $Pb_3As_2O_8 : 3PbCl_2 :: 100 : 92.731, \pm .0019$
  (11). $Pb_3As_2O_8 : 3PbBr_2 :: 100 : 122.441, \pm .0076$

To reduce these ratios we have—

$Ag = 107.880, \pm .00029$ $Na = 23.0108, \pm .00024$
$Cl = 35.4584, \pm .0002$ $K = 39.0999, \pm .0002$
$Br = 79.9197, \pm .0003$ $Cr = 52.0193, \pm .0013$
$S = 32.0667, \pm .00075$ $Pb = 206.970, \pm .0017$

Hence,

  From ratio 3 ....$As = 74.188, \pm .0389$
   " " 6 ....74.895, $\pm$ .0066
   " " 11 ....74.916, $\pm$ .0286
   " " 7 ....74.928, $\pm$ .0160
   " " 8 ....74.934, $\pm$ .0018
   " " 9 ....74.947, $\pm$ .0049
   " " 2 ....75.008, $\pm$ .0108
   " " 1 ....75.021, $\pm$ .0245
   " " 4 ....75.032, $\pm$ .0160
   " " 10 ....75.050, $\pm$ .0099
   " " 5 ....75.225, $\pm$ .0217

    General mean, $As = 74.957, \pm .0016$

This final mean is identical with the value found by Baxter and Coffin as the result of their determinations.

ANTIMONY.

After some earlier, unsatisfactory determinations, Berzelius,[1] 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 $Sb = 129.03$. The value 129 remained in general acceptance until 1855, when Kessler,[2] 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 dichromate 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
By oxidation of Sb with $K_2Cr_2O_7$................. " = 123.61
By oxidation of Sb with $KClO_3 + K_2Cr_2O_7$......... " = 123.72
By oxidation of Sb_2O_3 with $KClO_3 + K_2Cr_2O_7$...... " = 123.80
By oxidation of Sb_2S_3 with $K_2Cr_2O_7$............... " = 123.58
By oxidation of 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 different 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 also worthless.

Shortly after the appearance of Kessler's first paper, Schneider[3] 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:

[1] Poggend. Annalen, 8, 1.
[2] Poggend. Annalen, 95, 215.
[3] Poggend. Annalen, 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 Sb=120.55.

Immediately after the appearance of Schneider's memoir, Rose[1] 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,[2] 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
79.274
79.232
79.395
79.379

Mean, 79.283, ± .009

Hence Sb=122.46.

The determinations of Dumas[3] were published in 1859. This chemist

[1] Poggend. Annalen, 98, 455. 1856.
[2] Poggend. Annalen, 100, 363. 1857.
[3] Ann. Chim. Phys. (3), 55, 175.

sought to fix the ratio between silver and antimonious 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 is 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, ± .021

Hence $Sb = 121.83$.

In 1861 Kessler's second paper [1] 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 dichromate was prepared, containing 6.1466 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 standard solution of ferrous chloride. In some cases the titration was preceded by the addition of a definite weight of potassium chlorate, insufficient for complete oxidation; the dichromate 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 conversion 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

[1] Poggend. Annalen, 113, 145. 1861.

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 the dichromate and chlorate, the material used was found to be impure. Upon estimating the impurity 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 dichromate solution. Six experiments 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 :

$$10.985$$
$$10.939$$
$$10.951$$
$$10.936$$

Mean, 10.953, ± .0075

Hence $Sb = 122.08$.

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 dichromate was performed as usual. Calculated as above, the percentages of oxygen given in the last column correspond to 100 parts of antimony :

21

Sb.	KClO₃.	K₂Cr₂O₇ sol. cc.	Per cent. O.
1.636 grm.	.5000 grm.	18.3	13.088
3.0825 "	.9500 "	30.2	13.050
4.5652 "	1.4106 "	45.5	13.098

Mean, 13.079, ± .0096

Hence Sb = 122.33.

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. The third column gives the percentages of oxygen corresponding to 100 parts of $SbCl_3$:

						Per cent. O.
1.8576 grm. SbCl₃ needed	.5967 grm.	K₂Cr₂O₇ and	33.4 cc. sol.			7.0338
1.9118 "	.3019 "	KClO₃ "	16.2 "			7.0321
4.1235 "	.6801 "	KClO₃ "	23.2 "			7.0222

Mean, 7.0294, ± .0024

Hence Sb = 121.24.

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_2S 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. SbCl₃ 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 dichromate contained no evident errors, and was not accounted for. This series,[1] if we reduce all of Kessler's figures to a single common standard, gives a ratio between $K_2Cr_2O_7$ and $C_4H_4KSbO_7.\frac{1}{2}H_2O$. 100 parts of the former will oxidize of the latter:

$$336.64$$
$$338.01$$
$$336.83$$
$$337.93$$
$$338.59$$
$$335.79$$

Mean, $337.30, \pm .29$

From this $Sb = 118.68$.

The newer atomic weights found in other 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[2] 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[3] and were conclusive in favor of the lower value, approximately 120. For full details the original memoir must be consulted; only a few of the leading points can be cited here.

---

[1] Poggend. Annalen, 95, 217.
[2] Archiv der Pharmacie, 197, 194. Quoted by Cooke.
[3] Proc. Amer. Acad., 5, 13.

Schneider analyzed a sulphide of antimony which was already formed. Cooke, reversing the method, effected the synthesis of this compound. Known weights of pure antimony 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 compounds, tartaric acid was added, and then, with a supersaturated aqueous sulphhydric acid, antimony trisulphide was precipitated. The precipitate was collected by an ingenious process of reverse filtration, converted into the black modification by drying at 210°, and weighed. After weighing, the Sb_2S_3 was dissolved in hydrochloric acid, leaving a carbonaceous residue unacted upon. This was carefully estimated 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 trisulphide was weighed only in the red modification, and the results were uncorrected by conversion into the black variety 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 percentages 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, $28.5182, \pm .0120$

Hence $Sb = 120.55$.

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 as follows. 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, ± .0096

Hence $Sb = 121.82$.

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. It 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.[1]

---

[1] In Amer. Journ. Sci. (3), 21, 220, Cooke pointed out the errors due to the solubility of silver chloride, and gave two series of analyses of $SbCl_3$ to illustrate their magnitude.

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 resemble those of chlorine. 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. SbBr₃ 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 "	5.1398 "	63.890
2.3589 "	3.6959 "	63.825
1.3323 "	2.0863 "	63.859
2.6974 "	4.2285 "	63.791

Mean, 63.830, ± .008

Hence $Sb = 119.86$.

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. 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

Hence $Sb = 119.79$.

Although Cooke's work was practically conclusive, as between the rival values for antimony, his results were severely criticised by Kessler,[1] 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 well vindicated his own accuracy. In reply to Kessler, Cooke undertook still another series of experiments with antimony bromide,[2] 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 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, $\pm$ .0014

Hence $Sb = 119.85$.

Schneider,[3] 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, $\pm$ .0024

Hence $Sb = 120.43$.

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, $\pm$ .008
Schneider, late series........ 28.541, $\pm$ .0024
Cooke .... 28.5182, $\pm$ .0120

General mean .... 28.5385, $\pm$ .0023

[1] Berichte Deutsch. chem. Gesell., 12, 1044, 1879.
[2] Amer. Journ. Sci., May, 1880. Berichte, 13, 951.
[3] Journ. prakt. Chem. (2), 22, 131.

In 1881 Pfeifer[1] determined electrolytically the direct ratios between silver and antimony, and copper and antimony. With copper the following data were obtained:

			$3Cu:2Sb::100:x.$
1.412 grm. Sb =	1.1008 Cu.		128.270
1.902 "	1.4832 "		128.236
3.367 "	2.6249 "		128.272
			Mean, 128.259, ± .0077

Hence Sb = 122.27.

With silver he found—

			$3Ag:Sb::100:x.$
5.925 grm. Sb =	15.774 Ag.		37.562
6.429 "	17.109 "		37.577
10.116 "	26.972 "		37.506
4.865 "	13.014 "		37.383
4.390 "	11.697 "		37.531
9.587 "	25.611 "		37.433
4.525 "	12.097 "		37.406
			Mean, 37.485. ± .0198

Hence Sb = 121.32.

The latter ratio was also determined by Popper,[2] several years afterwards. The two metals were precipitated simultaneously by the same current; and in some experiments two portions of antimony were thrown down against one of silver. These are indicated in the subjoined table by suitable bracketing, and the ratio is given in the third column:

Sb.	Ag.	Ratio.
1.4856 ⎫		37.463
1.4788 ⎬	3.9655	37.292
2.0120 ⎫		37.503
2.0074 ⎬	5.3649	37.417
3.8882 ⎫		37.480
3.8903 ⎬	10.3740	37.500
4.1893 ⎫		37.455
4.1885 ⎬	11.1847	37.447
4.2710 ⎫		37.507
4.2752 ⎬	11.3868	37.545
5.6860 ⎫		37.460
5.6901 ⎬	15.1786	37.487
4.4117	11.8014	37.383
· 4.9999	13.3965	37.322
5.2409	14.0679	37.250
	Mean,	37.434, ± .0149
	Pfeifer found,	37.485, ± .0198
	General mean,	37.452, ± .0119

Popper's figures give in mean Sb=121.15.

The recent investigations by Cohen and Strengers[1] seem to prove that these electrolytic determinations are worthless. They effected the simultaneous precipitation of silver and antimony, using solutions of $SbCl_3$, and found that the apparent atomic weight of antimony increased with the concentration of the solutions. They give the results of 24 determinations, with full details, but only the end results need be cited here:

With 2.3 grm. $SbCl_3$ in 100 cc. of solution, Sb = 120.84 to 120.87
" 83.3 " Sb = 121.81 to 121.92

These values are calculated with old values for Cl and Ag, but they show the failure of the process to yield trustworthy figures. In any final discussion of the atomic weight of antimony, therefore, the work of Pfeifer and Popper must be disregarded.

The work done by Bongartz[2] in 1883 was quite different from any of the determinations which had preceded it. Carefully purified antimony was weighed as such, and then dissolved in a concentrated solution of potassium sulphide. From this, after strong dilution, antimony trisulphide was thrown down by means of dilute sulphuric acid. After thorough washing, this sulphide was oxidized by hydrogen peroxide, by Classen's method, and the sulphur in it was weighed as barium sulphate. The ratio measured, therefore, was $2Sb : 3BaSO_4$, and the data were as follows. The $BaSO_4$ equivalent to 100 parts of Sb is the ratio stated:

Sb taken.	BaSO₄ found.	Ratio.
1.4921	4.3325	290.362
.6132	1.7807	290.394
.5388	1.5655	290.553
1.2118	3.5205	290.518
.9570	2.7800	290.491
.6487	1.8855	290.349
.7280	2.1100	289.835
.9535	2.7655	290.036
1.0275	2.9800	290.024
.9635	2.7980	290.399
.9255	2.6865	290.275
.7635	2.2175	290.438

Mean, 290.306, ± .0436

Hence Sb = 120.61.

[1] Proc. Amsterdam Acad., Section of Sciences, 5 (2), 543. 1903. See also Cohen, Collins and Strengers, Zeitsch. phys. Chem., 50, 291.
[2] Ber. Deutsch. chem. Ges., 16, 1942. 1883.

Still another method of determination was adopted by Friend and Smith.[1] Potassium tartrylantimonite. $KSbC_4H_4O_7$, was heated in a stream of dry, gaseous hydrochloric acid, and so converted into potassium chloride. The results obtained, with vacuum weights. are subjoined:

$KSbC_4H_4O_7$.	KCl.	Per cent. KCl.
1.19481	.27539	23.049
1.57004	.36186	23.048
2.00912	.46307	23.048
2.04253	.47073	23.046
2.16646	.49935	23.049
2.25558	.51982	23.046
2.61255	.60215	23.048
2.95272	.68064	23.051

Mean, 23.048, $\pm$ .0006

Hence $Sb = 120.345$.

We have now before us the following ratios, good and bad, from which to calculate the atomic weight of antimony. The single analyses by Weber and Unger, being unimportant. are not included:

(1). Percentage of S in Sb_2S_3, 28.5385, $\pm$ .0023
(2). Percentage of Sb in Sb_2O_4. 79.283, $\pm$ .009
(3). O needed to oxidize 100 parts $SbCl_3$, 7.0294, $\pm$ .0024
(4). O needed to oxidize 100 parts Sb_2O_3, 10.953, $\pm$ .0075
(5). O needed to oxidize 100 parts Sb, 13.079, $\pm$ .0096
(6). $K_2Cr_2O_7$:tartar emetic::100:337.30, $\pm$ .29
(7). $3Ag:SbCl_3$::100:70.512, $\pm$ .021
(8). $3AgCl:SbCl_3$::100:53.2311, $\pm$ .008
(9). $3Ag:SbBr_3$::100:111.114, $\pm$ .0014
(10). $3AgBr:SbBr_3$::100:63.830, $\pm$ .008
(11). $3AgI:SbI_3$::100:71.060, $\pm$ .023
(12). $3Cu:2Sb$::100:128.259, $\pm$ .0077
(13). $3Ag:Sb$::100:37.452, $\pm$ .0119
(14). $2Sb:3BaSO_4$::100:290.306, $\pm$ .0436
(15). $KSbC_4H_4O_7:KCl$::100:23.048, $\pm$ .0006

To reduce these ratios we have—

Ag $= 107.880$, $\pm$ .00029	C $= 12.0038$. $\pm$ .0002	
Cl $= 35.4584$, $\pm$ .0002	K $= 39.0999$. $\pm$ .0002	
Br $= 79.9197$, $\pm$ .0003	Ba $= 137.363$. $\pm$ .0025	
I $= 126.9204$, $\pm$ .00033	Cr $= 52.0193$, $\pm$ .0013	
S $= 32.0667$, $\pm$ .00075	Cu $= 63.555$, $\pm$ .00063	

H $= 1.00779$, $\pm$ .00001

---

[1] Journ. Amer. Chem. Soc., 23, 502. 1901.

Hence,

From ratio	6	....	Sb = 118.678, ± .2844
"	" 11	....	119.786, ± .1621
"	" 9	....	119.850, ± .0047
"	" 10	....	119.858, ± .0451
"	" 15	....	120.345, ± .0086
"	" 1	....	120.444, ± .0108
"	" 14	....	120.612, ± .0182
"	" 13	....	121.210, ± .0386
"	" 3	....	121.240, ± .0777
"	" 7	....	121.830, ± .0680
"	" 4	....	122.078, ± .0100
"	" 12	....	122.272, ± .0075
"	" 5	....	122.333, ± .0898
"	" 2	....	122.462, ± .0550
"	" 8	....	122.527, ± .0345

General mean, Sb = 120.684, ± .0031

This mean has obviously very little significance except in so far as
it shows the relatively low weight attaching to the higher values. The
latter, say all over 121, are almost certainly in error, and ought to be
rejected. Taking only the seven lowest values, they give a general mean
of Sb = 120.048, ± .0038. Even this figure, however, is not quite satis-
factory, for the values derived from ratios 1 and 15, which seem to be
good, are not adequately accounted for. It is highly desirable that more
work should be done upon the atomic weight of antimony, by modern
methods, and for the purpose, in part at least, of explaining some of the
evident discrepancies which appear in the foregoing table.

BISMUTH.

Early in the last century the combining weight of bismuth was approximately fixed through the experiments of Lagerhjelm.[1] 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

Hence Bi = 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 Bi = 211.85, a figure still too high.

In 1851 the subject of the atomic weight of bismuth was taken up by Schneider,[2] 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, $\pm$ .0034

Hence Bi = 208.05.

---

[1] Annals of Philosophy, 4, 358. 1814. Adopted by Berzelius.
[2] Poggend. Annalen, 82, 303. 1851.

Next in order are the results obtained by Dumas.[1] Bismuth tri-chloride 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 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, with Ag = 108 and Cl = 35.5, Bi = 211.03.

The first three of the foregoing experiments were made with slightly discolored material. The remaining six percentages give a mean of 97.791, whence, on the same basis as before, Bi = 110.79. Evidently these results are now of slight value, for it is probable that the chloride of bismuth, like the corresponding antimony compound, contained traces of oxychloride. This assumption fully accounts for the discordance between Dumas' determination and the determinations of Schneider and still more recent investigators.

In 1883 Marignac[2] took up the subject, attacking the problem by two methods. His point of departure was commercial subnitrate of bismuth, which was purified by re-solution and reprecipitation, and from which he prepared the oxide. First, bismuth trioxide was reduced by heating in hydrogen, beginning with a moderate temperature and closing the operation at redness. The results were as follows, with the percentage of Bi in Bi_2O_3 added:

2.6460 grm. Bi_2O_3	lost .2730 grm. O.		89.683 per cent.
6.7057 "	.6910 "		89.696 "
3.6649 "	.3782 "		89.681 "
5.8024 "	.5981 "		89.692 "
5.1205 "	.5295 "		89.658 "
5.5640 "	.5742 "		89.680 "

Mean, 89.682. $\pm$ .0036

Hence Bi = 208.60.

---

[1] Ann. Chim. Phys. (3), 55, 176. 1859.
[2] Arch. Sci. Phys. Nat. (3), 10, 10. Oeuvres Complètes, 2, 717.

Marignac's second method of determination was by conversion of the oxide into the sulphate. The oxide was dissolved in nitric acid, and then sulphuric acid was added in slight excess from a graduated tube. The mass was evaporated to dryness with great care, and finally heated over a direct flame until fumes of SO_3 no longer appeared. The third column gives the sulphate formed from 100 parts of oxide:

2.6503	Bi_2O_3 gave	4.0218	$Bi_2(SO_4)_3$.	Ratio,	151.749
2.8025	"	4.2535	"	"	151.775
2.710	"	4.112	"	"	151.734
2.813	"	4.267	"	"	151.688
2.8750	"	4.3625	"	"	151.739
2.7942	"	4.2383	"	"	151.682

Mean, 151.728, $\pm$ .0099

Hence Bi = 208.16.

This result needs to be studied in the light of Bailey's observation,[1] that bismuth sulphate has a very narrow range of stability. It loses the last traces of free sulphuric acid at 405°, and begins to decompose at 418°, so that the foregoing ratio is evidently uncertain. The concordance of the data, however, is favorable to it.

Two analyses of bismuth sulphate, rather vaguely stated, are given by Bailey. The weights found, and the ratio derived from them are as follows:

$Bi_2(SO_4)_3$.	Bi_2O_3.	Ratio.
2.2155	1.4615	151.591
1.5635	1.0267	152.284

Mean, 151.937, $\pm$ .231

Hence Bi = 207.25. Combined with Marignac's series, the general mean becomes 151.729, $\pm$ .0099. Bailey's figures practically disappear.

The next determination of this atomic weight was by Löwe,[2] who oxidized the metal with nitric acid, and reduced the nitrate to oxide by ignition. Special care was taken to prepare bismuth free from arsenic, and the oxide was fused before weighing. In the paper just quoted Bailey calls attention to the volatility of bismuth oxide, which doubtless accounts for the low results found in this investigation. The data are as follows:

Bi taken.	Bi_2O_3 found.	Per cent. Bi.
11.309	12.616	89.640
12.2776	13.694	89.656

Mean, 89.648, $\pm$ .0040

Hence Bi = 207.84.

---

[1] Journ. Chem. Soc., 51, 676. 1887. Bailey deduces from his analyses Bi = 208.33 and 208.43. There may be some error in his printed figures, for his deductions do not agree with the data as given.

[2] Zeit. anal. Chem., 22, 498.

In Classen's [1] work upon the atomic weight of bismuth, the metal itself was first carefully investigated. Commercial samples, even those which purported to be pure, were found to be contaminated with lead and other impurities, and these were not entirely removable by many successive precipitations as subnitrate. Finally, pure bismuth was obtained by an electrolytic process, and this was converted into oxide by means of nitric acid and subsequent ignition to incipient fusion. Results as follows, with the percentage of Bi in Bi_2O_3 added:

Bi taken.	Bi_2O_3 found.	Per cent. Bi.
25.0667	27.9442	89.703
21.0691	23.4875	89.7035
27.2596	30.3922	89.693
36.5195	40.7131	89.700
27.9214	31.1295	89.6944
32.1188	35.8103	89.692
30.1000	33.5587	89.694
26.4825	59.5257	89.693
19.8008	22.0758	89.695

Mean, 89.696, $\pm$ .0009

Hence Bi = 208.92, or, reduced to a vacuum standard, 208.90.

Classen's paper was followed by a long controversy between Schneider and Classen, [2] in which the former upheld the essential accuracy of the work done by Marignac and himself. Schneider had started out with commercial bismuth, and Classen found that the commercial bismuth which he met with was impure. Schneider, by various analyses, showed that other samples of bismuth were so nearly pure that the common modes of purification were adequate; but Classen replied that the original sample used by Schneider in his atomic weight investigation had not been reëxamined. Accordingly, Schneider published a new series of determinations [3] made by the old method, but with metal which had been scrupulously purified. Results as follows:

Bi.	Bi_2O_3.	Per cent. Bi.
5.0092	5.5868	89.661
3.6770	4.1016	89.648
7.2493	8.0854	89.659
9.2479	10.3142	89.662
6.0945	6.7979	89.653
12.1588	13.5610	89.660

Mean, 89.657, $\pm$ .0015

Hence with O = 16, Bi = 208.05, a confirmation of the earlier determinations.

[1] Ber. Deutsch. chem. Ges., 23, 938. 1890.
[2] Journ. prakt. Chem., 42, 563; 43, 133; 44, 23 and 411.
[3] Journ. prakt. Chem., 50, 461. 1894.

According to Adie [1] the differences between the low and high values for bismuth are due to the presence of silicon in the metal. A preliminary determination of the atomic weight, made with pure bismuth, gave $Bi = 208.8$, approximately. Adie's explanation of the discrepancies remains to be substantiated by others.

Birckenbach,[2] working under the direction of Gutbier, effected the synthesis of bismuth oxide, and also studied its reduction. Bismuth from three distinct sources was employed in the investigation. First, the metal was converted into nitrate, and then calcined to oxide, which latter was proved to be free from occluded gases. The data obtained were as follows:

Preliminary Series.

Bi.	Bi_2O_3.	Per cent. Bi.
10.2899	11.4782	89.647
8.1023	9.0372	89.655
		Mean, 89.651, $\pm$ .0027

Hence $Bi = 207.905$.

Final Series.

Bi.	Bi_2O_3.	Per cent. Bi.
9.63289	10.74328	89.664
10.41101	11.61288	89.651
10.97914	12.24528	89.661
10.11990	11.28800	89.653
18.96770	21.15541	89.659
11.99601	13.38001	89.654
27.23022	30.37392	89.651
24.98170	27.86431	89.655
10.11284	11.27998	89.653
28.35991	31.63053	89.660
		Mean, 89.656, $\pm$ .0010

Hence $Bi = 208.02$.

The reduction of bismuth oxide to bismuth gave Birckenbach the following results:

Preliminary Series.

Bi_2O_3.	Bi.	Per cent. Bi.
2.43105	2.17994	89.671
2.9547	2.6488	89.647
1.65199	1.4810	89.671
2.4103	2.1609	89.653
		Mean, 89.660, $\pm$ .0041

Hence $Bi = 208.11$.

[1] Proc. Cambridge Phil. Soc., 12, 240. 1903.
[2] Inaug. Diss., Erlangen, 1905. The oxidation series also appears under the authorship of Gutbier and Birckenbach, in Journ. prakt. Chem. (2), 47, 457. 1908.

Final Series.

Bi_2O_3.	Bi.	Per cent. Bi.
1.45827	1.30751	89.662
2.12432	1.90461	89.657
3.0021	2.6918	89.664
2.1012	1.8840	89.663
3.0182	2.70620	89.663
1.9091	1.71171	89.661

Mean, 89.662, ± .0007

Hence Bi = 208.153.

Rejecting the work of Lagerhjelm, which has so high a probable error as to count for almost nothing, the data for the percentage of Bi in Bi_2O_3 combine as follows:

Schneider, 1851	89.655,	± .0034
Marignac	89.682,	± .0036
Löwe	89.648,	± .0040
Classen	89.696,	± .0009
Schneider, 1894	89.657,	± .0015
Birckenbach, preliminary oxidations	89.651,	± .0027
Birckenbach, final oxidations	89.656,	± .0010
Birckenbach, preliminary reductions	89.660,	± .0041
Birckenbach, final reductions	89.662,	± .0007

General mean .... 89.6683, ± .00044

If we omit the high value found by Classen, the general mean becomes 89.6594, ± .00052.

Mehler,[1] also under Gutbier's direction, studied the composition of bismuth tribromide, which was prepared by direct union of the metal with bromine, and afterwards sublimed. The bromine was precipitated with silver solution, and the silver bromide was weighed. The weights are given as reduced to a vacuum. In the third column I give the ratio $3AgBr : BiBr_3 :: 100 : x$:

$BiBr_3$.	AgBr.	Ratio.
3.77071	4.74323	79.497
4.37676	5.50932	79.443
3.64088	4.58160	79.467
4.57894	5.76183	79.470
4.53204	5.70410	79.452
2.85054	3.58682	79.473
4.58310	5.76618	79.482
6.47910	8.15465	79.453

Mean, 79.467, ± .0042

Hence Bi = 207.92.

---

[1] Inaug. Diss., Erlangen, 1905. Sitzungsb. phys. med. Soz. Erlangen, 37, 343.

Another research, carried out under Gutbier by Janssen,[1] involved the synthesis of bismuth sulphate. Bismuth was first dissolved in nitric acid, and then, with sulphuric acid, converted into sulphate. The latter compound was freed from moisture and excess of acid by heating to 380°, at which temperature its weight was constant. The results obtained were as follows:

Bi.	$Bi_2(SO_4)_3$.	Per cent. Bi.
2.4045	4.0706	59.070
2.41900	4.09445	59.081
2.20280	3.72745	59.096
2.57206	4.35444	59.066
5.79241	3.79987	59.106
3.65233	6.18143	59.086

Mean, 59.084, $\pm$ .0042

Hence Bi $= 208.085$.

The subjoined ratios are now available for discussion:

(1). $Bi_2O_3:2Bi::100:89.6683, \pm .00044$
(2). $Bi_2(SO_4)_3:2Bi::100:59.084, \pm .0042$
(3). $Bi_2O_3:Bi_2(SO_4)_3::100:151.729, \pm .0099$
(4). $3Ag:BiCl_3::100:98.003, \pm .090$
(5). $3AgBr:BiBr_3::100:79.467, \pm .0042$

To reduce these ratios we have—

Ag $= 107.880, \pm .00029$	Br $= 79.9197, \pm .0003$
Cl $= 35.4584, \pm .0002$	S $= 32.0667, \pm .00075$

Hence,

From ratio 5 .... Bi $= 207.921, \pm .0239$
"   "   2 ....208.085, $\pm$ .0260
"   "   3 ....208.171, $\pm$ .0445
"   "   1 ....208.295, $\pm$ .0095
"   "   4 ....210.802, $\pm$ .2914

General mean. Bi $= 208.224, \pm .0082$

This value is probably too high, mainly because of Classen's determinations. Rejecting them, and also the worthless determination by Dumas, the general mean becomes

$$Bi = 208.062, \pm .0096$$

which value is to be accepted. It is also sustained by Brauner's[2] statement that Kužma, by syntheses of bismuth sulphate from bismuth oxide, has obtained the value Bi $= 208.0, \pm .1$. The details of Kužma's work are yet to be published.

---

[1] Inaug. Diss., Erlangen, 1906.
[2] In Abegg's "Handbuch," 3 (3), 634.

COLUMBIUM.[1]

The atomic weight of this metal has been determined by several investigators. Rose[2] analyzed a compound which he supposed to be chloride, but which, according to Rammelsberg,[3] 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[4] results seem to have no present value, and Blomstrand's[5] are far from concordant. The latter chemist studied columbium pentachloride and sodium columbate. In the first case he weighed the columbium as columbium pentoxide, and the chlorine as silver chloride, the oxide being determined by several distinct processes. In some cases it was thrown down by water, in others by sulphuric acid, and in still others by sodium carbonate or ammonia jointly with sulphuric acid. The weights given are as follows:

$CbCl_5$.	Cb_2O_5.	$AgCl$.
.591	.294	....
.8085	.401	2.085
.633	.317	....
.195	.0974	.500
.507	.2505	1.302
.9415	.472	2.454
.563	.2796	....
.9385	.4675	2.465
.4788	.2378	....
.408	.204	1.067
.9065	.4515	....

Hence the subjoined percentages, and the ratios $5AgCl : CbCl_5 :: 100 : x$, and $10AgCl : Cb_2O_5 :: 100 : x$:

Per cent. Cb_2O_5.	$5AgCl : CbCl_5$.	$10AgCl : Cb_2O_5$.
49.788	.....	.....
49.598	38.777	19.233
50.079	.....	.....
49.949	39.000	19.435
49.408	38.940	19.240

[1] This name has forty years priority over "niobium," and therefore deserves preference.
[2] Poggend. Annal., 104, 439. 1858.
[3] Poggend. Annal., 136, 353. 1869.
[4] Journ. prakt. Chem., 68, 73. 1856.
[5] Acta Univ. Lund. 1864.

50.135	38.366	19.234
49.662	.....	.....
49.813	38.073	18.966
49.666	.....	.....
50.000	38.238	19.119
49.807	.....	.....

Mean, 49.806, ± .045   Mean, 38.566, ± .108   Mean, 19.205, ± .043

From these means the atomic weight of columbium may be computed, thus:

From $2CbCl_5 : Cb_2O_5$...................... Cb = 96.231
From $CbCl_5 : 5AgCl$...................... " = 99.107
From $5AgCl : Cb_2O_5$...................... " = 97.641

when $Ag = 107.88$, and $Cl = 35.4584$.

The series upon sodium columbate, which salt was decomposed with sulphuric acid, both Cb_2O_5 and Na_2SO_4 being weighed, is too discordant for discussion. The exact nature of the salt studied is not clear, and the data given, when transformed into the ratio $Na_2SO_4 : Cb_2O_5 :: 100 : x$, give values for x ranging from 151.65 to 161.20. Further consideration of this series would therefore be useless. It seems highly probable that Blomstrand's materials were not entirely free from tantalum, since the atomic weight of columbium derived from his analyses of the chloride is evidently too high.

Marignac[1] made about twenty analyses of the potassium fluoxycolumbate, $CbOF_3 . 2KF . H_2O$. One hundred 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	

From the mean percentage of Cb_2O_5, Cb = 93.478.

From the mean between the extremes given for K_2SO_4, Cb = 93.95.

The recent determinations by Balke and Smith[2] are much more satisfactory than those already cited. Their material was certainly purer, and the results obtained were highly concordant. Columbium pentachloride was decomposed by water, with the aid of a little nitric acid,

[1] Arch. Sci. Phys. Nat. (2), 23. 1865. Oeuvres Complètes, 2, 259.
[2] Journ. Amer. Chem. Soc., 30, 1644. 1908.

and the oxide so produced was finally ignited and weighed. Their data, with vacuum weights, are as follows:

$CbCl_5$.	Cb_2O_5.	Per cent. Cb_2O_5.
9.56379	4.71539	49.305
5.42742	2.65730	49.292
5.15992	2.54364	49.296
9.64854	4.75641	49.297
7.24572	3.57222	49.301
8.00559	3.94746	49.309
9.60763	4.73852	49.324
9.19732	4.53638	49.323
4.27456	2.10734	49.300

Mean, 49.305, $\pm$ .0026

Hence, if Cl$=35.4584$, Cb$=93.528$. It is not necessary to combine this value with the earlier determinations, for the reason that it supplants them. It is, however, near one of Marignac's values, which has confirmatory significance. The atomic weight of columbium appears to be quite near 93.5. The results obtained by Deville and Troost[1] for the vapor densities of columbium chloride and oxychloride are in harmony with this conclusion.

TANTALUM.

The results obtained for the atomic weight of this metal by Berzelius,[2] Rose,[3] and Hermann[4] 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."

Blomstrand's determinations,[5] as in the case of columbium, were made upon the pentachloride. His weights are as follows:

$TaCl_5$.	Ta_2O_5.	$AgCl$.
.9808	.598	. . . . .
1.4262	.867	2.906
2.5282	1.5375	5.0105
1.0604	.6455	2.156
2.581	1.577	. . . . .
.8767	.534	. . . . .

[1] Compt. Rend., 56, 891. 1863.
[2] Poggend. Annalen, 4, 14. 1825.
[3] Poggend. Annalen, 99, 80. 1856.
[4] Journ. prakt. Chem., 70, 193. 1857.
[5] Acta Univ. Lund, 1864.

Hence the subjoined percentages of Ta_2O_5 from $TaCl_5$, and the ratios $5AgCl : TaCl_5 :: 100 : x$, and $10AgCl : Ta_2O_5 :: 100 : x$:

Per cent. Ta_2O_5.	$5AgCl:TaCl_5$.	$10AgCl:Ta_2O_5$.
60.971	.....	.....
60.791	49.078	29.835
60.814	50.458	30.685
60.873	49.297	29.940
60.960	.....	.....
60.924	.....	.....
Mean, 60.889, $\pm$ .0208	49.611, $\pm$ .289	30.153, $\pm$ .180

From these ratios we get for the atomic weight of tantalum:

From per cent. Ta_2O_5.................... $Ta = 173.74$
From $5AgCl:TaCl_5$...................... " $= 178.27$
From $10AgCl:Ta_2O_5$.................... " $= 176.10$

These results are too low, and their "probable errors" are not worth computing. Probably Blomstrand's material still contained some columbium.

In 1866 Marignac's determinations appeared.[1] He 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 next dissolved out by water, while the residue was ignited and weighed as Ta_2O_5. One hundred 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, $\pm$ .037	Mean, 44.295, $\pm$ .026

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

[1] Arch. Sci. Phys. Nat. (2), 26, 89. 1866. Oeuvres Complètes, 2, 314.

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, ± .047

Hence we have four values for Ta:

From potassium salt, per cent. Ta_2O_5..... Ta $= 183.55$
From potassium salt, per cent. K_2SO_4.... " $= 182.93$
From potassium salt, $K_2SO_4 : Ta_2O_5$....... " $= 182.76$
From ammonium salt, per cent. Ta_2O_5.... " $= 182.66$

Average .... Ta $= 182.975$

The determinations by Hinrichsen and Sahlbom[1] were much simpler. Metallic tantalum was converted into pentoxide by heating in oxygen, and the composition of the oxide was so ascertained. The weights and percentages of tantalum are as follows:

Ta.	Ta_2O_5.	Per cent. Ta.
.37200	.45437	81.872
.41278	.50364	81.959
.33558	.40975	81.899
.35883	.43807	81.912
.47554	.58087	81.868

Mean, 81.902. ± .0111

Hence Ta $= 181.019$.

In this instance, as in the case of columbium, the latest determination supplants the others. Until further evidence is available the atomic weight of tantalum may be taken as 181. The uncertainty probably amounts to as much as a unit.

---

[1] Ber. Deutsch. chem. Ges., 39, 2600. 1906.

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 having any importance was that of Berzelius,[1] 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 weighing the lead chromate thus produced. The error in his determination 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 trustworthy.

In 1844 Berzelius' results were first seriously called in question. The figure for chromium deduced from his experiments was somewhat over 56; but Peligot[2] now showed, by his analyses of chromous acetate and of the chlorides of chromium, that the true number was near 52.5. Unfortunately, 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[3] work we may omit entirely. He gives an atomic weight for chromium which is notoriously too low (50.1), and prints none of the numerical details upon which his result rests. The researches which particularly command our attention begin with those of Berlin.[4] His starting point was normal silver chromate; but in one experiment the dichromate $Ag_2Cr_2O_7$ was used. These salts, which are easily obtained in a 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

[1] Schweigg. Journ., 22, 53, and Poggend. Annal., 8, 22.
[2] Compt. Rend., 19, 609 and 734; 20, 1187; 21, 74.
[3] Compt. Rend., 24, 679. 1847.
[4] Journ. prakt. Chem., 37, 509, and 38, 149. 1846.

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:

$$23.037$$
$$23.027$$
$$23.025$$
$$22.968$$
$$\overline{}$$

Mean, 23.014, $\pm$ .011

Hence $Cr = 52.46$.

And from the single experiment with $Ag_2Cr_2O_7$ the percentage of Cr_2O_3 was 35.306. Hence $Cr = 52.34$.

For the ratio between Ag_2CrO_4 and AgCl, putting the latter at 100, we have for the former:

$$115.917$$
$$115.883$$
$$115.992$$
$$116.033$$
$$\overline{}$$

Mean, 115.956, $\pm$ .023

Hence $Cr = 52.67$.

In the single experiment with dichromate 100AgCl is formed from $151.035 Ag_2Cr_2O_7$. Hence $Cr = 52.61$.

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:

$$26.705$$
$$26.685$$
$$26.707$$
$$26.650$$
$$26.662$$
$$\overline{}$$

Mean, 26.682, $\pm$ .0076

Hence $Cr = 52.49$.

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[1] appeared. His method simply consisted in the ignition of anhydrous chromic sulphate and of ammonium 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 braces 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, ± .0280

Hence $Cr = 53.42$.

From the alum, $NH_4.Cr(SO_4)_2.12H_2O$, 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,[2] 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 results were obtained quite near those of Berlin. Both of these series are discussed together, neither having any present 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, ± .0125

Hence $Cr = 53.46$.

The determinations made by Lefort[3] are even less valuable than those by Moberg. This chemist started out from barium chromate, which,

[1] Journ. prakt. Chem., 43, 114.
[2] This objection is suggested by Berlin in a note upon Lefort's paper. Journ. prakt. Chem., 71, 191.
[3] Journ. prakt. Chem., 51, 261. 1850.

to thoroughly free it from moisture, had been dried for several hours at 250°. The chromate was dissolved in 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 certainly 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
3.5570	"	3.2710	"	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, ± .0369

Hence Cr = 53.03.

Wildenstein,[1] in 1853, also made barium chromate the basis of his researches. A known weight of 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 of $BaCrO_4$ 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

[1] Journ. prakt. Chem., 59, 27.

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

Hence Cr = 53.56.

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 dichromate with that of the chlorate, and from his observations deduced the ratio between the molecular weights of the two salts.

In his earlier paper [1] 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 dichromate. 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

Hence Cr = 52.20.

In his later paper [2] Kessler substituted arsenic trioxide for the iron solution. In one series of experiments the quantity of dichromate needed to oxidize 100 parts of the arsenic trioxide was determined, and in another the latter substance was similarly compared with the chlorate.

[1] Poggend. Annalen, 95, 208. 1855.
[2] Poggend. Annalen, 113, 137. 1861.

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
	41.161
	41.193
	41.149
	41.126
	Mean, 41.172, $\pm$ .009

Hence $Cr = 52.31$.

Reducing the later series to the standard of the earlier, the two combine as follows:

(1). $2KClO_3 : K_2Cr_2O_7 : : 100 : 120.191$, $\pm$ .028
(2). $2KClO_3 : K_2Cr_2O_7 : : 100 : 120.282$, $\pm$ .043

General mean....120.216, $\pm$ .0235

Siewert's determinations, which do not seem to have attracted general attention, were published in 1861.[1] 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

---

[1] Zeit. gesammt. Wissenschaften, 17, 530.

parts of chloride of silver, the quantities of chromic chloride stated in the third of the subjoined columns:

.2367 grm. $CrCl_3$ 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, $\pm$ .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, $\pm$ .0031. Hence $Cr = 52.046$.

Siewert also made two analyses of silver dichromate 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

Hence $Cr = 52.14$.

Berlin's single determination of this ratio gave 151.035. Taking all three values together as one series, they give a mean of 150.816, $\pm$ .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, $\pm$ .0415

Hence $Cr = 51.983$.

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, $\pm$ .0335.

For the ratio between silver chloride and chromic oxide, Siewert's two analyses of the dichromate give as follows. For 100 parts of AgCl we have of Cr_2O_3:

52.948
53.150

Mean, 53.049, $\pm$ .068

Hence $Cr = 52.041$.

This figure, reduced to the standard of Berlin's work on the monochromate, becomes $26.525, \pm .034$. Berlin's mean was $26.682, \pm .0076$. The two means, combined, give a general mean of $26.676, \pm .074$.

By Baubigny[1] we have only three experiments upon the calcination of anhydrous chromic sulphate, as follows:

1.989 grm. $Cr_2(SO_4)_3$ gave .7715 grm. Cr_2O_3.   38.788 per cent.
3.958   "   1.535   "   38.782   "
2.6052   "   1.0115   "   38.826   "

Mean, 38.799, $\pm$ .0092

Hence $Cr = 52.14$.

Moberg found for the same ratio the percentage $39.195, \pm .028$. The general mean of both series, Moberg's and Baubigny's, is $38.838, \pm .0087$.

In Rawson's work[2] ammonium dichromate was the substance studied. Weighed quantities of this salt were dissolved in water, and then reduced by hydrochloric acid and alcohol. After evaporation to dryness the mass was treated with water and ammonia, reëvaporated, dried five hours at 140°, and finally ignited in a muffle. The residual chromic oxide was bright green, and was tested to verify its purity. The corrected weights are as follows:

$Am_2Cr_2O_7$.	Cr_2O_3.	Per cent. Cr_2O_3.
1.01275	.61134	60.365
1.08181	.65266	60.330
1.29430	.78090	60.334
1.13966	.68799	60.368
.98778	.59595	60.332
1.14319	.68987	60.346

Mean, 60.346, $\pm$ .0046

Hence $Cr = 52.15$.

Still later and most elaborate of all, we come to the determinations of the atomic weight of chromium made by Meineke,[3] who studied the chromate and ammonio-chromate of silver, and also the dichromates of potassium and ammonium. For the latter salt he measured the same ratio that Rawson determined, but by a different method. He precipi-

---

[1] Compt. Rend., 98, 146.
[2] Journ. Chem. Soc., 55, 213.
[3] Ann. Chem., 261, 339. 1891.

tated its solution with mercurous nitrate, and ignited the precipitate, with the subjoined results. Vacuum weights are given:

$Am_2Cr_2O_7.$	$Cr_2O_3.$	Per cent. $Cr_2O_3.$
2.0416	1.2316	60.325
2.1618	1.3040	60.320
2.0823	1.2562	60.328
2.1913	1.3221*	60.335
2.0970	1.2656	60.353

Mean, 60.332, ± .0037
Rawson found, 60.346, ± .0046

General mean, 60.337, ± .0029

From Meineke's figures $Cr = 52.11$.

The chromate of silver, Ag_2CrO_4, and the ammonio-chromate, Ag_2CrO_4. $4NH_3$, both prepared with all necessary precautions to insure purity, were first treated essentially as in Berlin's experiments, except that the traces of silver chloride held in solution by the chromic chloride were thrown out by sulphuretted hydrogen, estimated, and their amount added to the main portion. Thus the chief error in Berlin's work was avoided. I subjoin the data obtained, with vacuum standards, as usual. All of Meineke's results are so corrected:

$Ag_2CrO_4.$	$AgCl.$	$Cr_2O_3.$
2.7826	2.4047	.6384
3.2627	2.8199	.7480
3.6362	3.1416	.8338
4.6781	4.0414	1.0726
3.2325	2.7930	.7411
3.9137	3.3805	.8976

Hence we have the following ratios, as in the case of Berlin's data:

Per cent. $Cr_2O_3.$	$100AgCl:Ag_2CrO_4.$	$100AgCl:Cr_2O_3.$
22.943	115.715	26.548
22.926	115.703	26.526
22.931	115.744	26.602
22.928	115.754	26.601
22.924	115.736	26.531
22.935	115.773	26.552

| Mean, 22.931,±.0019 | Mean, 115.737,±.0072 | Mean, 26.560,±.0093 |
| Berlin, 23.014,±.0110 | | |

General mean, 22.934,±.0018

---

* Calculated back from Meineke's value for Cr. to replace an evident misprint in the original.

From Meineke's figures Cr = 52.10, 52.04 and 52.14.
With the ammonio-chromate Meineke found as follows:

$Ag_2CrO_4.4NH_3$.	$AgCl$.	Cr_2O_3.
4.1518	2.9724	.7904
4.2601	3.0592	.8125
5.9348	4.2654	1.1317

And the ratios become—

Per cent. Cr_2O_3.	$100 AgCl : Salt$.	$100 AgCl : Cr_2O_3$.
19.037	139.679	26.591
19.072	139.255	26.559
19.059	139.138	26.532
Mean, 19.059,±.0074	Mean, 139.357,±.1109	Mean, 26.561,±.0115
Cr = 52.27	Cr = 51.61	Cr = 52.144

The first of these three analyses is rejected by Meineke as suspicious, but for the present I shall allow it to remain. The data in the third column may now be combined with the corresponding figures from the normal chromate, as found by Meineke and his predecessors:

Berlin	26.682, ± .0076
Siewert, from $Ag_2Cr_2O_7$........	26.525, ± .0340
Meineke, from Ag_2CrO_4........	26.560, ± .0093
Meineke, from $Ag_2CrO_4.4NH_3$...	26.561, ± .0115
General mean	26.620, ± .0052

$$4AgCl : Cr_2O_3 : : 100 : 26.620, \pm .0052$$

Obviously, this mean is vitiated by the known error in Berlin's work, the ultimate effect of which is serious.

In all four of the salts studied by Meineke he determined volumetrically the oxygen in excess of the normal oxides by measuring the amount of iodine liberated in acid solutions. With the silver salts the process was essentially as follows: A weighed quantity of the chromate was dissolved in weak ammonia, and the solution was precipitated with potassium iodide. After the silver iodide had been filtered off, five or six grammes of potassium iodide were added to the filtrate, which was then acidulated with phosphoric acid and a little sulphuric. The liberated iodine was then titrated with sodium thiosulphate solution, which had been standardized by means of pure iodine, prepared by Stas' method. From the iodine thus measured the excessive oxygen was computed, and from that datum the atomic weight of chromium was found. For present purposes, however, the data may be used more directly, as giving the

23

ratios $3I : Ag_2CrO_4$ and $3I : Ag_2CrO_4.4NH_3$. Thus treated, the weights are as follows, reduced to a vacuum. Reckoning the salt as 100, the third column gives the percentage of iodine liberated:

Ag_2CrO_4.	I Set Free.	Percentage.
.43838	.50251	114.628
.90258	1.03432	114.595
.89858	1.02980	114.603
.89868	1.03072	114.693

Mean, 114.630, ± .015

Hence $Cr = 52.40$.

The next series, obviously, gives the ratio $3I : Ag_2CrO_4.4NH_3$:

$Ag_2CrO_4.4NH_3$.	I Set Free.	Percentage.[1]
.54356	.51784	95.267
.54856	.52046	94.877
.54926	.52322	95.258
.54906	.52376	95.392
.54466	.51910	95.307
.54536	.51891	95.150

Mean, 95.208, ± .0497

Hence $Cr = 52.02$.

In dealing with the two dichromates Meineke used the acid potassium iodate in place of potassium iodide, the chromate and the iodate reacting in the molecular ratio of $2:1$. The thiosulphate was standardized by means of the acid iodate, so that we have direct ratios between the latter and the two chromates. The data are as follows, with the amount of iodate proportional to one hundred parts of the dichromate in the third column:

$K_2Cr_2O_7$.	KHI_2O_6.	Percentage.
.25090	.16609	66.198
.25095	.16613	66.200
.25078	.16601	66.197
.24979	.16541	66.220
.24987	.16540	66.192
.24966	.16543	66.262
.25015	.16559	66.196
.25012	.16559	66.204
.24977	.16546	66.245
.25034	.16572	66.198
.25025	.16567	66.202
.25015	.16568	66.234

Mean, 66.212, ± .0044

Hence $Cr = 52.14$.

---

[1] These figures are not wholly in accord with the percentages of oxygen computed by Meineke. I suspect that there is a misprint among his data as published, probably in the second experiment, but I cannot trace it with certainty.

$Am_2Cr_2O_7$.	KHI_2O_6.	Percentage.
.21457	.16584	77.290
.21465	.16588	77.279
.21464	.16584	77.264
.21416	.16543	77.246
.21447	.16564	77.232
.21427	.16559	77.281
.22196	.17152	77.272
.22194	.17151	77.278
.22180	.17139	77.272

Mean, 77.268, ± .0041

Hence Cr = 52.13.

Baxter, Mueller and Hines [1] determined the atomic weight of chromium through the analysis of silver chromate. The weighed salt was dissolved in nitric acid and reduced either by sulphurous acid or hydrazine sulphate. The silver was then precipitated as chloride or bromide, by weak hydrochloric or hydrobromic acid, and the halide compound was weighed. All modern precautions were taken in this work, such as determining traces of moisture in the chromate, and also the traces of silver chloride or bromide remaining in solution. The chloride series, with vacuum weights, was as follows:

Ag_2CrO_4.	AgCl.	Ratio.
10.30985	8.90908	115.723
8.26920	7.14492	115.735
5.56679	5.67444	115.726

Mean, 115.728, ± .0024

Hence Cr = 52.005.

This combines with previous series as follows:

For the bromide series, all corrections applied, the data are these:

Ag_2CrO_4.	AgBr.	Ratio.
2.63788	2.98621	88.336
2.82753	3.20084	88.337
2.33454	2.64268	88.340
1.77910	2.01402	88.336
2.33198	2.63994	88.335
3.10402	3.51390	88.336

---

[1] Journ. Amer. Chem. Soc., 31, 529. 1909.

2.92751	3.31427	88.330
4.21999	4.77762	88.328
5.24815	5.94104	88.337
6.24014	7.06484	88.327
7.92313	8.96982	88.331

Mean, 88.334, $\pm$ .0009

Hence $Cr = 51.987$.

Similar determinations of the atomic weight of chromium were made by Baxter and Jesse,[1] who analyzed silver dichromate. In a single experiment 6.26657 grammes of $Ag_2Cr_2O_7$ gave 4.16076 of AgCl. Ratio, 150.611. Giving this the weight of a single determination in the following bromide series, $\pm$.0024, it combines with the earlier measurements by Berlin and Siewert to a general mean of 150.612, $\pm$.0024. The older work vanishes. Hence $Cr = 52.003$.

The dichromate-bromide series of determinations gave the subjoined data:

$Ag_2Cr_2O_7$.	$AgBr$.	Ratio.
5.71554	4.97149	114.966
4.87301	4.23888	114.960
7.45476	6.48425	114.967
4.75269	4.13420	114.960
8.15615	7.09495	114.957
6.15412	5.35309	114.964
6.83662	5.94768	114.963
5.39883	4.69631	114.959

Mean, 114.962, $\pm$ .0008

Hence $Cr = 51.995$.

The following ratios are now available for computing the atomic weight of chromium:

(1). Percentage Cr_2O_3 from Ag_2CrO_4, 22.934, $\pm$ .0018
(2). Percentage Cr_2O_3 from $Ag_2Cr_2O_7$, 35.236, $\pm$ .0335
(3). $2AgCl : Ag_2CrO_4 :: 100 : 115.731$, $\pm$ .0023
(4). $2AgCl : Ag_2Cr_2O_7 :: 100 : 150.612$, $\pm$ .0024
(5). $4AgCl : Cr_2O_3 : 100 : 26.620$, $\pm$ .0052
(6). Percentage Cr_2O_3 in $Cr_2(SO_4)_3$, 38.838, $\pm$ .0087
(7). Percentage Cr_2O_3 in $AmCr(SO_4)_2.12H_2O$, 16.143, $\pm$ .0125
(8). $BaSO_4 : BaCrO_4 :: 100 : 108.9815$, $\pm$ .0369
(9). $BaCrO_4 : BaCl_2 :: 100 : 81.702$, $\pm$ .014
(10). $3AgCl : CrCl_3 :: 100 : 36.842$, $\pm$ .0031
(11). $2KClO_3 : K_2Cr_2O_7 :: 100 : 120.216$, $\pm$ .0235
(12). Percentage Cr_2O_3 in $Ag_2CrO_4.4NH_3$, 19.059, $\pm$ .0074
(13). $2AgCl : Ag_2CrO_4.4NH_2 :: 100 : 139.357$, $\pm$ .1109
(14). Percentage Cr_2O_3 in $Am_2Cr_2O_7$, 60.337, $\pm$ .0029

---

[1] Journ. Amer. Chem. Soc., 31, 541. 1909.

(15). $Ag_2CrO_4:3I::100:114.630, \pm .015$

(16). $Ag_2CrO_4.4NH_3:3I::100:95.208, \pm .0497$

(17). $2K_2Cr_2O_7:KHI_2O_6::100:66.212, \pm .0044$

(18). $2Am_2Cr_2O_7:KHI_2O_6::100:77.268, \pm .0041$

(19). $2AgBr:Ag_2CrO_4::100:88.334, \pm .0009$

(20). $2AgBr:Ag_2Cr_2O_7::100:114.962, \pm .0008$

To reduce these we have the following atomic weights:

$Ag = 107.880, \pm .00029$	$S = 32.0667, \pm .00075$
$Cl = 35.4584, \pm .0002$	$N = 14.0101, \pm .0001$
$Br = 79.9197, \pm .0005$	$K = 39.0999, \pm .0002$
$I = 126.9204, \pm .00033$	$Ba = 137.363, \pm .0025$

$$H = 1.00779, \pm .00001$$

Hence,

From ratio 13	$Cr = 51.610,$	$\pm .3180$
" " 19	$51.987,$	$\pm .0035$
" " 20	$51.995,$	$\pm .0016$
" " 4	$52.010,$	$\pm .0069$
" " 3	$52.014,$	$\pm .0067$
" " 16	$52.020,$	$\pm .2088$
" " 10	$52.046,$	$\pm .0134$
" " 2	$52.104,$	$\pm .0824$
" " 1	$52.111,$	$\pm .0063$
" " 14	$52.125,$	$\pm .0066$
" " 18	$52.126,$	$\pm .0067$
" " 17	$52.137,$	$\pm .0098$
" " 11	$52.235,$	$\pm .0285$
" " 6	$52.264,$	$\pm .0203$
" " 12	$52.267,$	$\pm .0240$
" " 5	$52.312,$	$\pm .0149$
" " 15	$52.404,$	$\pm .0499$
" " 8	$53.031,$	$\pm .0862$
" " 7	$53.456,$	$\pm .0611$
" " 9	$53.563,$	$\pm .0437$

General mean, $Cr = 52.0193, \pm .0013$

In this combination the work of Baxter and his colleagues carries overwhelming weight, and yet the good work of Siewert, Baubigny, Rawson, and, in part, Meineke's, is not entirely ignored. The high values, with their large probable errors, practically vanish from the general mean. The ten lowest values give a mean of $Cr = 52.007, \pm .0013$: the ten highest give $Cr = 52.194, \pm .0050$. The unimportance of the last value is perfectly evident.

MOLYBDENUM.

If we leave out of account the inaccurate determination made by Berzelius,[1] 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 investigations, together with considerations based upon the periodic classification, point conclusively to the higher.

The earliest investigation which we need especially to consider is that of Svanberg and Struve.[2] 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 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:

$$
\begin{aligned}
&89.7919 \left.\right\} A \\
&89.7291 \\
&89.6436 \left.\right\} \\
&89.7082 \\
&89.7660 \left.\right\} B \\
&89.7640 \\
&89.8635
\end{aligned}
$$

Mean, $89.7523, \pm .0176$

[1] Poggend. Annalen, 8, 1. 1826.
[2] Journ. prakt. Chem., 44, 301. 1848.

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.

> From the CO_2 series.............. Mo = 91.93
> From the MoS_2 series........... Mo = 93.30

Berlin,[1] 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 $(NH_4)_4Mo_5O_{17}.3H_2O$, and in it these percentages of MoO_3 were found:

> 81.598
> 81.612
> 81.558
> 81.555
> ————
> Mean, 81.581, ± .0095

Hence Mo = 92.16.

Until 1859 the value 92 was generally accepted on the basis of the foregoing researches, but in this year Dumas[2] 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 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, ± .030

Hence Mo = 95.924.

---

[1] Journ. prakt. Chem., 49, 444. 1850.
[2] Ann. Chem. Pharm., 105, 84; and 113, 23.

In 1868 the same method was employed by Debray.[1] His trioxide was purified by sublimation in a platinum tube. His data 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

Hence $Mo = 95.524$.

For the same ratio we have also a single experiment by Rammelsberg,[2] who, closely following Dumas' method, found in molybdenum trioxide 66.708 per cent. of metal. As this figure falls within the limits of Dumas' series, we may assign it equal weight with one experiment in the latter.

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 a 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.

In 1873, Lothar Meyer[3] discussed the analyses made by Liechti and Kemp[4] of four chlorides of molybdenum, and in the first edition of this work the same data were considered in detail. The analyses, however, were not intended as determinations of atomic weight, and since good determinations have been more recently published, the work on the chlorides will be omitted from further consideration. It is enough to state here that they gave values for Mo ranging near 96, both above and below that number, with an extreme range of over eight-tenths of a unit.

In 1893 the determinations by Smith and Maas appeared,[5] representing an entirely new method. Sodium molybdate, purified by many recrystallizations and afterwards dehydrated, was heated in a current of pure, dry, gaseous hydrochloric acid. The compound $MoO_3.2HCl$ was thus distilled off, and the sodium molybdate was quantitatively transformed into sodium chloride. The latter salt was afterwards carefully examined, and proved to be free from molybdenum. The data, with all weights reduced to a vacuum standard, are subjoined:

Na_2MoO_4.	$NaCl$.	Per cent. $NaCl$.
1.14726	.65087	56.733
.89920	.51023	56.743
.70534	.40020	56.739

[1] Compt. Rend., 66, 734.
[2] Berlin Monatsbericht, 1877, p. 574.
[3] Ann. Chem. Pharm., 169, 365. 1873.
[4] Ann. Chem. Pharm., 169, 344.
[5] Journ. Amer. Chem. Soc., 15, 397 1893.

.70793	.40182	56.760
1.26347	.71695	56.745
1.15217	.65367	56.734
.90199	.51188	56.750
.81692	.46358	56.747
.65098	.36942	56.748
.80563	.45717	56.747

Mean, 56.745, $\pm$ .0017

Hence Mo $= 96.055$.

In 1895, Seubert and Pollard [1] determined the atomic weight of molybdenum by two methods. First, the carefully purified trioxide, in weighed amounts, was dissolved in an excess of a standard solution of caustic soda. This solution was standardized by means of hydrochloric acid, which in turn had been standardized gravimetrically as silver chloride. Hence, indirectly, the ratio $2AgCl : MoO_3$ was measured. Sulphuric acid and lime water were also used in the titrations, so that the entire process was rather complicated. Ignoring the intermediate data, the end results, in weights of MoO_3 and $AgCl$, were as follows. The third column gives the MoO_3 proportional to 100 parts of $AgCl$:

MoO_3.	$AgCl$.	Ratio.
3.6002	7.1709	50.206
3.5925	7.1569	50.196
3.7311	7.4304	50.214
3.8668	7.7011	50.211
3.9361	7.8407	50.201
3.8986	7.7649	50.208
3.9630	7.8941	50.202
3.9554	7.8806	50.192
3.9147	7.7999	50.189
3.8543	7.6767	50.208
3.9367	7.8437	50.190

Mean, 50.202, $\pm$ .0018

Hence Mo $= 95.92$.

The second method adopted by Seubert and Pollard was the old one of reducing the trioxide to metal by heating in a current of hydrogen. The weights and percentages of metal are subjoined:

MoO_3.	Mo.	Per cent.
1.8033	1.2021	66.661
1.9345	1.1564	66.670
3.9413	2.6275	66.666
1.5241	1.0160	66.662
4.0533	2.7027	66.679

Mean, 66.668, $\pm$ .0022

Hence Mo $= 96.006$.

[1] Zeitsch. anorg. Chem., 8, 434. 1895.

Vandenberghe[1] prepared molybdenum dibromide, which was next reduced to metal by heating in hydrogen. The metal was then oxidized to trioxide by means of nitric acid. The data are as follows:

Mo.	MoO_3.	Per cent. Mo.
.7143	1.0711	66.689
.3453	.5177	66.699
.9693	1.4533	66.696
.5089	.7631	66.689
1.7212	2.5820	66.689

Mean, 66.692, ± .0015

Corrected to a vacuum this becomes $66.687, \pm .0015$.

Hence Mo = 96.088.

This mean may be combined with former determinations thus:

Dumas	66.649, ± .0300
Debray	66.556, ± .0200
Rammelsberg	66.708, ± .0680
Seubert and Pollard..........	66.668, ± .0022
Vandenberghe	66.687, ± .0015
General mean	66.681, ± .0012

Neglecting all determinations made before 1859, there are now three ratios from which to compute the atomic weight of molybdenum, as follows:

(1). $MoO_3:Mo::100:66.681, \pm .0012$
(2). $2AgCl:MoO_3::100:50.202, \pm .0018$
(3). $Na_2MoO_4:2NaCl::100:56.745, \pm .0017$

Reducing these ratios with $Ag = 107.880, \pm .00029$, $Cl = 35.4584, \pm .0002$, and $Na = 23.0108, \pm .00024$, we have—

From ratio 2 ....Mo =	95.917, ± .0052
" " 3	96.055, ± .0036
" " 1	96.062, ± .0039
General mean, Mo =	96.029, ± .0024

In this combination the actual uncertainty is greater than the decimals. For practical purposes the round number 96 can be used.

---

[1] Acad. Roy. Belge, Mém. Couronnés, T. 56.

TUNGSTEN.

The atomic weight of tungsten has been determined from analyses of the trioxide, the hexchloride, and the tungstates of iron, silver, sodium and barium.

The composition of the trioxide has been the subject of many investigations. Malaguti[1] 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 probably accurate, provided that the trioxide used be pure.

The first experiments which we need consider are, as usual, those of Berzelius.[2] 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, $\pm$ .0880

Hence $W = 189.324$.

These figures are far too high, the error being probably due to the presence of alkaline impurity in the trioxide employed.

Next in order of time comes the work of Schneider,[3] 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

[1] Journ. prakt. Chem., 8, 179. 1836.
[2] Poggend. Annalen, 8, 1. 1826.
[3] Journ. prakt. Chem., 50, 152. 1850.

Oxidation Series.

79.329
79.324
79.328
———
Mean, 79.327
Mean of all, 79.320, $\pm$ .0068

Hence $W = 184.108$.

Closely agreeing with these figures are those of Marchand,[1] published in the following year:

Reduction Series.

79.307
79.302
———
Mean, 79.3045

Oxidation Series.

79.321
79.352
———
Mean, 79.3365
Mean of all, 79.3205, $\pm$ .0073

Hence $W = 184.114$.

The figures obtained by v. Borch[2] agree approximately 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

Oxidation Series.

79.359
79.339
———
Mean, 79.349
Mean of all, 79.293, $\pm$ .0108

Hence $W = 183.806$.

---

[1] Ann. Chem. Pharm., 77, 261. 1851.
[2] Journ. prakt. Chem., 54, 254. 1851.

Dumas[1] gives only a reduction series, based upon trioxide obtained by the ignition of a pure ammonium tungstate. The reduction was effected in a porcelain boat, platinum being objectionable on account of the tendency of tungsten 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

Hence W = 184.019.

The data furnished by Bernoulli[2] 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

Oxidation Series.

79.558
79.656
79.555
79.554

Mean, 79.581
Mean of all, 79.480, $\pm$ .056

Hence W = 185.918.

Two reduction experiments by Persoz[3] 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

Hence W = 184.041.

[1] Ann. Chem. Pharm., 113, 23. 1860.
[2] Poggend. Annalen, 111, 573. 1860.
[3] Zeit. anal. Chem., 3, 260. 1864.

Next in order is the work done by Roscoe.[1] 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

Oxidation Series.

79.230
79.299
———
Mean, 79.2645
Mean of all, 79.264, $\pm$ .0146

Hence $W = 183.482$.

In Waddell's experiments[2] especial precautions were taken to procure tungstic oxide free from silica and molybdenum. Such oxide, elaborately purified, was reduced in hydrogen, with the following results:

1.4006 grm. WO_3 gave	1.1115 W.	79.359 per cent.	
.9900 "	.7855 "	79.343 "	
1.1479 "	.9110 "	79.362 "	
.9894 "	.7847 "	79.311 "	
4.5639 "	3.6201 "	79.320 "	

Mean, 79.339, $\pm$ .0069

Hence $W = 184.332$.

The investigation by Pennington and Smith[3] started from the supposition that the tungsten compounds studied by their predecessors had not been completely freed from molybdenum. Accordingly, tungstic oxide, carefully freed from all other impurities, was heated in a stream of gaseous hydrochloric acid, so as to volatilize all molybdenum as the compound $MoO_3.2HCl$. The residual WO_3, was then reduced in pure hydrogen, and the tungsten so obtained was oxidized in porcelain crucibles. Care was taken to exclude reducing gases, and the trioxide was finally cooled in vacuum desiccators over sulphuric acid. The oxida-

[1] Ann. Chem. Pharm., 162, 368. 1872.
[2] Amer. Chem. Journ., 8, 280. 1886.
[3] Read before the Amer. Philos. Soc., Nov. 2, 1894.

tion data are as follows, with the usual percentage column added. The weights are reduced to a vacuum:

Tungsten.	Oxygen gained.	Percentage.
.862871	.223952	79.394
.650700	.168900	79.392
.597654	.155143	79.390
.666820	.173103	79.391
.428228	.111168	79.390
.671920	.174406	79.392
.590220	.153193	79.394
.568654	.147588	79.394
1.080973	.280600	79.392

Mean, 79.392, ± .0004

Hence $W = 184.92$.

The very high value for tungsten found by Pennington and Smith, nearly a unit higher than that which was commonly accepted, seems to have at once attracted the attention of Schneider,[1] who criticized the paper somewhat fully, and gave some new determinations of his own. The tungsten trioxide employed in this new investigation was heated in gaseous hydrochloric acid, and the absence of molybdenum was proved. The data obtained, both by reduction and by oxidation, are as follows:

Reduction Series.

2.0738 grm. WO_3 gave 1.6450 W.	79.323 per cent.
4.0853 "	3.2400 "	79.309 "
6.1547 "	4.8811 "	79.307 "

Oxidation Series.

1.5253 grm. W gave 1.9232 WO_3.	79.311 per cent.
3.1938 "	4.0273 "	79.304 "
4.7468 "	5.9848 "	79.314 "

Mean of all, 79.311, ± .0018

Hence $W = 184.007$.

In order to account for the difference between this result and that of Pennington and Smith, an impurity of molybdenum trioxide amounting to about one per cent. would be necessary. Schneider suggests that the quantities of material used by Pennington and Smith were too small, and that there may have been mechanical loss of small particles during the long heatings. Such losses would tend to raise the atomic weight computed from the experiments. On the other hand, the losses could hardly have been uniform in extent, and the extremely low probable error of Pennington and Smith's series renders Schneider's supposition improbable. The error, if error exists, must be accounted for otherwise.

---

[1] Journ. prakt. Chem. (2), 53, 288. 1896.

Soon after Schneider's paper appeared, another set of determinations by Shinn [1] was published from Smith's laboratory. Attempts to verify the results obtained by Smith and Desi having proved abortive, and other experiments having failed, Shinn resorted to the oxidation method and gives the subjoined data. The percentage column is added by myself:

.22297 grm. W gave .28090 WO_3.	79.377
.17200 " .21664 "	79.394
.10989 " .13844 "	79.377
.10005 " .12598 "	79.417

Mean, 79.391, $\pm$ .0066

Hence $W = 184.908$.

This figure is very close to that found in Pennington and Smith's series.

The great discordance between the determinations so far cited, led Hardin [2] to a very careful investigation of tungsten trioxide. The substance was prepared from various sources, and manipulated by various methods; and although concordant results were sometimes obtained in succession, the discordance between different series of experiments was very great. Hardin therefore concluded that a discussion of his figures, with reference to the atomic weight of tungsten, would be useless. Nevertheless, partly for the sake of completeness, and partly because this calculation is in great measure a study of the compensation of errors, I prefer to cite Hardin's determinations, in order that they may be compared with others. For this purpose I give his sixty-four determinations as one series. The letters o and r indicate oxidation and reduction experiments, respectively. The atomic weights found were as follows:

r 184.05	r 184.01	o 184.86	o 184.20
r 184.04	r 184.66	o 184.27	r 183.58
r 183.98	r 183.99	o 184.07	r 183.51
r 184.33	r 183.93	r 183.83	r 183.83
r 183.94	r 183.91	r 183.80	o 184.05
r 183.91	o 184.53	r 183.67	o 184.22
r 183.66	o 184.01	r 183.56	o 184.06
o 184.94	o 184.65	r 183.72	r 184.03
o 184.86	r 183.55	r 183.71	r 183.81
o 185.00	r 184.34	r 183.80	o 183.85
o 184.91	r 184.21	r 183.87	o 184.14
o 184.75	r 183.95	o 183.83	r 183.89
o 184.15	o 183.70	o 183.75	r 183.63
r 184.88	o 184.30	o 184.13	o 184.17
r 184.85	o 183.99	o 183.90	o 184.08
r 184.94	o 184.07	o 183.82	r 184.13

[1] Thesis, University of Pennsylvania, 1896. "The atomic mass of tungsten."
[2] Journ. Amer. Chem. Soc., 19, 657. 1897.

The mean of all is $W = 184.105, \pm .0337$. This gives a percentage of W in WO_3 of $79.320, \pm .0185$. The discordances were shown by Hardin to be due partly to impurities in his material, such as nitrogen retained by trioxide prepared from ammonium tungstate, and partly to volatility of the oxide at high temperatures. In a later memoir [1] he discusses these errors at some length, and gives a few other determinations which are even more discordant, and therefore not worth citation now.

Taylor's thesis,[2] representing work done in Smith's laboratory, is essentially a study of errors. He found that constant weight could not be secured during reduction experiments with the trioxide, and he also found, like Hardin, that the oxidations generally gave the higher values for the atomic weight of tungsten. Furthermore, he ascertained that tungstic oxide derived from colloidal ammonium tungstate gave different values dependent upon whether the latter compound was dialyzed or undialyzed. Oxide from the dialyzed salt gave the highest atomic weights. Some of the discrepancies were ultimately traced to the presence in the material studied, of a complex salt containing manganese and iron, and the influence of these impurities was studied. Iron, and also molybdenum, tend to lower the apparent atomic weight of tungsten; manganese, and in much greater measure, raises it. The errors are in opposite directions, but do not absolutely compensate one another.

One new method for measuring the atomic weight of tungsten was tested by Taylor, but the results were not satisfactory. Sodium carbonate was heated in a glass bulb with tungsten trioxide and water, the latter was distilled off after effervescence had ceased, and the residue was then heated to $300°$ in a vacuum. The weights of carbonate and oxide being known, the loss in weight represented carbon dioxide. The ratio between WO_3 and CO_2 was thus determined. I cite the weights, and also the values for the ratio $WO_3 : CO_2 :: 100 : x:$

Weight WO_3.	Weight CO_2.	Ratio.
2.0802	.3952	18.998
2.1937	.4173	19.023
4.0818	.7762	19.016
3.3629	.6394	19.013

Mean, $19.0125, \pm .0034$

Hence $W = 183.45$; a determination which Taylor regards as worthless, while admitting that the method is one of some promise.

Several of the investigations so far described were carried out under the direction of, or in coöperation with Professor Edgar F. Smith. The

---

[1] Journ. Amer. Chem. Soc., 21, 1017. 1899.
[2] Thesis, University of Pennsylvania, 1901. " Atomic weight of tungsten."

experience obtained in their conduct gave a sound basis for further researches, which were undertaken by Smith and Exner.[1] These authors discuss at length the sources of error in former determinations of the atomic weight of tungsten, and point out the difficulty of preparing pure material, a difficulty which was at last overcome. From a pure ammonium tungstate they prepared pure tungsten, the pure trioxide, and pure tungsten hexchloride, free from oxychloride, and with these substances their atomic weight determinations were made. At this point only their syntheses of the trioxide will be considered, their other series being discussed later. Their figures, with vacuum weights, and the usual percentage column are given below:

Weight W.	Weight WO₃.	Per cent.
2.24552	2.83144	79.306
1.78151	2.24619	79.313
1.63590	2.06270	79.309
1.38534	1.74665	79.314
1.29903	1.63774	79.318
2.01302	2.53781	79.321
2.18607	2.75632	79.311
2.36755	2.98478	79.323
1.94958	2.45781	79.322
4.43502	5.59141	79.318
2.37603	2.99548	79.321
2.58780	3.26260	79.314
2.58503	3.25886	79.322
2.38298	3.00441	79.316
2.05578	2.59169	79.322
3.60828	4.54915	79.318
6.22621	7.84949	79.320
5.28444	6.66239	79.317
3.99095	5.03138	79.321
7.30166	9.20647	79.309
3.44143	4.33870	79.319
2.67709	3.37541	79.312
4.96735	6.26229	79.322

Mean, 79.3169, ± .0007

Hence $W = 184.075, \pm .0064$.

There are still other experiments by Riche,[2] 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:

[1] Proc. Amer. Phil. Soc., 43, 123. 1904.
[2] Journ. prakt. Chem., 69, 10. 1857.

1. Berzelius .... 79.7745, ± .0880
2. Schneider, 1850 .... 79.320, ± .0068
3. Marchand .... 79.3205, ± .0073
4. Borch .... 79.293, ± .0108
5. Dumas .... 79.312, ± .0090
6. Bernoulli .... 79.480, ± .0560
7. Persoz .... 79.314, ± .0070
8. Roscoe .... 79.264, ± .0146
9. Waddell .... 79.339, ± .0069
10. Pennington and Smith........... 79.392, ± .0004
11. Schneider, 1896 .... 79.311, ± .0018
12. Shinn .... 79.391, ± .0066
13. Hardin .... 79.320, ± .0185
14. Smith and Exner................ 79.3169, ± .0007

General mean .... 79.3706, ± .00034

In this combination only two values carry much weight; the tenth and the fourteenth. The series by Pennington and Smith is evidently much overvalued, and exerts an undue influence upon the general mean. In reality the series by Smith and Exner is by far the most trustworthy of all, and the figures given by Schneider, Marchand, Dumas and Persoz are in harmony with it. The other series are more doubtful. The weighted mean of twelve series, omitting Nos. 10 and 14, is 79.3160; a value almost identical with that of Smith and Exner. The latter, therefore, is abundantly confirmed.

In 1861 Scheibler[1] deduced the atomic weight of tungsten from analyses of barium metatungstate. $BaO.4WO_3.9H_2O$. 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 better result was attained. The percentages of water are as follows:

13.053
13.054
13.045
13.010
13.022

Mean, 13.0368, ± .0060

Hence $W = 184.05$.

The work of Zettnow,[2] published in 1867. was more complicated than any of the foregoing researches. He prepared the tungstates of silver and of iron, and from their composition determined the atomic weight of tungsten.

---

[1] Journ. prakt. Chem., 83, 324.
[2] Poggend. Annalen, 130, 30.

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 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, $Am_2Fe(SO_4)_2.6H_2O$, 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 gramme 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:

$$\left.\begin{array}{l}.028301\\.028291\\.028311\\.028301\end{array}\right\}\text{First set}$$

$$\left.\begin{array}{l}.028367\\.028368\\.028367\\.028367\end{array}\right\}\text{Second set}$$

$$\left.\begin{array}{l}.028438\\.028438\end{array}\right\}\text{Third set}$$

Mean, .0283549, $\pm$ .0000115

Hence $W = 184.41$.

With the silver tungstate, Ag_2WO_4, Zettnow employed two methods. In two experiments the substance was decomposed 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, $\pm$ .021

By Second Method.

161.687
161.651
161.613

Mean, 161.650, $\pm$ .014
General mean from both series, 161.645, $\pm$ .012

Hence $W = 183.64$.

For tungsten hexchloride we have first, two analyses by Roscoe, 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 : [1]

53.610
53.632

Mean, 53.621, $\pm$ .0074

Hence $W = 184.02$.

The investigation of tungsten hexchloride by Smith and Exner was much more elaborate. They prepared the substance from scrupulously pure materials, and further purified it by repeated sublimations. They decomposed the chloride by means of water, and weighed the residual tungsten trioxide. Their figures, with vacuum weights, are as follows, with a percentage column added by myself:

---

[1] The actual figures are as follows:

19.5700 grm. WCl_6 gave 42.4127 grm. AgCl.
10.4326 grm. WCl_6 gave 4.8374 grm. tungsten.

Weight WCl_6.	Weight WO_3.	Per cent. WO_3.
3.18167	1.86085	58.487
2.66612	1.55903	58.476
3.52632	2.06244	58.487
1.52117	.88972	58.489
1.22299	.71523	58.482
2.28445	1.33603	58.484
3.25404	1.90337	58.493
3.37078	1.97133	58.483
7.76488	4.54082	58.479
2.08764 ·	1.22114	58.494
2.80141	1.63859	58.492
3.24328	1.89681	58.484
4.97475	2.91262	58.489
3.04036	1.77838	58.492
4.31046	2.52133	58.493
3.21201	1.29381	58.490
2.70368	1.58135	58.489
3.60658	2.10934	58.486
2.63037	1.53835	58.484
3.41668	1.99808	58.480
3.49940	2.04675	58.489
3.86668	2.26145	58.486
3.40202	1.98970	58.486
3.20661	1.87533	58.483
3.26386	1.90909	58.492
6.73833	3.94031	58.476
7.37889	4.31643	58.497

Mean, 58.4868, ± .0007

Hence $W = 184.11$.

The syntheses of WO_3 by Smith and Exner give $W = 184.007, \pm .0079$. If we substitute that value in the hexchloride ratio we can compute an independent figure for the atomic weight of chlorine, namely, $Cl = 35.454$, $\pm .0028$. This figure is good, and furnishes additional corroboration of Smith and Exner's determinations.

Smith and Exner also made a series of determinations of Taylor's ratio between WO_3 and CO_2. Their figures, with the ratio added, are as follows:

Weight WO_3.	Weight CO_2.	Ratio.
2.45645	.46775	19.041
2.72292	.51785	18.974
3.32953	.63288	19.008
3.97620	.75473	18.981
3.44944	.65489	18.985
3.41273	.64796	18.986
6.10309	1.16087	19.021

6.39735	1.21644	19.015
2.17450	.41332	19.008
1.57903	.29966	18.977

Mean, 18.9996, ± .0046

Hence $W = 183.60$.

Combined with Taylor's mean, $19.0125, \pm .0034$, the general mean is $19.0073, \pm .0027$. This ratio, however, is affected by constant errors, as Smith and Exner have shown. There is not only a possibility of action of the sodium carbonate upon the glass bulb, but also a loss due to slight decomposition of the carbonate itself at the temperature employed in the experiments. Smith and Exner therefore discard the method as too inaccurate.

The work done by Smith and Desi[1] probably ought to be considered in connection with that of Pennington and Smith on the trioxide. Smith and Desi started with tungsten trioxide, freed from molybdenum by means of gaseous hydrochloric acid. This material was reduced in a stream of carefully purified hydrogen, and the water formed was collected in a calcium chloride tube and weighed. To the results found I add the percentage of water obtained from 100 parts of WO_3. Vacuum weights are given:

WO_3.	H_2O.	Per cent. H_2O.
.983024	.22834	23.228
.998424	.23189	23.226
1.008074	.23409	23.221
.911974	.21184	23.229
.997974	.23179	23.226
1.007024	.23389	23.226

Mean, 23.226, ± .0008

Hence $W = 184.70$. This method is also criticized by Smith and Exner, and rejected.

Still another method for determining the atomic weight of tungsten was tested by Thomas,[2] also in Smith's laboratory. Sodium tungstate, $Na_2WO_4.2H_2O$, was dehydrated between 180° and 200°, and the percentage of water so determined. In this series of experiments the tungstate contained traces of carbonate and silicate. With purer material other determinations were made between 268° and 295°, and these were divided

---

[1] Read before Amer. Phil. Soc., Nov. 2, 1894.

[2] Journ. Amer. Chem. Soc. 21, 373. 1899. Thomas cites some work on tungsten trioxide, but his figures appear in Hardin's series.

by the author into two series. I give below the percentage of water computed from Thomas' weights:

Preliminary.	*First Series.*	*Second Series.*
10.920	10.895	10.918
10.919	10.886	10.971
10.941	10.900	10.800
10.931	10.894	10.926
10.937	10.861	10.860
10.929	10.891	———
10.926	10.878	Mean, 10.895, $\pm$ .0200
10.945	———	
10.924	Mean, 10.886, $\pm$ .0034	
10.935		
———		
Mean, 10.931, $\pm$ .0020		

The general mean of the three series is 10.919, $\pm$ .0017. Hence $W =$ 183.93, but with a very wide range of values in the individual experiments. This method, again, is rejected by the author himself as unsuited to exact atomic weight determinations.

The ratios, good and bad, rejecting nothing, from which to calculate the atomic weight of tungsten are now as follows:

(1). $WO_3 : W : : 100 : 79.3706$, $\pm$ .00034
(2). $BaW_4O_{13}.9H_2O : 9H_2O : : 100 : 13.0368$, $\pm$ .0060
(3). $WO_3 : 3H_2O : : 100 : 23.226$, $\pm$ .0008
(4). $Am_2Fe(SO_4)_2.6H_2O : FeWO_4 : : 0.0365457$, $\pm$ .0000012 : 0.0283549, $\pm$ .0000115
(5). $2AgCl : Ag_2WO_4 : : 100 : 161.645$, $\pm$ .012
(6). $WCl_6 : 6Cl : : 100 : 53.621$, $\pm$ .0074
(7). $WCl_6 : WO_3 : : 100 : 58.4868$, $\pm$ .0007
(8). $WO_3 : CO_2 : : 100 : 19.0073$, $\pm$ .0027
(9). $Na_2WO_4.2H_2O : 2H_2O : : 100 : 10.919$, $\pm$ .0017

The values to use in reducing these ratios are—

Ag = 107.880, $\pm$ .00029	C = 12.0038, $\pm$ .0002
Cl = 35.4584, $\pm$ .0002	Na = 23.0108, $\pm$ .00024
S = 32.0667, $\pm$ .00075	Ba = 137.363, $\pm$ .0025
N = 14.0101, $\pm$ .0001	Fe = 55.880, $\pm$ .0012
	H = 1.00779, $\pm$ .00001

Hence,

From ratio 8	....	$W =$ 183.510, $\pm$ .0329
" " 5	....	183.639, $\pm$ .0345
" " 9	....	183.934, $\pm$ .0491
" " 6	....	184.016, $\pm$ .0309
" " 2	....	184.052, $\pm$ .0819
" " 7	....	184.112, $\pm$ .0067
" " 4	....	184.409, $\pm$ .1236
" " 1	....	184.678, $\pm$ .0031
" " 3	....	184.700, $\pm$ .0080

General mean, $W =$ 184.575, $\pm$ .0026

This combination is evidently of very little significance. It includes data which are confessedly defective, and which do not tend to compensation of errors. The abnormally high value derived from ratio 1, which dominates the combination, is due to the excessive weight given to the determinations by Pennington and Smith, which Smith himself has discarded. If, in place of ratio 1 we take the determinations of Smith and Exner alone, namely, $WO_3 : W :: 100 : 79.3169, \pm .0007$, we have the more trustworthy value, $W = 184.075, \pm .0064$. This, combined with the value from ratio 7, also due to Smith and Exner, gives a general mean of $W = 184.092, \pm .0046$. This seems to be the most probable value now available, and it is checked by the fact, already pointed out, that the two ratios of Smith and Exner, combined, give a good value for the atomic weight of chlorine.

URANIUM.

The earlier attempts to determine the atomic weight of uranium were all vitiated by the erroneous supposition that 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,[1] by Arfvedson,[2] and by Marchand[3] 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_8 to UO_2. Rammelsberg's[4] results also, although very suggestive, need no full discussion. He analyzed the green chloride, UCl_4; 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_2, 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_8 from several different sources were reduced to UO_2 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

[1] Schweigg. Journ., 22, 336. 1818. Poggend. Annalen, 1, 359. 1825.

[2] Poggend. Annalen, 1, 245. Berz. Jahr., 3, 120. 1822.

[3] Journ. prakt. Chem., 23, 497. 1841.

[4] Poggend. Annalen, 55, 318, 1842; 56, 125, 1842; 59, 9, 1843; 60, 91, 1845. Journ. prakt. Chem., 29, 324.

weight of uranium ranging from 185.74 to 235.84, or, in mean, 216.17. 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 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 [1] showing that the atomic weight of uranium must be somewhere near 240. 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 [2] 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_8 by heating in oxygen. The following weights are reduced to a vacuum standard:

10.1644 grm. oxalate gave	7.2939 grm. UO_2.				
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_2 in the oxalate, while B represents the amount of U_3O_8 formed from 100 parts of UO_2:

A.	B.
71.924	. . . . . .
71.787	103.949
71.767	103.867
71.621	103.920

---

[1] Compt. Rend., 12, 735. 1841. Ann. Chim. Phys. (3), 55. 1842.
[2] Journ. prakt. Chem., 27, 385. 1842.

71.794	103.900
71.793	. . . . . .
71.778	. . . . . .
71.790	103.930

Mean, 71.782, ± .019   Mean, 103.913, ± .009

Hence U = 237.70.   Hence U = 240.25.

Wertheim's[1] 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, ± .0076

Hence U = 239.29.

The final results of Peligot's[2] 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 was weighed as U_3O_8, and the carbon as CO_2. From the ratio between the CO_2 and U_3O_8 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_8 proportional to 100 parts of CO_2:

CO_2.	U_3O_8.	Ratio.
1.456	4.649	319.299
1.369	4.412	322.279
2.209	7.084	320.688
1.019	3.279	321.786
1.069	3.447	322.461
1.052	3.389	322.148

Mean, 321.443, ± .338

Hence U = 240.23.

[1] Journ. prakt. Chem., 29, 209. 1843.
[2] Compt. Rend., 22, 487. 1846.

From the acetate, $UO_2(C_2H_3O_2)_2.2H_2O$, the following percentages of U_3O_8 were obtained:

5.061 grm. acetate gave 3.354 grm. U_3O_8.			66.2715 per cent.
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

Hence U = 239.73.

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	Mean, 11.24	Mean, 41.222, ± .092

From these data we get the following values for the molecular weight of uranyl acetate:

From percentage of U_3O_8	425.827, ± .1678
From percentage of CO_2	426.993, ± .9530
From percentage of H_2O	423.603, ± 3.7250
General mean	425.861, ± .1651

Hence U = 239.77.

In the posthumous paper of Zimmermann, edited by Krüss and Alibegoff,[1] the atomic weight of uranium is determined by two methods. First, UO_2, prepared by several methods, is converted into U_3O_8 by heating in oxygen. To begin with, U_3O_8 was prepared, and reduced to UO_2 by ignition in hydrogen. When the reduction takes place at moderate temperatures, the UO_2 is somewhat pyrophoric, but if the operation is performed over the blast lamp this difficulty is avoided. After weighing the UO_2, the oxidation is effected, and the gain in weight observed. The preliminary U_3O_8 was derived from the following sources: A, from uranium tetroxide; B, from the oxalate; C, from uranyl nitrate; D, by

---

[1] Ann. Chem., 232, 299. 1886.

precipitation with mercuric oxide. The full data, lettered as indicated above, are subjoined:

	UO_2.	U_3O_8.	Per cent. of Gain.
A	8.9363	9.2872	3.927
	7.9659	8.2789	3.929
	12.4385	12.9270	3.927
B	12.8855	13.3913	3.925
	5.7089	5.9331	3.927
	9.6270	10.0051	3.928
C	13.1855	13.7036	3.929
	9.9973	10.3901	3.929
D	15.8996	16.5242	3.928
	7.4326	7.7245	3.927

Mean, 3.9276, ± .0003
Ebelmen found, 3.913, ± .009

General mean, 3.9276, ± .0003

In short, Ebelmen's mean vanishes when combined with Zimmermann's. From Zimmermann's mean U = 239.58.

Zimmermann's second method was essentially that of Wertheim, namely, the ignition of the double acetate $UO_2(C_2H_3O_2)_2 . NaC_2H_3O_2$, the residue being sodium uranate, $Na_2U_2O_7$.

Double Acetate.	Uranate.	Per cent. Uranate.
4.272984	2.886696	67.557
5.272094	3.560770	67.540
2.912283	1.967428	67.556
3.181571	2.149309	67.555

Mean, 67.552, ± .0027
Wertheim found, 67.523, ± .0076

General mean, 67.549, ± .0025

From Zimmermann's figures U = 239.71.

An entirely different method for determining the atomic weight of uranium was adopted by Aloy.[1] Pure uranyl nitrate was ignited in a suitable apparatus, and the nitrogen evolved was collected and measured. The residual green oxide of uranium was reduced to uranous oxide, which was weighed. From this weight and that of the nitrogen, as computed from its volume, the atomic weight of the metal was calculated. Unfortunately, Aloy gives only the volumes of gas and the corresponding atomic weight, but not the weight of the oxide. His data, therefore, as

[1] Ann. Chim. Phys. (7), 24, 418. Preliminary paper in Compt. Rend., 182, 551. 1901.

published, are radically defective.   Assuming $N = 14.04$, Aloy gives the following values for uranium:

<div align="center">

239.3
239.4
239.6
239.3
239.4
239.5
239.4
239.4

Mean, 239.412, $\pm$ .0235
</div>

If $N = 14.0101$, this reduces to $U = 238.902$.

The important memoir by Richards and Merigold[1] begins with a careful criticism of former determinations.   In Aloy's work, they show that the residual oxide probably contained some unexpelled nitrogen, and they also point out the difficulty of exactly measuring small volumes of gas.   Their own work was based upon careful analyses of uranous bromide by the best established methods, and their results, with vacuum weights, are as follows.   First, analyses to determine the ratio $4AgBr : UBr_4$:

<div align="center">

Preliminary Series.

</div>

Weight UBr_4.	Weight $AgBr$.	Ratio.
2.2058	2.9699	74.272
1.4418	1.9401	74.316
1.4050	1.8910	74.299
1.1749	1.5818	74.276

<div align="right">

Mean, 74.291, $\pm$ .0070
</div>

<div align="center">

Second Series.

</div>

Weight UBr_4.	Weight $AgBr$.	Ratio.
1.7999	2.4226	74.296
1.0662	1.4352	74.290
1.8551	2.4967	74.302

<div align="right">

Mean, 74.296, $\pm$ .0029
</div>

General mean of both series, 74.295, $\pm$ .0027.   Hence $U = 238.424$. Second, measurements of the ratio $4Ag : UBr_4$:

Weight UBr_4.	Weight Ag.	Ratio.
1.7999	1.3918	129.322
1.0662	.8245	129.315
1.8551	1.4342	129.347

<div align="right">

Mean, 129.328, $\pm$ .0066
</div>

Hence $U = 239.397$.

---

[1] Proc. Amer. Acad., 37, 365. 1902.

The two ratios, combined, give the cross ratio $Ag : Br :: 100 : 74.074$.
Oechsner de Coninck,[1] in order to establish the molecular weight of uranyl oxide, reduced UO_2Br_2 by heating. His results were as follows:

UO_2Br_2.	UO_2.	Per cent. UO_2.
.737	.466	63.229
.900	.566	62.889
.720	.452	62.778
.818	.519	63.447
1.080	.681	63.056

Mean, 63.080, ± .0805

Hence $U = 241.1$.

In a second brief paper[2] he gives three reductions of the chloride, UO_2Cl_2, by heating in hydrogen:

UO_2Cl_2.	UO_2.	Per cent. UO_2.
.523	.414	79.159
.5763	.456	79.098
1.048	.830	79.198

Mean, 79.152, ± .0197

Hence $U = 237.24$.

These determinations are of no real importance, and are included in this discussion merely for the sake of completeness. Summing up, the following ratios are now available for uranium:

(1). Per cent. UO_2 from uranyl oxalate, 71.782, ± .019
(2). $6CO_2 : U_3O_8 :: 100 : 321.443$, ± .338
(3). Molecular weight of uranyl acetate, 425.861, ± .1650
(4). $3UO_2 : U_3O_8 :: 100 : 103.9276$, ± .0003
(5). Per cent. $Na_2U_2O_7$, from $UO_2.Na(C_2H_3O_2)_3$, 67.549, ± .0025
(6). $N : U :: 14.04 : 239.412$, ± .0235
(7). $4AgBr : UBr_4 :: 100 : 74.295$, ± .0027
(8). $4Ag : UBr_4 :: 100 : 129.328$, ± .0066
(9). $UO_2Br_2 : UO_2 :: 100 : 63.080$, ± .0805
(10). $UO_2Cl_2 : UO_2 :: 100 : 79.152$, ± .0197

To reduce these ratios we have—

$Ag = 107.880$, ± .00029		$C = 12.0038$, ± .0002
$Cl = 35.4584$, ± .0002		$N = 14.0101$, ± .0001
$Br = 79.9197$, ± .0003		$Na = 23.0108$, ± .00024
	$H = 1.00779$, ± .00001	

[1] Bull. Acad. Belg., Classe des Sciences, 1907, 1041.
[2] *Ibid.*, 1908, 163. In another paper, Compt. Rend., 147, 1477, Oechsner de Coninck describes attempts to determine the atomic weight of chlorine by reductions of UO_2Cl_2. His results have no value and need not be considered here.

Hence,

```
From ratio 10 ...................U = 237.244, ± .2665
    "      "   1 .......................237.705, ± .1951
    "      "   8 .......................238.397, ± .0285
    "      "   7 .......................238.424, ± .0203
    "      "   6 .......................238.902, ± .0235
    "      "   4 .......................239.582, ± .0207
    "      "   5 .......................239.663, ± .0279
    "      "   3 .......................239.768, ± .1651
    "      "   2 .......................240.228, ± .2975
    "      "   9 .......................241.094, ± .6900
```

General mean, U = 238.977, ± .0104

Ratios 1, 2, 3, 9 and 10 are evidently worthless; but their omission would only change the general mean by about 0.001, a negligible quantity. The final result is higher than the values obtained by Richards and Merigold, which are probably the best of all the separate determinations. It would hardly be safe, however, to reject the work of Zimmermann, at least until more evidence is available. The radio-active properties of uranium may possibly affect its atomic weight, but that possibility remains to be tested.

SELENIUM.

The atomic weight of this element was first determined by Berzelius,[1] who, saturating 100 parts of selenium with chlorine, found that 179 of chloride were produced. Hence $Se = 79.24$. 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,[2] and pass on to the experiments published by Sacc[3] 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 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

Hence $Se = 78.68$.

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

Hence $Se = 78.59$.

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

[1] Poggend. Annalen, 8, 1. 1826.
[2] Poggend. Annalen, 9, 623. 1827.
[3] Ann. Chim. Phys. (3), 21, 119.

weight under consideration.[1] They analyzed 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, ± .003

Hence Se = 78.88.

The next determinations were made by Dumas,[2] 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, ± .125

Dumas' figures alone give Se = 79.39.

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.

Still later, Ekman and Pettersson[3] investigated several methods for the determination of this atomic weight, and finally decided upon the two following:

First, pure silver selenite, Ag_2SeO_3, was ignited, leaving behind metallic

[1] Journ. prakt. Chem., 55, 202. 1852.
[2] Ann. Chem. Pharm., 113, 32. 1860.
[3] Ber. Deutsch. chem. Gesell., 9, 1210, 1876. Published in detail by the society at Upsala.

silver, which, however, sometimes retained minute traces of selenium. The data obtained were as follows:

Ag_2SeO_3.	Ag.	Per cent. Ag.
5.2102	3.2787	62.929
5.9721	3.7597	62.954
7.2741	4.5803	62.967
7.5390	4.7450	62.939
6.9250	4.3612	62.978
7.3455	4.6260	62.978
6.9878	4.3992	62.955

Mean, 62.957, ± .0048

Hence Se = 78.95.

Secondly, 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.

SeO_2.	Se.	Per cent. Se.
11.1760	7.9573	71.199
11.2453	8.0053	71.185
24.4729	17.4232	71.193
20.8444	14.8383	71.187
31.6913	22.5600	71.191

Mean, 71.191, ± .0016
Sacc found, 71.088, ± .0320

General mean, 71.1907, ± .0016

Ekman and Pettersson's series alone give Se = 79.076.

Lenher,[1] in order to determine the atomic weight of selenium, studied two of its compounds. First, silver selenite was heated in a stream of gaseous hydrochloric acid, and so transformed into silver chloride. In a second series of experiments the silver chloride was afterwards reduced to metal by heating in hydrogen. Two ratios were thus determined. For convenience I now treat the two series as one. Lenher's data, with vacuum weights, and with the corresponding percentages added by myself, are as follows:

Ag_2SeO_3.	$AgCl$.	Ag.	Per cent. Ag.	Per cent. $AgCl$.
.98992	.82715	......	.....	83.557
1.59912	1.33600	......	.....	83.560
2.70573	2.26087	......	.....	83.559
.26204	.21897	.16480	62.891	83.564
.58078	.48522	.36534	62.906	83.546
.70614	.58999	.44417	62.901	83.551

[1] Journ. Amer. Chem. Soc., 20, 355. 1898. Thesis, University of Pennsylvania.

.80811	.67532	.50821	62.889	83.568
.98396	.82232	.61882	62.891	83.572
1.29685	1.08350	.81562	62.892	83.549
1.63103	1.36288	1.02588	62.898	83.559
2.00162	1.67234	1.25884	62.891	83.549
			Mean, 62.895,	83.558,
			± .0014	± .0017

From Ag ratio, Se = 79.288.
From AgCl ratio, Se = 79.328.

Secondly, ammonium bromoselenate was studied. From this salt the selenium was precipitated by hydroxylamine hydrochloride, and then collected and weighed in a Gooch crucible. The vacuum weights and percentages of selenium follow:

Am_2SeBr_6.	Se.	Per cent. Se.
1.00059	.13324	13.3161
1.50153	.20022	13.3344
2.00059	.26649	13.3209
2.00126	.26657	13.3201
3.00125	.39958	13.3138
4.00216	.53346	13.3293
5.00218	.66656	13.3254
5.03001	.66998	13.3196
	Mean,	13.3224, ± .0017

Hence Se = 79.25.

Steiner's[1] determinations, two in number, were made incidentally to his work on tellurium. Phenyl selenide was burned in a combustion tube, and the carbon dioxide so produced was weighed. To his figures I add the ratio $(C_6H_5)_2Se : 12CO_2 :: 100 : x$:

Selenide.	CO_2.	Ratio.
.2812	.6375	226.707
.5371	1.2158	226.365
	Mean,	226.536, ± .0485

Hence Se = 78.97. This determination is of trifling significance.

Julius Meyer[2] analyzed silver selenite electrolytically. The silver was precipitated from a solution of the salt in potassium cyanide. With vacuum weights the data are as follows:

Ag_2SeO_3.	Ag.	Per cent. Ag.
.5152	.3241	62.907
.5237	.3295	62.915
1.6964	1.0672	62.910
1.8793	1.1826	62.928
2.1460	1.3503	62.922
	Mean,	62.9164, ± .0082

[1] Ber. Deutsch. chem. Ges., 34, 570. 1901.
[2] Ber. Deutsch. chem. Ges., 35, 1591. 1902.

From the solutions 0.0002 gramme of silver was recovered, to be added to the sum of the silver weights given above. This raises the percentage to 62.9193. Hence Se = 79.155.

Combining Meyer's series with its predecessors we have—

Ekman and Pettersson........	62.957, ± .0048
Lenher	62.895, ± .0014
Meyer	62.9193, ± .0082
General mean	62.9003, ± .0013

There are now eight ratios from which to deduce the atomic weight of selenium:

(1). $SeO_2 : Se :: 100 : 71.1907, \pm .0016$
(2). $BaSeO_3 : BaSO_4 :: 100 : 88.437, \pm .013$
(3). $HgSe : Hg :: 100 : 71.7327, \pm .003$
(4). $Se : 4Cl :: 100 : 178.696, \pm .125$
(5). $Ag_2SeO_3 : 2Ag :: 100 : 62.9003, \pm .0013$
(6). $Ag_2SeO_3 : 2AgCl :: 100 : 83.558, \pm .0017$
(7). $Am_2SeBr_6 : Se :: 100 : 13.3224, \pm .0017$
(8). $C_{12}H_{10}Se : 12CO_2 :: 100 : 226.536, \pm .0486$

The atomic weights used in reducing these ratios are as follows:

Ag = 107.880, ± .00029		C = 12.0038, ± .0002
Cl = 35.4584, ± .0002		Ba = 137.363, ± .0025
Br = 79.9197, ± .0003		Hg = 200.054, ± .0017
N = 14.0101, ± .0001		H = 1.00779, ± .00001

Hence,

From ratio	2	....	Se = 78.587, ± .0388
"	" 3	....	78.883, ± .0124
"	" 8	....	78.972, ± .0501
"	" 1	....	79.075, ± .0047
"	" 7	....	79.248, ± .0102
"	" 5	....	79.259, ± .0052
"	" 6	....	79.328, ± .0070
"	" 4	....	79.373, ± .0555
		General mean,	Se = 79.176, ± .0029

This mean is slightly lower than the values obtained by Lenher, but near that given by Meyer. In default of more evidence it seems to be as trustworthy as any value which might be arbitrarily chosen.

TELLURIUM.

Particular interest attaches to the atomic weight of tellurium on account of its relations to the periodic system. According to that system, tellurium should lie between antimony and iodine, having an atomic weight greater than 120 and less than 126. Theoretically, Mendeléef assigns it a value of $Te = 125$, but all of the best determinations lead to a mean number higher than is admissible under the currently accepted hypotheses. 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.[1] 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:

$$80.057$$
$$80.036$$
$$80.034$$

Mean, 80.042, $\pm .005$

Hence $Te = 128.34$.

The next determinations were made by von Hauer,[2] 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, we get from von Hauer's analyses, for 100 parts of the salt, the quantities of AgBr which are put in the third column:

2.000 grm.	K_2TeBr_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, $\pm .045$

Hence $Te = 127.64$.

Dumas,[3] by a method for which he gives absolutely no particulars, found $Te = 129$.

[1] Poggend. Annalen, 28, 395. 1833.
[2] Sitzungsb. Wien. Akad., 25, 142.
[3] Ann. Chim. Phys. (3), 55, 129. 1859.

In 1879, with direct reference to Mendeléef's theory, the subject of the atomic weight of tellurium was taken up by Wills.[1] The methods of 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 $Te = 126.64$ to 129.66:

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

Hence $Te = 128.12$.

In the second series tellurium was oxidized by aqua regia to TeO_2, with results varying from $Te = 128.10$ to 128.32:

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

Hence $Te = 128.22$.

By von Hauer's process, the analysis of $TeBr_4.2KBr$, Wills' figures give results ranging from $Te = 126.36$ to 127.90. 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

Hence $Te = 127.10$.

Combined with von Hauer's mean, 164.408, ± .045, this gives a general mean of 164.468, ± .0324.

The next determinations in order of time were those of Brauner.[2] This chemist tried various unsuccessful methods for determining the

[1] Journ. Chem. Soc., Oct., 1879, p. 704.
[2] Journ. Chem. Soc., 55, 382. 1889.

atomic weight of tellurium, among them being the synthetic preparation of silver, copper and gold tellurides, and the basic sulphate, Te_2SO_7. None of these methods gave sufficiently concordant results, and they were therefore abandoned. The oxidation of tellurium to dioxide by means of nitric acid was also unsatisfactory, but a series of oxidations with aqua regia gave data as follows. The third column contains the percentage of tellurium in the dioxide:

Te.	TeO_2.	Per cent. Te.
2.3092	2.9001	79.625
2.8153	3.5332	79.681
4.0176	5.0347	79.798
3.1613	3.9685	79.660
.8399	1.0526	79.793

Mean, 79.711, ± .0239

Hence Te = 125.72.

In a single analysis of the dioxide, by reduction with SO_2, 2.5489 grammes TeO_2 gave 2.0374 of metal. If we give this experiment the weight of one observation in the synthetic series, the percentage of tellurium found by it becomes—

79.932, ± .0534

Hence Te = 127.46.

Brauner's best results were obtained from analyses of tellurium tetrabromide, prepared from pure tellurium and pure bromine, and afterwards sublimed in a vacuum. This compound was titrated with standard solutions of silver, and three series of experiments, made with samples of bromide of different origin, gave results as follows. The $TeBr_4$ equivalent to 100 parts of silver appears in the third column:

First Series.

$TeBr_4$.	$4Ag$.	Ratio.
2.14365	2.06844	103.636
1.76744	1.70531	103.643
1.47655	1.42477	103.634
1.23354	1.19019	103.642

Second Series.

$TeBr_4$.	$4Ag$.	Ratio.
3.07912	2.97064	103.651
5.47446	5.28157	103.652
3.30927	3.19313	103.637
7.26981	7.01414	103.645
3.52077	3.39667	103.654

Third Series.

$TeBr_4$.	$4Ag$.	Ratio.
2.35650	2.27363	103.645
1.51931	1.46564	103.662
1.43985	1.38942	103.630

Mean of all as one series, 103.644, $\pm$ .0018

Hence $Te = 127.57$. A reduction of the weighings to a vacuum raises this by 0.07 to 127.64.

Still another series of analyses, made with fractionated material, gave values for tellurium running up to as high as 137. These experiments led Brauner to believe that he had found in tellurium a higher homologue of that element, a view which he has since abandoned.[1] Brauner also made a series of analyses of tellurium dibromide, but the results were unsatisfactory.

In the series of determinations by Gooch and Howland[2] an alkaline solution of tellurium dioxide was oxidized by means of standard solutions of potassium permanganate. This was added in excess, the excess being measured, after acidification with sulphuric acid, by back titration with oxalic acid and permanganate. Two series are given, varying in detail, but for present purposes they may be treated as one. The ratio $TeO_2 : O :: 100 : x$ is given in the third column:

TeO_2 taken.	O required.	Ratio
.1200	.01202	10.017
.0783	.00785	10.026
.0931	.00940	10.097
.1100	.01119	10.149
.0904	.00909	10.055
.1065	.01078	10.122
.0910	.00915	10.055
.0910	.00910	10.000
.0911	.00924	10.143
.0913	.00915	10.022
.0912	.00915	10.033
.0914	.00923	10.098

Mean, 10.068, $\pm$ .0100

Hence $Te = 126.92$.

In Staudenmaier's[3] determinations of the atomic weight of tellurium,

[1] Journ. Chem. Soc., 67, 549. 1895.

[2] Amer. Journ. Sci., 58, 375. 1894. Some misprints in the original publication have been kindly corrected by Professor Gooch; hence the differences between these data and the figures formerly given.

[3] Zeitsch. anorg. Chem., 10, 189. 1895.

crystallized telluric acid, H_6TeO_6 was the starting point. By careful heating in a glass bulb this compound can be reduced to TeO_2, and by heating in hydrogen, to metal. In the latter case finely divided silver was added to prevent volatilization of tellurium. The telluric acid was fractionally crystallized, but the different fractions gave fairly constant results. I therefore group Staudenmaier's data so as to bring them into series more suitable for the present discussion:

First.—H_6TeO_6 to TeO_2.

H_6TeO_6.	Loss in Weight.	Per cent. TeO_2.
1.7218	.5260	69.451
2.8402	.8676	69.453
4.0998	1.2528	69.442
3.0916	.9450	69.433
1.1138	.3405	69.429
4.9843	1.5236	69.432
4.6716	1.4278	69.437

Mean, 69.440, $\pm$ .0024

Hence $Te = 127.16$.

Second.—H_6TeO_6 to Te.

H_6TeO_6.	Loss in Weight.	Per cent. Te.
1.2299	.5471	55.517
1.0175	.4526	55.518
2.5946	1.1549	55.488

Mean, 55.508, $\pm$ .0068

Hence $Te = 127.31$.

Staudenmaier also gives four reductions of TeO_2 to Te, in presence of finely divided silver. The data are as follows:

TeO_2.	Loss in Weight.	Per cent. Te.
.9171	.1839	79.948
1.9721	.3951	79.966
2.4115	.4835	79.950
1.0172	.2041	79.935

Mean, 79.950, $\pm$ .0043

Hence $Te = 127.60$.

Chikashige[1] resorted to Brauner's method, giving the ratio between silver and $TeBr_4$. In all essential particulars the work resembles that of Brauner, except that the tellurium, instead of being extracted from metallic tellurides, was derived from Japanese native sulphur, in which

---

it exists as an impurity. This difference of origin in the material studied gives the chief interest to the investigation. The data are as follows:

$TeBr_4$.	Ag.	Ratio.
4.1812	4.0348	103.628
4.3059	4.1547	103.639
4.5929	4.4319	103.633

Mean, 103.633, ± .0023
Brauner found, 103.644, ± .0018

General mean, 103.640, ± .0014

From Chikashige's mean, Te = 127.42.

Metzner [1] determined the atomic weight of tellurium by two methods, using tellurium which had been prepared from the hydride. First, tellurium was treated with sulphuric acid and converted into the basic sulphate, Te_2SO_7. I give his weights, and also the percentage of tellurium in the compound:

Te.	Sulphate.	Per cent. Te.
790.2	1245.0	63.982
414.3	647.5	63.985
1098.3	1717.0	63.966

Mean, 63.978, ± .0040

Hence Te = 127.94.

Secondly, Metzner prepared tellurium dioxide by hydrolysis of the tetrachloride, and reduced it to tellurium by heating in a current of carbon monoxide. The reduction was effected in presence of silver, in order to avoid volatilization. His data follow, with the usual percentage of Te in TeO_2 stated in the third column:

TeO_2.	Loss.	Per cent. Te.
743.2	148.8	79.978
1106.7	221.3	80.004
988.5	197.0	80.073
1312.5	262.5	79.962

Mean, 80.004, ± .0165

Hence Te = 128.032.

The determinations by Heberlein [2] represent three distinct methods, starting with crystallized telluric acid, H_6TeO_6. First, the acid was treated with hydrochloric acid, by which chlorine was liberated. The

---

[1] Compt. Rend., 126, 1716. 1898. Metzner fails to state what his weights mean. Are they milligrammes?

[2] Inaug. Diss., Basel. Printed at Strassburg, 1898.

latter was distilled off and collected in a solution of potassium iodide. Iodine was set free and determined by titration with a tenth normal thiosulphate solution. If W = the weight of telluric acid, and n the number of cubic centimetres of the thiosulphate solution, the atomic weight of tellurium is given by the subjoined formula:

$$Te = \frac{20000\ W}{n} - H_6O_6$$

The first term on the right of the equation obviously represents the molecular weight of H_6TeO_6. The figures are as follows:[1]

Weight H_6TeO_6.	Vol. thiosulphate, cc.	Mol. W. H_6TeO_6.
.22911	20.00	229.100
.5736	50.02	229.348
.4038	35.21	229.367
.4393	38.30	229.400
.32331	28.22	229.135

Mean, 229.270, ± .0425

Hence $Te = 127.223$.

Secondly, Heberlein employed Staudenmaier's method of reducing H_6TeO_6 to TeO_2 by careful heating in a glass bulb:

Weight Acid.	Loss.	Per cent. TeO_2.
1.35236	.41431	69.364
1.76859	.54122	69.398

Mean, 69.381, ± .0115

Hence $Te = 126.72$.

Finally, tellurium dioxide was reduced to tellurium by heating in a current of hydrogen in presence of silver. Heberlein's two experiments are as follows:

TeO_2.	Loss.	Per cent. Te.
1.35908	.27353	79.874
1.94038	.39050	79.875

Mean, 79.8745, ± .0034

Hence $Te = 127.002$. Heberlein's determinations assign low values to the atomic weight of tellurium.

Steiner's determination[2] of the atomic weight was made by combustion

---

[1] The formula given by Heberlein probably involves the old atomic weights of chlorine and iodine. With modern atomic weights the value for Te would be raised. The data as printed are, however, incomplete. A correction would be uncertain, and the probable error of the determinations is so high that the change could exert no appreciable effect upon the final combination of values.

[2] Ber. Deutsch. chem. Ges., 34, 570. 1901.

of phenyl telluride, $(C_6H_5)_2Te$. I give his weights, and also the ratio $C_{12}H_{10}Te : 12CO_2 :: 100 : x$:

Weight telluride.	Weight CO_2.	Ratio.
.2925	.5512	188.440
.2559	.4811	188.003
.23065	.4341	188.207
.2140	.4031	188.364
.2578	.4849	188.092

Mean, 188.221, ± .0549

Hence Te = 126.42, a very low value. This determination only claims a rough approximation to the truth, and is not entitled to much consideration.

Pellini,[1] in his determinations of this atomic weight, returned to the time-honored methods with the dioxide. First, carefully purified tellurium was oxidized by nitric acid. Secondly, tellurium dioxide was reduced by hydrogen in presence of metallic silver. The data are as follows:

Oxidation Series.

Weight Te.	Weight TeO_2.	Per cent. Te.
1.0679	1.3353	79.968
1.5469	1.9354	79.926
2.2386	2.7980	80.007
2.4522	3.0665	79.967
2.0977	2.6239	79.945
2.0442	2.5575	79.929
2.0434	2.5556	79.957

Mean, 79.957, ± .0071

Hence Te = 127.657.

Reduction Series.

Weight TeO_2.	Loss.	Per cent. Te.
1.4680	.2944	79.945
1.9968	.3993	80.000
1.9575	.3932	79.913

Mean, 79.953, ± .0171

Hence Te = 127.625.

Koethner,[2] after some preliminary, but inconclusive experiments with tellurium sulphate and telluric acid, finally resorted to analyses of the

[1] Ber. Deutsch. chem. Ges., 34, 3807. 1901. Gazz. Chim. Ital., 32, 131. 1902. In Gazz. Chim. Ital., 33 (2), 35, Pellini discusses the possibility of an admixture in ordinary tellurium, of an element having a higher atomic weight.

[2] Liebig's Annalen, 319, 1. 1901. Thesis, Halle, 1901. For a critical discussion of the subject, see Koethner, Zeitsch. anorg. Chem., 34, 402, 1903. See also Seubert, Zeitsch. anorg. Chem., 33, 247; and 35, 206.

basic nitrate, Te_2HNO_7. This compound was reduced by careful heating to TeO_2. In series II, as given below, the tellurium was purified by distillation in a vacuum; in series I that precaution was not taken. Weights not reduced to a vacuum:

Series I.

Nitrate.	TeO₂.	Per cent. TeO₂.
2.9373	2.4522	83.485
2.7982	2.3361	83.486
2.8554	2.3840	83.491

Mean, 83.487, ± .0014

Hence Te = 127.30.

Series II.

Nitrate.	TeO₂.	Per cent. TeO₂.
5.30270	4.42824	83.510
6.00600	5.01543	83.507
5.58039	4.65990	83.505
28.66904	23.94259	83.513
3.83859	3.20560	83.510
5.85449	4.88930	83.514
25.65029	21.412146	83.513

Mean, 83.5103, ± .0009

Hence Te = 127.57.

In 1902 Scott[1] published a preliminary note on the atomic weight of tellurium. Analyses of trimethyl tellurium iodide and bromide were made, the ratio with silver iodide being determined in the first case and the titration ratio with silver in the second. I subjoin Scott's figures, with the ratio to 100AgI and 100Ag, respectively. Vacuum weights are given:

$(CH_3)_3TeI.$	AgI.	Ratio.
1.7461	1.3688	127.564
6.6425	5.20575	127.570
8.0628	6.3181	127.614

Mean, 127.583, ± .0105

Hence Te = 127.56.

$(CH_3)_3TeBr.$	Ag.	Ratio.
2.4294	1.0373	234.204
6.8424	2.9201	234.321

Mean, 234.263, ± .0391

Hence Te = 127.72.

---

[1] Proc. Chem. Soc., 18, 112. 1902.

Gutbier's[1] determinations began with telluric acid, H_6TeO_6. First, the acid was dehydrated by heating in a stream of dry air, and the water was collected in a calcium chloride tube and weighed:

H_6TeO_6.	H_2O.	Per cent. H_2O.
.4937	.1162	23.537
.9910	.2335	23.562
		Mean, 23.550, ± .0083

Hence $Te = 127.45$.

Secondly, telluric acid was reduced to tellurium by precipitation with hydrazin hydrate. Gutbier's data are as follows:

H_6TeO_6.	Te.	Per cent. Te.
.9380	.5204	55.480
.4963	.2754	55.491
1.0485	.5829	55.594
.8865	.4915	55.443
.4339	.2411	55.566
.3492	.1937	55.470
		Mean, 55.507, ± .0165

Hence $Te = 127.31$. Staudenmaier found $55.508, ±.0068$ per cent. The general mean of both series is $55.5079, ±.0067$.

Finally, tellurium dioxide was reduced to tellurium by the same process:

TeO_2.	Te.	Per cent. Te.
.1662	.13287	79.946
.3136	.2507	79.942
.2799	.2238	79.957
		Mean, 79.948, ± .0031

Hence $Te = 127.585$. All of Gutbier's weights were reduced to a vacuum standard.

In a later memoir Gutbier[2] gives two more series of reductions of tellurium dioxide. In series I the oxide was reduced by hydrogen, and in series II by hydrazin. Vacuum weights are given:

Series I.

TeO_2.	Te.	Per cent. Te.
2.99688	2.39585	79.944
1.30740	1.04527	79.950
2.04325	1.63380	79.955
2.61725	2.09249	79.949
3.61725	2.89222	79.956
		Mean, 79.951, ± .0015

Hence $Te = 127.609$.

[1] Liebig's Annalen, 320, 52. 1902.
[2] Liebig's Annalen, 342, 266. 1905.

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

Series II.

</div>

TeO_2.	Te.	Per cent. Te.
1.90601	1.52390	79.952
1.03532	.82784	79.959
2.2200	1.77480	79.945

Mean, 79.952, ± .0031

Hence $Te = 127.617$.

In a more extended memoir, which includes the results of the last mentioned investigation, Gutbier [1] gives a series of analyses of basic tellurium nitrate, like those of Koethner. His figures are as follows, not reduced to a vacuum standard:

Nitrate.	TeO_2.	Per cent. TeO_2.
4.70704	3.92380	83.360
6.23210	5.20285	83.484
5.65043	4.71132	83.379
2.86977	2.39211	83.355
4.43213	3.69833	83.443
9.25691	7.73205	83.505
7.09070	5.91930	83.481
12.2400	10.2216	83.508

Mean, 83.439, ± .0156

Hence $Te = 126.74$.

Gallo's [2] investigation was an attempt to determine the electrochemical equivalent of tellurium in terms of silver. Silver and tellurium were thrown down by the same current, but in different receptacles, and so were directly compared. In the third column I give the ratio $4Ag : Te :: 100 : x$:

Weight Ag.	Weight Te.	Ratio.
.74117	.218412	29.469
1.03801	.304514	29.336
.91704	.27256	29.722
1.041101	.307117	29.499
1.09064	.321952	29.519
1.16302	.34582	29.666
.968903	.28646	29.565
1.518712	.44767	29.477
.906561	.26836	29.534
.995511	.29586	29.720
.86596	.25656	29.627
1.11282	.328318	29.503

Mean, 29.553, ± .0221

---

[1] Sitzungsb. phys. med. Soz. Erlangen, 37, 276. 1906. Gutbier regards these determinations as unsatisfactory.

[2] Atti Acad. Lincei (5), 14, 23, 1905. Also Gazz. Chim. Ital., 35, 245. See also Pellini, Gazz. Chim. Ital., 34, 132, on the electrolytic determination of tellurium.

Hence Te = 127.53. All of Gallo's weights are on a vacuum basis. Gallo also made a series of electrolytic analyses of tellurium dioxide as follows. The precipitation was effected in a hydrofluoric acid solution:

Weight TeO$_2$.	Weight Te.	Per cent. Te.
.4624	.3694	79.888
.7429	.5938	79.930
.7995	.6390	79.925
.9610	.7664	79.750
1.0043	.8025	79.906
1.9891	1.5890	79.885

Mean, 79.881, ± .0220

Hence Te = 127.053.

Two determinations by Lenher,[1] although not next in chronological order, may be conveniently inserted here. One was by reduction of TeO$_2$, the other by oxidation of Te:

TeO$_2$.	Te.	Per cent. Te.
.85035	.6845	79.932
.2119	.1694	79.943

Mean, 79.938, ± .0037

Hence Te = 127.50.

The percentage of tellurium in the dioxide is now fixed by 15 series of determinations, which, arranged in the order of ascending magnitude may be combined, as usual, into a general mean:

Brauner, oxidation	79.711,	± .0239
Heberlein	79.8745,	± .0034
Gallo	79.881,	± .0220
Brauner, reduction	79.932,	± .0534
Lenher	79.938,	± .0037
Gutbier, 1902	79.948,	± .0031
Staudenmaier	79.950,	± .0043
Gutbier, 1905, 1	79.951,	± .0015
Gutbier, 1905, 2	79.952,	± .0031
Pellini, reduction	79.953,	± .0171
Pellini, oxidation	79.957,	± .0071
Metzner	80.004,	± .0165
Wills, 1	80.015,	± .0410
Wills, 2	80.028,	± .0040
Berzelius	80.042,	± .0050

General mean, 79.9498, ± .0010

The determinations by Staudenmaier, Pellini and Gutbier are in close agreement, and very near the general mean of all.

---

[1] Journ. Amer. Chem. Soc., 30, 741. 1908.

Norris,[1] in the course of an investigation which proved the unity of tellurium as an element, made a series of atomic weight determinations by Koethner's method. The element itself was purified by various modes of fractionation, and different fractions were found to be identical. The basic nitrate was reduced by heating to TeO_2, which was fused before weighing; a precaution which eliminated the possibility of contamination by enclosed gases. The uncorrected data are as follows:

Nitrate.	TeO_2.	Per cent. TeO_2.
2.28215	1.90578	83.508
2.35429	1.96615	83.513
1.86853	1.56042	83.512
1.77348	1.48110	83.514
2.31048	1.92938	83.506
2.14267	1.78936	83.511
2.35523	1.96676	83.506
2.18860	1.82780	83.515
3.29158	2.74881	83.510
3.27516	1.89993	83.508
2.53164	2.11410	83.507
2.01327	1.68121	83.506

Mean, 83.5097, $\pm$ .0006

A vacuum correction to the weights reduces this mean by 0.0074 to 83.5023. Hence Te = 127.48. Assuming the same correction to previous series of determinations, the final value for the percentage of TeO_2 is given by the subjoined combination:

Koethner, 1 .... 83.480, $\pm$ .0014
Koethner, 2 .... 83.5003, $\pm$ .0009
Gutbier .... 83.432, $\pm$ .0156
Norris .... 83.5023, $\pm$ .0006

General mean .... 83.5000, $\pm$ .00047

The investigation by Baker and Bennett[2] was also intended to determine the definiteness of tellurium as an element. Different preparations from different sources were studied by several methods, and all gave sensibly the same atomic weight. The results obtained by two methods are given in detail, with vacuum weights throughout. First, tellurium dioxide was heated with sulphur in tubes of glass, the two ends of the tube being packed with silver leaf to avoid loss of tellurium. Sulphur dioxide was expelled, and from its amount, as measured by the loss in weight of the apparatus, the atomic weight of tellurium was com-

---

[1] Journ. Amer. Chem. Soc., 28, 1675. 1906.
[2] Journ. Chem. Soc., 91, 1849. 1907.

puted. The determinations by this method may be arranged in three principal series, representing differences in the source of the initial substance, as follows: 1. Fractional crystallization of telluric acid from barium tellurate. 2. Fractional crystallization of telluric acid produced by oxidation of the element. 3. Tellurium dioxide prepared from tellurium hydride.

Series 1.

Weight TeO₂.	Loss. SO₂.	Per cent. SO₂.
1.51509	.60838	40.155
1.09875	.44074	40.113
1.02150	.40993	40.130
.90835	.36472	40.152
1.00702	.40451	40.169
1.01515	.40733	40.125

Series II.

Weight TeO₂.	Loss. SO₂.	Per cent. SO₂.
1.56837	.62938	40.130
1.07852	.43257	40.108
1.72627	.69246	40.142
2.09253	.83927	40.108
.83335	.33465	40.157
1.15372	.46284	40.117
.68618	.67661	40.127
.90835	.36472	40.152

Series III.

Weight TeO₂.	Loss, SO₂.	Per cent. SO₂.
1.02217	.41050	40.160
.80697	.32392	40.140
1.32003	.52992	40.145
1.05207	.42221	40.131
1.37043	.54969	40.111
.95944	.38511	40.139

Mean of all as one series, 40.136, ± .0028

Hence $Te = 127.62$. Several other determinations, concordant with these, are cited, but without the detailed weighings.

Baker and Bennett also determined the atomic weight of tellurium by synthesis of the tetrabromide. Tellurium and bromine were directly combined in an atmosphere of nitrogen, and the excess of bromine was expelled by a current of nitrogen at a temperature of 50°. The deter-

minations fall into several series, representing different samples of material, but they are given here as one series:

Weight Te.	Weight TeBr₄.	Per cent. Te.
.61273	2.14933	28.508
.56866	1.99354	28.525
.59884	2.09951	28.523
.57894	2.03040	28.514
.54743	1.91899	28.527
.33859	1.18732	28.517
.56866	1.99354	28.526
.47643	1.67025	28.525
.56622	1.98597	28.511
.44271	1.55205	28.524
.41671	1.46177	28.508
.50611	1.77489	28.515
.37382	1.31081	28.519
.31895	1.11868	28.512
.48931	1.71554	28.522
.47156	1.65404	28.510
.40748	1.42867	28.523
.62013	2.17449	28.518
.37382	1.31081	28.519
.50822	1.78207	28.518
.12928	.45354	28.505
.42926	1.50540	28.515
.80348	2.81715	28.511
.95309	3.34193	28.512

Mean, $\overline{28.517}$, ± .0009

Hence Te = 127.53. If Br = 79.96, Te = 127.60, in accord with the SO_2 ratio.

Baker and Bennett furthermore report a few analyses of tellurium tetrachloride which gave values for Te ranging from 127.58 to 127.64, but without weights or details. These determinations, therefore, are unavailable for discussion here.

In the determinations by Marckwald [1] telluric acid was the starting point. This compound was reduced to TeO_2 by heating, as in several former investigations, with the following results:

Weight H_6TeO_6.	TeO_2.	Per cent. TeO_2.
8.6277	5.9884	69.409
12.2680	8.5135	69.396
13.0051	9.0244	69.390
8.6415	5.9947	69.371
8.4588	5.8696	69.390
8.0113	5.5599	69.401

Mean, 69.393, ± .0035

---

[1] Ber. Deutsch. chem. Ges., 40, 4730, 1907. For a criticism of Marckwald by Baker, see Chem News, 97, 209.

Hence Te = 126.81, a figure which falls below the atomic weight of iodine. The error which suggests itself is the possible retention of water or mother liquor by the telluric acid; but Marckwald obtained an acid of constant weight after prolonged drying over phosphorus pentoxide. Still, water may have been retained as an enclosure within the particles of acid, so enveloped as to be prevented from escaping. Marckwald's figures combine with other similar determinations thus:

Staudenmaier	69.440, ± .0024
Heberlein	69.381, ± .0115
Marckwald	69.393, ± .0035
General mean	69.424, ± .0020

Lenher's investigations,[1] like those of his recent predecessors, had special reference to the homogeneity of tellurium. The tellurium was obtained from three distinct sources; first, from the telluride ores of Colorado; second, from the residues of an electrolytic copper refinery; and third, from Bohemian material. From these the double bromide K_2TeBr_6 was prepared, and this, by heating first in chlorine and afterwards in gaseous hydrochloric acid, was converted into potassium chloride. That is, the ratio $K_2TeBr_6 : 2KCl$ was measured, all weights being reduced to a vacuum. In the following table I have treated the three series as one, for the results obtained are sensibly uniform:

	K_2TeBr_6.	$KCl.$	Per cent. $KCl.$
1	2.33360	.50779	21.7599
	1.27372	.27716	21.7599
	1.47573	.32111	21.7594
	1.65715	.36059	21.7596
	1.54006	.33513	21.7608
2	1.82810	.39778	21.7592
	1.87342	.40765	21.7595
	1.48045	.32214	21.7596
	2.24775	.48911	21.7600
3	2.37899	.51767	21.7601
	1.79926	.39146	21.7562
	.94102	.20476	21.7594
	1.55357	.33806	21.7602
	1.95038	.42440	21.7599
	1.73248	.37698	21.7596
	1.81923	.39586	21.7598

Mean, 21.7596, ± .00017

Hence Te = 127.57.

---

[1] Journ. Amer. Chem. Soc., 31, 20. 1909. See also Lenher's figures for TeO_2, previously cited.

The ratios for tellurium are now as follows:

(1). $TeO_2 : Te : : 100 : 79.9498, \pm .0010$
(2). $TeO_2 : O : : 100 : 10.068, \pm .0100$
(3). $H_6TeO_6 : 3H_2O : : 100 : 23.550, \pm .0083$
(4). $H_6TeO_6 : TeO_2 : : 100 : 69.424, \pm .0020$
(5). $H_6TeO_6 : Te : : 100 : 55.5079, \pm .0067$
(6). Molecular weight H_6TeO_6, 229.270, $\pm .0425$.   (Heberlein)
(7). $4Ag : Te : : 100 : 29.553, \pm .0021$
(8). $4Ag : TeBr_4 : : 100 : 103.640, \pm .0014$
(9). $K_2TeBr_6 : 6AgBr : : 100 : 164.468, \pm .0324$
(10). $TeBr_4 : Te : : 100 : 28.517, \pm .0009$
(11). $TeO_2 : SO_2 : : 100 : 40.136, \pm .0028$
(12). $Te_2SO_7 : Te : : 100 : 63.978, \pm .0040$
(13). $Te_2HNO_7 : TeO_2 : : 100 : 83.5000, \pm .00047$
(14). $C_{12}H_{10}Te : 12CO_2 : : 100 : 188.221, \pm .0549$
(15). $AgI : C_3H_9TeI : : 100 : 127.583, \pm .0105$
(16). $Ag : C_3H_9TeBr : : 100 : 234.263, \pm .0391$
(17). $K_2TeBr_6 : 2KCl : : 100 : 21.7596, \pm .00017$

To reduce these ratios we have—

$Ag = 107.880, \pm .00029$	$N = 14.0101, \pm .0001$
$Cl = 35.4584, \pm .0002$	$C = 12.0038, \pm .0002$
$Br = 79.9197, \pm .0003$	$S = 32.0667, \pm .00075$
$I = 126.9204, \pm .00033$	$K = 39.0999, \pm .0002$

$$H = 1.00779, \pm .00001$$

Hence,

From ratio 14	$Te = 126.418, \pm .0820$
" " 2	$126.919, \pm .1579$
" " 4	$127.044, \pm .0114$
" " 6	$127.223, \pm .0425$
" " 5	$127.313, \pm .0247$
" " 9	$127.392, \pm .1350$
" " 3	$127.451, \pm .0583$
" " 13	$127.453, \pm .0046$
" " 7	$127.527, \pm .0954$
" " 10	$127.531, \pm .0045$
" " 8	$127.548, \pm .0063$
" " 15	$127.563, \pm .0247$
" " 17	$127.572, \pm .0064$
" " 1	$127.599, \pm .0066$
" " 11	$127.614, \pm .0113$
" " 16	$127.722, \pm .0422$
" " 12	$127.937, \pm .0163$

General mean, $Te = 127.520, \pm .0023$

In short, the atomic weight of tellurium is near 127.5, at least so far as the element is now known. The general mean given above is between the values determined by Norris and Gallo.

It has already been stated that several of the more important investigations relative to the atomic weight of tellurium, have had for their purpose the establishment of its homogeneity. Up to this point all the evidence has gone to show that it is not a mixture of two elements. Tellurium from widely different sources, as in Lenher's recent work, gives one and the same value for its atomic weight. Fractionations by different methods have also given constant results, and it seemed as if the question had been definitely settled. Very recently, however, even since this chapter was in great part written, Browning and Flint[1] have secured evidence upon the other side, which deserves some attention. When tellurium tetrachloride is mixed with water and hydrolyzed, a large part of it is precipitated as tellurium dioxide. A part, however, remains in solution, from which it can be thrown down by ammonia and a slight excess of acetic acid. Carefully purified tellurium was treated by the process thus briefly suggested, and converted, with all due precautions, into the basic nitrate. The portion precipitated by hydrolysis gave, on analysis of the nitrate, a mean value of $Te = 126.53$. From the portion afterwards thrown down the value 128.97 was obtained. Other determinations, by other methods, gave similar results. The *alpha*, or first precipitate, gave mean values, in two additional series, of 126.64 and 126.31. The *beta* portion, that not precipitated during hydrolysis of the chloride, gave $Te = 128.77$ and 128.81. Browning and Flint intend to continue their research; but until that is finished it is not practicable to discuss their atomic weights in connection with previous determinations. Their fractionations are evidently not perfect, but preliminary; and their atomic weights are not given as being anything more than approximations. So far they have established a reasonable probability; nothing more.

[1] Amer. Journ. Sci. (4), 28, 347. 1909.

FLUORINE.

The atomic weight of fluorine has been commonly determined by two general methods; namely, the conversion of fluorides into sulphates. There are, however, two exceptions, which will be considered in due time.

Excluding the early results of Davy,[1] we have to consider first the experiments of Berzelius, Louyet, Dumas, De Luca and Moissan with reference to the fluorides of calcium, sodium, potassium, barium and lead.

The ratio between calcium fluoride and sulphate has been determined by the five 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 insure 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,[2] 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, $1.750, \pm .0004$

Hence $F = 18.85$.

Louyet's researches[3] 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.

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

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

Mean, $1.7437, \pm .0003$

Hence $F = 18.99$.

---

[1] Phil. Trans., 64. 1814.
[2] Poggend. Annalen, 8, 1. 1826.
[3] Ann. Chim. Phys. (3), 25, 300. 1849.

A second series, upon artificial fluoride, gave:

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

Mean, 1.7417, ± .0004

Hence F = 19.03.

Dumas[1] published but one result for calcium fluoride. .495 grm. gave .864 grm. sulphate, the ratio being 1 : 1.7455. Hence F = 18.95.

De Luca[2] 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

Hence F = 18.97.

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

Moissan[3] unfortunately gives no details nor weighings, but merely states that four experiments with calcium fluoride gave values for F ranging from 19.02 to 19.08. To S he assigned the value 32.074, and probably Ca was taken as = 40. With these data his extreme values as given may be calculated back into uniformity with the ratio as stated above, becoming—

$$1.7444$$
$$1.7410$$

Mean, 1.7427

Hence F = 19.011.

If we assign this equal weight with Berzelius' series, the data for this ratio combine thus:

Berzelius	1.7500, ± .0004
Louyet, first series............	1.7437, ± .0003
Louyet, second series..........	1.7417, ± .0004
De Luca with Dumas..........	1.7459, ± .0011
Moissan	1.7427, ± .0004
General mean	1.7444, ± .00018

[1] Ann. Chem. Pharm., 113, 28. 1860.
[2] Compt. Rend., 51, 299. 1860.
[3] Compt. Rend., 111, 570. 1890.

For the ratio between the two sodium salts we have experiments by Dumas, Louyet and Moissan. According to Louyet, one gramme of NaF gives of Na_2SO_4—

<div align="center">

1.686
1.683
1.685

———

Mean, 1.6847, ± .0006
</div>

Hence F = 19.06.

The weighings published by Dumas are as follows:

<div align="center">

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

———

Mean, 1.688, ± .0007
</div>

Hence F = 19.08.

Moissan says only that five experiments with sodium fluoride gave F = 19.04 to 19.08. This was calculated with Na = 23.05 and S = 32.074. Hence, reckoning backward, the two values give for the standard ratio—

<div align="center">

1.6889
1.6873

———

Mean, 1.6881
</div>

Hence F = 19.07.

Giving this equal weight with Dumas' mean, we have—

<div align="center">

Louyet .... 1.6847, ± .0006
Dumas .... 1.688, ± .0007
Moissan .... 1.6881, ± .0007

—————————

General mean .... 1.6867, ± .00038
</div>

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

<div align="center">

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

———

Mean, 1.4991, ± .0007
</div>

Hence F = 19.02.

The ratio between barium fluoride and barium sulphate was measured by Louyet and Moissan. According to Louyet, one gramme of BaF_2 gives of $BaSO_4$—

<div align="center">

1.332
1.331
1.330

———

Mean, 1.331, ± .0004
</div>

Hence F = 19.01.

Moissan, in five experiments, found F = 19.05 to 19.09. Assuming that he put Ba = 137, and S = 32.074 as before, these two extremes become—

$$1.3311$$
$$1.3305$$

Mean, 1.3308

Hence F = 19.02.

Giving this equal weight with Louyet's mean, we get the subjoined combination:

Louyet .... 1.331, ± .0004
Moissan .... 1.3308, ± .0004

General mean .... 1.3309, ± .00028

The experiments with lead fluoride are due to Louyet, and 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, ± .0002

Hence F = 19.14.

In Christensen's determinations [1] we find a method adopted which is radically unlike anything in the work of his predecessors. He started out with the salt $(NH_4)_2MnF_5$. When this is added to a mixture, in solution, of potassium iodide and hydrochloric acid, iodine is set free, and may be titrated with sodium thiosulphate. One molecule of the salt (as written above) liberates one atom of iodine. In four experiments Christensen obtained the following data:

3.1199 grm. Am_2MnF_5 gave 2.12748 I.	68.191 per cent.
3.9190 "	2.67020 "	68.135 "
3.5005 "	2.38429 "	68.113 "
1.2727 "	.86779 "	68.185 "

Mean, 68.156, ± .0128

Hence F = 19.038.

---

[1] Journ. prakt. Chem. (2), 35, 541. Christensen assigns to the salt double the formula here given.

Still another method for determining the atomic weight of fluorine was adopted by Julius Meyer.[1] Carefully purified calcium oxide was weighed, slaked with water and then converted into chloride by means of hydrochloric acid. The chloride solution was then repeatedly evaporated with pure hydrofluoric acid. The calcium fluoride so produced was finally ignited to constant weight. On a vacuum basis his weights were as follows. The third column gives the ratio $CaO : CaF_2 :: 100 : x$:

Weight CaO.	Weight CaF_2.	Ratio.
6.1883	8.6215	139.320
4.2736	5.9548	139.339
6.2931	8.7658	139.292
5.7767	8.0485	139.327
4.9836	6.9426	139.309

Mean, 139.317, $\pm$ .0054

Hence $F = 19.035$.

The ratios from which to compute the atomic weight of fluorine are now—

(1). $CaO : CaF_2 :: 100 : 139.317$, $\pm$ .0054
(2). $CaF_2 : CaSO_4 :: 1.0 : 1.7444$, $\pm$ .00018
(3). $2NaF : Na_2SO_4 :: 1.0 : 1.6867$, $\pm$ .00038
(4). $2KF : K_2SO_4 :: 1.0 : 1.4991$, $\pm$ .0007
(5). $BaF_2 : BaSO_4 :: 1.0 : 1.3309$, $\pm$ .00028
(6). $PbF_2 : PbSO_4 :: 5.0 : 6.1783$, $\pm$ .0002
(7). $Am_2MnF_5 : I :: 100 : 68.156$, $\pm$ .0128

To reduce these ratios we have—

$Ca = 40.1323$, $\pm$ .0005	$Na = 23.0108$, $\pm$ .00024
$Ba = 137.363$, $\pm$ .0025	$S = 32.0667$, $\pm$ .00075
$Pb = 206.970$, $\pm$ .0017	$I = 126.9204$, $\pm$ .00033
$Mn = 54.947$, $\pm$ .0005	$N = 14.0101$, $\pm$ .0001
$K = 39.0999$, $\pm$ .0002	$H = 1.00779$, $\pm$ .00001

Hence,

From ratio 2	.... $F = 18.973$, $\pm$ .0041
" " 5	.... 19.015, $\pm$ .0185
" " 4	.... 19.024, $\pm$ .0271
" " 1	.... 19.035, $\pm$ .0016
" " 7	.... 19.038, $\pm$ .0070
" " 3	.... 19.109, $\pm$ .0085
" " 6	.... 19.136, $\pm$ .0041

General mean, $F = 19.041$, $\pm$ .00135

[1] Zeitsch. anorg. Chem., 36, 313. 1903.

This mean is near the values deduced from Meyer's and Christensen's determinations, which are presumably the best. If it is applied to Christensen's ratio, No. 7, it gives for the atomic weight of manganese $Mn = 54.933$, which agrees well with the results obtained by Baxter and Hines. From this we may fairly infer that the value for fluorine is not far from the truth.

MANGANESE.

The earliest experiments of Berzelius [1] and of Arfvedson [2] gave values for Mn ranging between 56 and 57, and therefore need no farther consideration here. The first determinations to be noticed are those of Turner [3] and a later measurement by Berzelius, [4] who both determined gravimetrically the ratio between the chlorides of manganese and silver. The manganese chloride was fused in a current of dry hydrochloric acid, and afterwards precipitated with a silver solution. I give the $MnCl_2$ equivalent to 100 parts of AgCl in the third column :

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 $Mn = 55.07$, Berzelius; or 54.87, Turner.

Many years later Dumas [5] 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. One hundred 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 $Mn = 54.916$.

[1] Poggend. Annalen, 8, 185. 1826.
[2] Berz. Jahresbericht, 9, 136. 1829.
[3] Trans. Roy. Soc. Edinb., 11, 143. 1831.
[4] Lehrbuch, 5 Aufl., 3, 1224.
[5] Ann. Chem. Pharm., 113, 25. 1860.

An entirely different method of investigation was followed by von Hauer,[1] 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:

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, $\pm$ .008

Hence Mn = 54.915.

This method of von Hauer, which seemed to give good results with cadmium, is, according to Schneider,[2] 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_3O_4 equivalent to one gramme of water:

4.149 grm. Mn_3O_4 gave	.330 grm. H_2O.	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, $\pm$ .0034

Hence Mn = 54.08.

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 von Hauer.

[1] Journ. prakt. Chem., 72, 360, 1857.
[2] Poggend. Annalen, 107, 605.

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, ± .0122

Hence Mn = 54.03.

Up to this point the data give two distinct values for Mn—one near 54, the other approximately 55—and with no sure guide to preference between them. The higher value, however, has been confirmed by later testimony.

In 1883 Dewar and Scott [1] published the results of their work upon silver permanganate. This salt is easily obtained pure by recrystallization, and has the decided advantage of not being hygroscopic. Two sets of experiments were made. First, the silver permanganate was heated to redness in a glass bulb, first in air, then in hydrogen. Before weighing, the latter gas was replaced by nitrogen. The data are as follows:

$AgMnO_4$.	$Ag + MnO$.	Per cent. $Ag + MnO$.
5.8696	4.63212	78.917
5.4988	4.33591	78.852
7.6735	6.05395	78.894
13.10147	10.31815	78.756
12.5799	{ 9.91065	78.782
	{ 9.91435	78.811

Mean, 78.835, ± .0174

Hence Mn = 55.009.

The duplication of the last weighing is not explained.

In the second series the permanganate was dissolved in dilute nitric acid, reduced by sulphur dioxide, potassium nitrite, or sodium formate,

---

[1] Proc. Roy. Soc., 35, 44. 1883.

and titrated with potassium bromide. The $AgMnO_4$ equivalent to 100 KBr appears in the third column:

$AgMnO_4$.	KBr.	Ratio.
6.5289	3.42385	190.686
7.5378	3.9553	190.575
6.1008	3.20166	190.559
5.74647	3.00677	191.117
6.16593	3.23602	190.540
5.11329	2.6828	190.596
5.07438	2.66204	190.624
13.4484	7.05603	190.604
12.5799	6.60065	190.588
12.27025	6.43808	190.584

Mean, 190.647. ± .0361

Vacuum weights are given throughout. To the first series of experiments the authors attach little importance, and numbers 1 and 4 of the second series they also regard as questionable. These experiments represent the use of sulphur dioxide as the reducing agent, and were attended by the formation of an insoluble residue, apparently of a sulphide. Excluding them, the remaining eight experiments of the second series give in mean—

KBr:$AgMnO_4$::100:190.584, ± .0062, and Mn = 54.95

which will be used for the present calculation. Dewar and Scott also made determinations with manganese chloride and bromide. With the first salt they found Mn=54.91, and with the second, Mn=54.97; but they give no details.

Marignac's work upon the atomic weight of manganese also appeared in 1883.[1] He prepared the oxide, MnO, by ignition of the oxalate and subsequent reduction of the resulting Mn_3O_4 in hydrogen. The oxide, with various precautions, was then converted into sulphate. The percentage of MnO in $MnSO_4$ is appended:

2.6587 grm. MnO gave	5.6530 $MnSO_4$.	47.032 per cent.
2.5185 "	5.3600 "	46.987 "
2.5992 "	5.5295 "	47.006 "
2.8883 "	6.1450 "	47.002 "

Mean, 47.007, ± .0025

Hence Mn=55.022.

J. M. Weeren, in 1890,[2] published determinations made by two methods, the one Marignac's, the other von Hauer's. From manganese sulphate

---

[1] Arch. Sci. Phys. Nat. (3), 10, 21. 1883.
[2] Atom-Gewichtsbestimmung des Mangans. Inaugural Dissertation. Halle, 1890.

he threw down the hydrated peroxide electrolytically, and the latter compound was then reduced in hydrogen which had been proved to be free from oxygen. The resulting monoxide was cooled in a stream of purified nitrogen. After the oxide had been treated with sulphuric acid, converted into sulphate, and weighed, a few drops of sulphuric acid and a little sulphurous acid were added to it, after which it was reheated and weighed again. This process was repeated until four successive weighings absolutely agreed. The results of this set of experiments were as follows, reduced to a vacuum standard:

15.2349 grm. MnO gave	32.4142 MnSO₄.	47.005 per cent.
13.9686 "	29.7186 "	47.004 "
13.7471 "	29.2493 "	47.000 "
15.5222 "	33.0246 "	47.001 "
14.9824 "	31.8755 "	47.002 "
14.6784 "	31.2304 "	47.000 "

Mean, 47.002, $\pm$ .0006

Hence $Mn = 55.008$.

Marignac's mean, combined with this, hardly affects either the percentage itself or its probable error. Fortunately, both Marignac and Weeren are completely in agreement as to the ratio, and either set of measurements would be valid without the other. In order, therefore, to give Marignac's work some proper recognition, we can assume a general mean of 47.004, $\pm$ .0006, without danger of serious error.

The manganese sulphate produced in the foregoing series of experiments was used, with many precautions, for the next series carried out by von Hauer's method. It was transferred to a porcelain boat, dried at 260° to avoid errors due to retention of water taken up in the process of transfer, and then heated to constant weight in a stream of hydrogen sulphide. Before weighing, the sulphide was heated to redness in hydrogen and cooled in the same gas. The results, with vacuum weights, were as follows:

16.0029 grm. MnSO₄ gave	9.2228 MnS.	57.632 per cent.
16.3191 "	9.4048 "	57.631 "
15.9307 "	9.1817 "	57.634 "
15.8441 "	9.1315 "	57.634 "
16.2783 "	9.3819 "	57.635 "
17.0874 "	9.8477 "	57.633 "

Mean, 57.633, $\pm$ .0004
von Hauer found, 57.608, $\pm$ .0080

Hence the general mean is identical with Weeren's to the third decimal place, which is unaffected by combination with von Hauer's data.

27

From Weeren's figures alone $Mn = 54.994$.

The determinations by Baxter and Hines[1] were based upon analyses of manganese bromide and chloride, both fused in order to eliminate moisture. The usual Harvard methods were employed, giving two ratios for each salt. With vacuum weights the data obtained were as follows, first with the bromide:

$MnBr_2$.	$AgBr$.	Ag.	Ag ratio.	$AgBr$ ratio.
5.58416	9.76561	......	.....	57.181
5.63432	9.85345	......	.....	57.181
6.53738	11.43300	6.56765	99.539	57.180
4.81005	8.41206	4.83238	99.538	57.180
4.88097	8.53642	4.90354	99.540	57.178
5.63219	9.85008	5.65813	99.542	57.179
6.52626	11.41293	......	.....	57.180
5.79924	10.14206	5.82600	99.541	57.180
3.59809	6.29271	3.61478	99.538	57.179
5.16334	9.02959	5.18711	99.542	57.182
3.92226	6.85968	3.94042	99.539	57.178
4.49158	7.85571	4.51250	99.536	57.176
3.60071	6.29740	3.61736	99.540	57.178
4.77392	8.34915	4.79620	99.535	57.179
3.57660	6.25569	3.59319	99.538	57.174
5.69972	9.96840	5.72641	99.534	57.178
			Mean, 99.539,	57.179,
			$\pm$ .0005	$\pm$ .0004

From Ag ratio, $Mn = 54.926$.
From AgBr ratio, $Mn = 54.925$.
And Ag : Br :: 100 : 74.083.

Secondly, for the chloride series:

$MnCl_2$.	$AgCl$.	Ag.	Ag ratio.	$AgCl$ ratio.
4.62970	10.54641	7.93740	58.328	43.898
3.52899	8.03868	6.05041	58.326	43.900
3.30881	7.53731	5.67279	58.328	43.899
3.56843	8.12932	6.11818	58.325	43.896
3.45083	7.86129	5.91637	58.327	43.896
4.47948	10.20372	7.67995	58.327	43.900
3.92089	8.93140	6.72227	58.327	43.900
			Mean, 58.327,	43.898,
			$\pm$ .0003	$\pm$ .0005

From Ag ratio, $Mn = 54.928$.
From AgCl ratio, $Mn = 54.928$.
And Ag : Cl :: 100 : 32.869.

---

[1] Journ. Amer. Chem. Soc., 28, 1560. 1906.

The chloride ratios, as determined by different chemists, combine thus:

<div align="center">

Ag ratio.

Dumas	58.321, ± .0010
Baxter and Hines...........	58.327, ± .0003
General mean	58.3265, ± .0003

AgCl ratio.

Berzelius with Turner........	43.924, ± .0150
Baxter and Hines.............	43.898, ± .0005
General mean	43.898, ± .0005

</div>

In this instance the early work does not even effect the fourth decimal place.

We have now to consider the following ratios for manganese:

(1). $2Ag : MnCl_2 : : 100 : 58.3265, \pm .0003$
(2). $2AgCl : MnCl_2 : : 100 : 43.898, \pm .0005$
(3). $2Ag : MnBr_2 : : 100 : 99.539, \pm .0005$
(4). $2AgBr : MnBr_2 : : 100 : 57.179, \pm .0004$
(5). $H_2O : Mn_3O_4 : : 100 : 1255.82, \pm .3400$
(6). $2CO_2 : Mn : : 100 : 61.3943, \pm .0122$
(7). $AgMnO_4 : Ag + MnO : : 100 : 78.835, \pm .0174$
(8). $KBr : AgMnO_4 : : 100 : 190.584, \pm .0062$
(9). $MnSO_4 : MnO : : 100 : 47.004, \pm .0006$
(10). $MnSO_4 : MnS : : 100 : 57.633, \pm .0004$

The antecedent atomic weights are—

Ag = 107.880, ± .00029	S = 32.0667, ± .00075
Cl = 35.4584, ± .0002	K = 39.0999, ± .0002
Br = 79.9197, ± .0003	C = 12.0038, ± .0002
	H = 1.00779, ± .00001

Hence,

From ratio 6	Mn =	54.032, ± .0108
" " 5		54.081, ± .0610
" " 4		54.925, ± .0020
" " 3		54.926, ± .0014
" " 1		54.928, ± .0008
" " 2		54.928, ± .0015
" " 8		54.953, ± .0074
" " 10		54.994, ± .0013
" " 7		55.009, ± .1522
" " 9		55.014, ± .0014
General mean, Mn =		54.947, ± .0005

In this combination the best work is evidently that of Baxter and Hines, as shown by the concordant values derived from ratios 1 to 4. But Weeren's work also appears to be excellent, and ought not to be ignored. The general mean takes all the trustworthy determinations into account, and seems to be preferable to any selection among them.

IRON.

The atomic weight of iron has been mainly determined from the composition of ferric oxide, ferrous bromide and the two 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.[1] The first work deserving of present consideration is that of Wackenroder,[2] who reduced the oxide in hydrogen at a moderate red heat. The following percentages of iron were thus found:

$$69.62$$
$$69.954$$
$$69.98$$
$$69.98$$
$$69.99$$
$$70.04$$

Mean, 69.927, ± .0905

If we reject the first of these figures the mean becomes 69.988, ±.0099, which is more trustworthy. Hence Fe = 55.97.

In 1844 Berzelius[3] 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, ± .0013

Hence Fe = 56.05. The " probable error " assigned to this pair of measurements greatly overvalues them. It is better, therefore, to give the mean equal weight with Wackenroder's, making it 70.020, ±.0099.

About the same time Svanberg and Norlin[4] published 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

---

[1] For details concerning these earlier researches, see Oudeman's monograph, pp. 140, 141.

[2] Arch. Pharm., 35, 279, and 36, 22. 1843.

[3] Berz. Jahresb., 25, 43. Ann. Chem. Pharm., 30, 432.

[4] Berz. Jahresb., 25, 42.

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. Fe₂O₃.	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

Hence Fe = 55.875.

In the second series ferric oxide was reduced by ignition in a current of hydrogen, yielding the subjoined percentages of metal:

2.98353 grm. Fe₂O₃ 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

Hence Fe = 56.093.

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.

In 1844 there was also published an important paper by Erdmann and Marchand.[1] These chemists prepared ferric oxide by the ignition of pure ferrous oxalate, and submitted 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 Fe₂O₃ are as follows:

70.013 ⎤
69.962 ⎟
69.979 ⎬ A
70.030 ⎟
69.977 ⎦
70.044 ⎤
70.015 ⎬ B
70.055 ⎦

Mean, 70.0094, ± .0080

Hence Fe = 56.025.

[1] Journ. prakt. Chem., 33, 1.

In 1850 Maumené's [1] 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, $\pm$ .0019

Hence Fe = 56.003.

The two determinations by Rivot [2] are quite unimportant. This chemist reduced ferric oxide in hydrogen, and obtained the subjoined percentages of iron:

69.31
69.35

Mean, 69.33, $\pm$ .0130

Hence Fe = 54.25.

Richards and Baxter [3] also reduced ferric oxide by hydrogen. Iron was purified electrolytically and then converted into oxide by two processes. First, by solution, precipitation as hydroxide, and ignition of the latter compound. With the oxide thus prepared, the two subjoined reductions were made:

Fe_2O_3.	Fe.	Per cent. Fe.
3.17485	2.22096	69.954
3.61235	2.52750	69.968

Mean, 69.961, $\pm$ .0047

Hence Fe = 55.900.

Secondly, iron was converted into nitrate, and that into oxide by calcination. The oxide was free from occluded gases. The data, with vacuum weights for both series, are as follows:

[1] Compt. Rend., Oct. 17, 1850.
[2] Ann. Chem. Pharm., 78, 214. 1851.
[3] Proc. Amer. Acad., 35, 253. Zeitsch. anorg. Chem., 23, 245. 1900.

Fe_2O_3.	Fe.	Per cent. Fe.
3.97557	2.78115	69.956
4.89655	3.42558	69.959
4.35955	3.04990	69.959
7.14115	4.99533	69.951
6.42021	4.49130	69.956

Mean, 69.9562, ± .0010

Hence $Fe = 55.883$.

The nine series of figures for this ratio combine thus:

Wackenroder	69.988, ± .0099
Berzelius	70.020, ± .0099
Erdmann and Marchand.............	70.0094, ± .0080
Svanberg and Norlin, oxidation.......	69.9534, ± .0050
Svanberg and Norlin, reduction......	70.0354, ± .0055
Maumené	70.0008, ± .0019
Rivot	69.33, ± .013
Richards and Baxter, 1..............	69.961, ± .0047
Richards and Baxter, 2..............	69.9562, ± .0010
General mean	69.9728, ± .00083

Although they are not in chronological order, the analyses of ferrous bromide by Baxter [1] may conveniently be considered here. He made two sets of analyses, fixing the two usual ratios, by the established Harvard methods. His figures, with all corrections and vacuum weights, follow:

$FeBr_2$.	$AgBr$.	Ag.	Ag ratio.	$AgBr$ ratio.
3.55929	6.19873	......	.....	57.420
3.07448	5.35450	......	.....	57.419
2.96102	5.15696	2.96234	99.956	57.418
4.00791	6.97983	4.00937	99.964	57.421
			Mean, 99.960, ± .0027	57.4195, ± .00044

From Ag ratio, $Fe = 55.836$.

From $AgBr$ ratio, $Fe = 55.828$.

And $Ag : Br : : 100 : 74.087$.

Dumas' [2] 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, they must be included.

Pure ferrous chloride, ignited in a stream of hydrochloric acid gas, was dissolved in water and titrated with a silver solution in the usual

[1] Proc. Amer. Acad., 39, 245. 1903.
[2] Ann. Chem. Pharm., 113, 26. 1860.

way. One hundred parts of silver are equivalent to the amounts of $FeCl_2$ given in the third column:

$$3.677 \text{ grm. } FeCl_2 = 6.238 \text{ grm. Ag.} \qquad 58.945$$
$$3.924 \qquad \text{``} \qquad 6.675 \qquad \text{``} \qquad 58.787$$

Mean, 58.866, $\pm$ .053

Ferric chloride, titrated in the same way, gave these results:

$$1.179 \text{ grm. } FeCl_3 = 2.3475 \text{ grm. Ag.} \qquad 50.224$$
$$1.242 \qquad \text{``} \qquad 2.471 \qquad \text{``} \qquad 50.263$$

Mean, 50.2435, $\pm$ .0132

These give us two additional values for Fe, as follows:

From $FeCl_2$ .... Fe $= 56.092$
From $FeCl_3$ .... " $= 56.231$

A series of determinations of the equivalent of iron, made by students by measuring the hydrogen evolved when the metal is dissolved in an acid, was published by Torrey in 1888.[1] The data have, of course, slight value, but may be considered as being in some measure confirmatory. They are as follows:

$$56.40$$
$$55.60$$
$$55.38$$
$$55.56$$
$$55.48$$
$$55.50$$
$$55.86$$
$$56.06$$
$$56.22$$
$$55.80$$
$$55.78$$
$$55.60$$
$$55.70$$
$$55.94$$

Mean, 55.777, $\pm$ .0532

These values undoubtedly depend on Regnault's value for the weight of hydrogen. Correcting by the later value, as found in the chapter of this work relating to the density ratio H : O, the mean becomes Fe $= 55.608, \pm .0532$. With O $= 16$, Fe $= 56.042$. The probable error in the weight of the hydrogen is ignored as having no practical significance.

_____

[1] Am. Chem. Journ., 10, 74.

A few determinations of the atomic weight of iron by Winkler[1] still need to be mentioned, not as directly significant, but as relating to the validity of a method which he applied to nickel and cobalt. Iron, not absolutely pure, was dissolved in a solution of iodine and potassium iodide. The quantity of iodine was known, and after the reaction ended the amount unconsumed was measured by titration with thiosulphate solution. A ratio between iodine and iron was thus determined, which can be expressed as $I_2 : Fe :: 100 : x$. Two series are given, one with iron cleaned by scrubbing, the other with iron which had been heated in hydrogen. The weights of iron given below are corrected for known impurities.

Series I.

Fe.	I.	Ratio.
.5726	2.585609	22.146
.5778	2.608375	22.152
.5721	2.582935	22.149

Mean, 22.149, $\pm$ .0012

Hence $Fe = 56.223$.

Series II.

Fe.	I.	Ratio.
.8252	3.727316	22.139
.8430	3.809144	22.131
.8349	3.771613	22.137

Mean, 22.136, $\pm$ .0017

Hence $Fe = 56.190$. The weighted mean of both series is $22.145, \pm$ .0010, which gives $Fe = 56.213$. This value is high, and so are the values found for cobalt and nickel by the same method. The process is probably affected by serious constant errors, and the results obtained by it are not good. For comparative purposes, however, the iodine ratio is included in the following tabulation of ratios:

(1). $Fe_2O_3 : 2Fe :: 100 : 69.9728, \pm$ .00083
(2). $2Ag : FeBr_2 :: 100 : 99.960, \pm$ .0027
(3). $2AgBr : FeBr_2 :: 100 : 57.4195, \pm$ .00044
(4). $2Ag : FeCl_2 :: 100 : 58.866, \pm$ .0530
(5). $3Ag : FeCl_3 :: 100 : 50.2435, \pm$ .0132
(6). $I_2 : Fe :: 100 : 22.145, \pm$ .0010
(7). $H : Fe :: 1 : 55.608, \pm$ .0532

[1] Zeitsch. anorg. Chem., 8, 291. 1895.

The antecedent atomic weights are—

$$Ag = 107.880, \pm .00029 \qquad Br = 79.9197, \pm .0003$$
$$Cl = 35.4584, \pm .0002 \qquad I = 126.9204, \pm .00033$$
$$H = 1.00779, \pm .00001$$

Hence,

From ratio 3	....	Fe $= 55.828, \pm .0018$
" " 2	....	$55.836, \pm .0062$
" " 1	....	$55.927, \pm .0018$
" " 7	....	$56.042, \pm .0532$
" " 4	....	$56.092, \pm .1144$
" " 6	....	$56.213, \pm .0026$
" " 5	....	$56.231, \pm .0428$

General mean, Fe $= 55.943, \pm .0011$

The last four of these values are evidently not to be trusted. The first three, which are good, give a general mean of Fe $= 55.880, \pm .0012$. This agrees well with the oxide series of Richards and Baxter, and is probably near the truth.

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,[1] 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 $Ni = 59.05$. The same process was applied also to cobalt, 269.2 parts of the oxide being found equivalent to 1029.9 of AgCl; hence $Co = 58.93$. These values are so nearly equal that their differences were naturally ascribed 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 [2] published some figures, but without details, concerning the atomic weight of nickel. They reduced the oxide by heating in a current of hydrogen, and obtained values ranging from 58.2 to 58.6, when $O = 16$.

In 1856, incidentally to other work, Deville [3] found that 100 parts of pure metallic nickel yielded 262 of sulphate; whence $Ni = 59.26$.

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 [4] 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 estimated, 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

---

[1] Cited by Berzelius. Poggend. Annalen, 8, 184. 1826.
[2] Journ. prakt. Chem., 55, 202. 1852.
[3] Ann. Chim. Phys. (3), 46, 182. 1856.
[4] Poggend. Annalen, 101, 387. 1857.

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

$$CoC_2O_4.2H_2O.$$

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 [1] 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.

---

[1] Poggend. Annalen, 107, 616.

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 1858.[1] He worked with the chlorides and sulphates of nickel and cobalt, using various methods, but publishing few details, as he did not consider the determinations final. The sulphates, taken as anhydrous, were calcined to oxides. From the ratio $NiSO_4 : NiO$, he found $Ni = 58.4$ to 59.0, and from five measurements of the ratio $CoSO_4 :$ Co, $Co = 58.64$ to 58.76. If oxygen is taken as 16, these give for the percentages of oxide in sulphate:

CoO in CoSO₄.	NiO in NiSO₄.
CoO in $CoSO_4$.	NiO in $NiSO_4$.
48.267	48.187
48.307	48.387
Mean, 48.287, $\pm$ .0135	Mean, 48.287, $\pm$ .0675

Hence $Co = 58.706$.　　　　　　　　　　　Hence $Ni = 58.706$.

The chlorides were dried at 100°, but found to retain water; and in most cases were then either fused in a stream of chlorine or of dry, gaseous hydrochloric acid, or else calcined gently with ammonium chloride. The determinations were then made by titration with a standard solution of silver in nitric acid. Five experiments with anhydrous $CoCl_2$ gave $Co = 58.72$ to 58.84. Three more with $CoCl_2$ dried at 100° gave $Co = 58.84$ to 59.02. Three with anhydrous $NiCl_2$ gave $Ni = 58.80$ to 59.00. If the calculations were made with $Ag = 108$ and $Cl = 35.5$, then these data give as proportional to 100 parts of silver:

NiCl₂.	CoCl₂.
$NiCl_2$.	$CoCl_2$.
60.093	60.056
60.185	60.111
	60.111
Mean, 60.139, $\pm$ .0310	60.194
	Mean, 60.118, $\pm$ .0192

Hence $Ni = 58.84$.　　　　　　　　　　　Hence $Co = 58.79$.

In one more experiment $NiCl_2$ was precipitated with a known quantity of silver. The filtrate was calcined, yielding NiO; hence the ratio $2Ag : NiO$, giving $Ni = 59.29$. This experiment needs no farther attention.

In short, according to Marignac, and contrary to Schneider's views, the two atomic weights are approximately the same. Marignac criticises Schneider's earlier paper, holding that the nickel oxalate may have con-

---

[1] Arch. Sci. Phys. Nat. (nouv. série), 1, 372. 1858. Oeuvres Complètes, 1, 575.

tained 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 criticises 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'[1] 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:

.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

Hence $Ni = 58.97$.

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

Hence $Co = 59.03$.

These values for Co and Ni differ by less than a tenth of a unit; here, as elsewhere, the figure for Ni being a trifle the lower.

Combining these data for nickel with Marignac's series, we have—

$$2Ag : NiCl_2 :: 100 : x.$$

Marignac	60.139, $\pm$ .0310
Dumas	60.199, $\pm$ .0062
General mean	60.194, $\pm$ .0061

The cobalt figures will be combined with others later.

---

[1] Ann. Chem. Pharm., 113, 25. 1860.

In 1863 [1] 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 data. The separate samples are indicated by lettering:

Nickel.

	NiO.	Ni.	Per cent. Ni.
A	2.0820	1.6364	78.597
	2.0956	1.6468	78.584
	2.0148	1.5838	78.608
B	2.2069	1.7342	78.581
	2.2843	1.7952	78.589
	2.1329	1.6761	78.583
C	2.2783	1.7911	78.616
	2.1434	1.6845	78.590
	2.4215	1.9030	78.588
D	2.1859	1.7179	78.590
	2.0088	1.5788	78.594
	2.0839	1.6379	78.597
	2.6560	2.0873	78.588

Mean, 78.593, ± .0018

Cobalt.

	CoO.	Co.	Per cent. Co.
A	2.1211	1.6670	78.591
	2.0241	1.5907	78.588
	2.1226	1.6673	78.550
	1.9947	1.5678	78.598
	3.0628	2.4078	78.614
B	2.1167	1.6638	78.603
	1.7717	1.3924	78.591
	1.7852	1.4030	78.591
C	1.6878	1.3264	78.588
	2.2076	1.7350	78.592
D	2.6851	2.1104	78.597
	2.1461	1.6868	78.598
E	3.4038	2.6752	78.595
	2.2778	1.7901	78.589
	2.1837	1.7163	78.596

Mean, 78.592, ± .0023

---

[1] Journ. Chem. Soc. (2), 1, 51. 1863.

These percentages are practically identical, and lead to essentially the same mean value for each atomic weight, namely,

$$Ni = 58.742$$
$$Co = 58.738$$

In a later paper Russell [1] 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 his 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. The data obtained were as follows; the last column giving the weight of hydrogen, computed from its volume, yielded by 100 parts of cobalt or nickel:

Nickel.

	Wt. Ni.	Vol. H in cc.	Ratio.
A	.0906	153.62	3.420
	.1017	172.32	3.418
	.1990	337.06	3.416
	.0997	168.93	3.417
	.1891	319.86	3.412
	.1859	314.75	3.415
	.1838	311.25	3.416
B	.1892	318.75	3.398
	.1806	305.28	3.409
	.2026	333.81	3.404
C	.1933	325.93	3.401
D	.1890	319.77	3.412
	.1942	328.15	3.408
	.1781	301.09	3.410

Mean, 3.411, ± .001

Cobalt.

	Wt. Co.	Vol. H in cc.	Ratio.
•A	.1958	321.36	3.395
	.1905	312.95	3.398
	.1946	319.63	3.397
	.2002	328.96	3.398
B	.1996	328.43	3.403
	.2000	329.55	3.401
	.1721	290.17	3.401
C	.1877	308.97	3.404
	.1935	318.60	3.405
D	.1909	314.73	3.410
	.1834	305.40	3.407

Mean, 3.4017, ± .0009

[1] Journ. Chem. Soc. (2), 7, 294. 1869.

The weight of the hydrogen in these determinations was doubtless computed from Regnault's figures for the density of that gas. Correcting by the new value for the weight of a litre of hydrogen, .089872 gramme, the ratios become:

For nickel .... 3.4211, ± .0010
For cobalt .... 3.4112, ± .0009

Hence Ni = 58.92 and Co = 59.09.

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,[1] 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 $BaSO_4$:

.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, ± .001

Hence Ni = 58.79.

For cobalt Sommaruga used the purpureocobalt 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

Hence Co = 59.91.

---

[1] Sitzungsb. Wien. Akad., 54, 2 Abth., 50. 1866.

28

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,[1] 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,[2] who determined the amount of gold which pure metallic nickel and cobalt could precipitate from a neutral solution of sodio-auric chloride.

In order to obtain pure cobalt Winkler prepared purpureocobalt 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. One hundred 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 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, ± .019

Hence Ni = 59.46.

.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, ± .025

Hence Co = 59.38.

Weselsky's paper,[3] already quoted, 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, ± .029

Hence Co = 59.09.

[1] Poggend. Annalen, 130, 310.
[2] Zeit. anal. Chem., 6, 18. 1867.
[3] Ber. Deutsch. chem. Gesell., 2, 592. 1868.

.8529 grm. $(C_5H_8N)_6Co_2Cy_{12}$ gave .1010 grm. Co. 11.842 per cent.

.6112	"	.0723	"	11.829 "
.7140	"	.0850	"	11.905 "
.9420	"	.1120	"	11.890 "

Mean, 11.8665, ± .0124

Hence Co = 59.04.

Next in order is the work done by Lee [1] in the laboratory of Wolcott Gibbs. Like Weselsky, Lee ignited certain cobalticyanides and also 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 purpureocobalt 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 appeared to be 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, when O = 16. The cobalt results agree remarkably well with those of Weselsky. The following are the data obtained:

Brucia nickelocyanide, $Ni_3Cy_{12}(C_{23}H_{26}N_2O_4)_6H_6.10H_2O.$

Salt.	Ni.	Per cent. Ni.
.3966	.0227	5.724
.5638	.0323	5.729
.4000	.0230	5.750
.3131	.01795	5.733
.4412	.0252	5.712
.4346	.0249	5.729

Mean, 5.7295, ± .0034

Hence Ni = 58.027.

Strychnia nickelocyanide, $Ni_3Cy_{12}(C_{21}H_{22}N_2O_2)_6H_6.8H_2O.$

Salt.	Ni.	Per cent. Ni.
.5358	.0354	6.607
.5489	.0363	6.613
.3551	.0234	6.589
.4495	.0297	6.607
.2530	.0166	6.561
.1956	.0129	6.595

Mean, 6.595, ± .005

Hence Ni = 58.085.

[1] Am. Journ. Sci. (3), 2, 44. 1871.

Brucia cobalticyanide, $Co_2Cy_{12}(C_{23}H_{26}N_2O_4)_6H_6.20H_2O.$

Salt.	Co.	Per cent. Co.
.4097	.0154	3.759
.3951	.0147	3.720
.5456	.0204	3.739
.4402	.0165	3.748
.4644	.0174	3.747
.4027	.0151	3.749

Mean, 3.7437, $\pm$ .0036

Hence $Co = 59.20.$

Strychnia cobalticyanide, $Co_2Cy_{12}(C_{21}H_{22}N_2O_2)_6H_6.8H_2O.$

Salt.	Co.	Per cent. Co.
.4255	.0195	4.583
.4025	.0185	4.596
.3733	.0170	4.554
.4535	.0207	4.564
.2753	.0126	4.577
.1429	.0065	4.549

Mean, 4.5705, $\pm$ .005

Hence $Co = 59.10.$

Purpureocobalt chloride, $Co_2(NH_3)_{10}Cl_6.$

Salt.	Co.	Per cent. Co.
.9472	.2233	23.575
.8903	.2100	23.587
.6084	.1435	23.586
.6561	.1547	23.579
.6988	.1647	23.569
.7010	.1653	23.581

Mean, 23.5795, $\pm$ .0019

Hence $Co = 59.10.$

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

Baubigny's [1] determinations of the atomic weight of nickel are limited

---

[1] Compt. Rend., 97, 951. 1883.

to two experiments upon the calcination of nickel sulphate, and his data are as follows:

$$6.2605 \text{ grm. NiSO}_4 \text{ gave } 3.0225 \text{ NiO.} \quad 48.279 \text{ per cent.}$$
$$4.4935 \qquad " \qquad\quad 2.1695 \quad " \qquad 48.281 \quad "$$

Mean, 48.280

Hence $Ni = 58.741$.

Zimmermann's work, published after his death by Krüss and Alibegoff,[1] was based, like Russell's, upon the reduction of cobalt and nickel oxides in hydrogen. The materials used were purified with great care, and the results were as follows:

Nickel.

NiO.	Ni.	Per cent. Ni.
6.0041	4.7179	78.578
6.4562	5.0734	78.582
8.5960	6.7552	78.585
4.7206	3.7096	78.583
8.2120	6.4536	78.587
9.1349	7.1787	78.585
10.0156	7.8702	78.579
4.6482	3.6526	78.580
8.9315	7.0184	78.580
10.7144	8.4196	78.582
3.0036	2.3602	78.579

Mean, 78.582, $\pm$ .0006

Hence $Ni = 58.704$.

Cobalt.

CoO.	Co.	Per cent. Co.
6.3947	5.0284	78.634
6.6763	5.2501	78.638
5.6668	4.4560	78.633
2.9977	2.3573	78.637
8.7446	6.8763	78.635
3.2625	2.5655	78.636
6.3948	5.0282	78.630
8.2156	6.4606	78.638
9.4842	7.4580	78.636
9.9998	7.8630	78.632

Mean, 78.635, $\pm$ .0002

Hence $Co = 58.889$.

Shortly after the discovery of nickel carbonyl, NiC_4O_4, Mond, Langer and Quincke[2] made use of it with reference to the atomic weight of

---

[1] Ann. Chem., 232, 324. 1886.
[2] Journ. Chem. Soc., 57, 753. 1890.

nickel. The latter was purified by distillation as nickel carbonyl, then converted into oxide, and that was reduced by hydrogen in the usual way.

NiO.	Ni.	Per cent. Ni.
.2414	.1896	78.542
.3186	.2503	78.562
.3391	.2663	78.531

Mean, 78.545, ± .0061

Hence Ni = 58.575.

Schutzenberger's experiments,[1] published in 1892, were also few in number. First, nickel sulphate, dehydrated at 440°, was calcined to oxide.

3.505 grm. NiSO₄ gave 1.690 NiO.	48.217 per cent.

3.505 grm. $NiSO_4$ gave 1.690 NiO.   48.217 per cent.
2.6008 " 1.2561 "   48.297   "

Mean, 48.257, ± .027

Hence Ni = 58.672.

Secondly, nickel oxide was reduced in hydrogen, as follows:

1.6865 grm. NiO gave 1.3245 Ni.   78.535 per cent.
1.2527 " $.9838$ "   78.533   "

Mean, 78.534

Hence Ni = 58.536.

In one experiment with cobalt oxide, 3.491 grm. gave 2.757 Co, or 78.975 per cent. Hence Co = 60.1. In view of the many determinations of this ratio by other observers, this single estimation may be neglected. The experiments on nickel sulphate, however, should be combined with those of Marignac and Baubigny, giving the latter equal weight with Schutzenberger's, thus:

Marignac .... 48.287, ± .0675
Baubigny .... 48.280, ± .027
Schutzenberger .... 48.257, ± .027

General mean .... 48.269, ± .018

From this point on the determination of these atomic weights was temporarily complicated by the questions raised by Krüss as to the truly elementary character of nickel and cobalt. If that which has been called nickel really contains an admixture of some other hitherto unknown element, then all the determinations made so far are worthless, and the investigations now to be considered bear directly upon that question.

---

[1] Compt. Rend., 114, 1149. 1892.

First in order comes Remmler's research upon cobalt.[1] This chemist, asking whether cobalt is homogeneous, prepared cobaltic hydroxide in large quantity, and made a series of successive ammoniacal extracts from it, twenty-five in all. Each extract represented a fraction, from which, by a long series of operations, cobalt monoxide was prepared, and the latter was reduced in hydrogen after the manner of Russell. The actual determinations began with the second fraction, and the data are subjoined, the number of the fraction being given with each experiment:

	CoO.	Co.	Per cent. Co.
2	.09938	.07837	78.859
3	.15021	.11814	78.650
4	.22062	.17360	78.687
5	.39011	.30681	78.647
6	.28820	.22661	78.629
7	.34304	.26968	78.615
8	.43703	.34321	78.532
9	.91477	.71864	78.560
10	.63256	.49661	78.508
11	.32728	.25701	78.529
12	.38042	.29899	78.595
13	.16580	.13027	78.571
14	1.01607	.79873	78.610
15	1.31635	1.03545	78.661
16	.91945	.72315	78.650
17	.53100	.41773	78.668
18	.82381	.64728	78.572
19	.81139	.63754	78.574
20	.76698	.60292	78.610
21	1.13693	.89412	78.643
22	2.00259	1.57495	78.646
23	1.04629	.82185	78.549
24	.48954	.38466	78.576
25	.69152	.54326	78.560

Mean, 78.613, $\pm$ .0099

Hence Co = 58.812.

Considered with reference to the purpose of the investigation, this mean and its probable error have no real significance. But it is very close to the means of other experimenters, and a study of the variations represented by the several fractions seems to indicate fortuity rather than system. Remmler regards his results as indicating lack of homogeneity in his material; but it seems more probable that such differences as exist are due to experimental errors and to impurities acquired in the long process of purification to which each fraction was submitted, rather than to any uncertainty regarding the nature of cobalt itself.

[1] Zeit. anorg. Chem., 2, 221. Also more fully in an Inaugural Dissertation, Erlangen, 1891.

From the same point of view—that is, with reference to the supposed heterogeneity of nickel—Krüss and Schmidt [1] carried out a series of fractionations of the metal by distillation in a stream of carbon monoxide. Nickel oxide, free from obnoxious impurities, was first reduced to metal by heating in hydrogen, after which the current of carbon monoxide was allowed to flow. The latter, carrying its small charge of nickel tetracarbonyl was then passed through a Winkler's absorption apparatus containing pure aqua regia, from which, by evaporation, nickel chloride was obtained, and from that, by reduction in hydrogen, the nickel. Ten such fractions were successively prepared and studied; first, by preparation of NiO and its reduction in hydrogen; and, secondly, in some cases, by the reoxidation of the reduced metal, so as to give a synthetic value for the ratio Ni : O. The data obtained are as follows, the successive fractions being numbered:

<h3 align="center">*Reduction of NiO.*</h3>

	NiO.	Ni.	Per cent. Ni.
1	.3722	.2926	78.614
	.7471	.5870	78.571
2	.7659	.60085	78.450
	.7606	.5961	78.372
3	1.0175	.7984	78.467
	1.2631	.99065	78.430
	1.2582	.9868	78.429
4	.5193	.4076	78.490
	.9200	.7215	78.424
5	.4052	.3179	78.455
	.6518	.5111	78.414
6	.5623	.4399	78.232
	.5556	.4350	78.294
7	.9831	.7724	78.568
	.9765	.7646	78.300
	.9639	.7557	78.400
8	.5756	.4538	78.839
	.56765	.4451	78.411
	.5663	.4438	78.368
	.5449	.4272	78.400
9	.3174	.2491	78.481
	.3148	.2467	78.367
10	.4976	.3904	78.457
	.4961	.3891	78.432

Mean, 78.444, ± .0166

Hence Ni = 58.225.

[1] Zeit. anorg. Chem., 2, 235. 1892.

Oxidation of Ni.

	Ni.	NiO.	Per cent. Ni.
1	.5870	.7471	78.571
2 {	.6011	.7659	78.372
	.5961	.7606	78.359
3 {	.7988	1.0175	78.506
	.9913	1.2631	78.482
	.9868	1.2582	78.429
4 {	.4093	.5193	78.818
	.7216	.9200	78.435
5 {	.3194	.4052	78.825
	.5111	.6518	78.414
6 {	.4415	.5623	78.517
	.4350	.5556	78.294
7 {	.7752	.9831	78.853
	.7667	.9765	78.515
	.7558	.9639	78.411
8 {	.4555	.5756	79.135
	.4456	.56765	78.499
	.44415	.5663	78.430
	.4423	.5642	78.394
9 {	.2508	.3174	79.015
	.2467	.3148	78.367
10 {	.3918	.4976	78.738
	.3891	.4961	78.432

Mean, 78.557, ± .0319

Hence Ni = 58.616.

To these data of Krüss and Schmidt the remarks already made concerning Remmler's work seem also to apply. The variations appear to be fortuitous, and not systematic, although the authors seem to think that they indicate a compositeness in that substance which has been hitherto regarded as elementary nickel. In view of all the evidence, however, I prefer to regard their varying estimations as affected by accidental errors, and to treat their means like others. On this basis, their work combines with previous work as follows, Schutzenberger's measurements of the ratio NiO : Ni being assigned equal weight with those of Mond, Langer and Quincke:

Russell	78.593, ± .0018
Zimmermann	78.582, ± .0006
Mond, Langer, and Quincke...........	78.545, ± .0061
Schutzenberger	78.534, ± .0061
Krüss and Schmidt, reduction series..	78.444, ± .0166
Krüss and Schmidt, oxidation series..	78.557, ± .0319

General mean	78.570, ± .0006

In 1889 Winkler [1] published a short paper concerning the gold method for determining the atomic weights in question, but gave in it no actual measurements. In 1893 [2] he returned to the problem with a new line of attack, and at the same time he took occasion to criticise Krüss and Schmidt somewhat severely. He utterly rejects the notion that either nickel or cobalt contain any hitherto unknown element, and ascribes the peculiar results obtained by Krüss and Schmidt to impurities derived from the glass apparatus used in their experiments. For his own part he now works with pure nickel and cobalt precipitated electrolytically upon platinum, and avoids the use of glass or porcelain vessels so far as possible. With material thus obtained he operates by two distinct but closely related methods, both starting with the metal, nickel or cobalt, converting it next into neutral chloride, and then measuring the chloride gravimetrically in one process, volumetrically in the other.

After precipitation in a platinum dish, the nickel or cobalt is washed with water, rinsed with alcohol and ether, and then weighed. It is next dissolved in pure hydrochloric acid, properly diluted, and by evaporation to dryness and long heating to 150° converted into anhydrous chloride. The nickel chloride thus obtained dissolves perfectly in water, but the cobalt salt always gave a slight residue in which the metal was electrolytically determined and allowed for. In the redissolved chloride, by precipitation with silver nitrate, silver chloride is obtained, giving a direct ratio between that compound and the nickel or cobalt originally taken. The gravimetric data are as follows, with the metal equivalent to 100 parts of silver chloride given in a final column:

Nickel.

Ni.	AgCl.	Ratio.
.3011	1.4621	20.594
.2242	1.0081	20.605
.5166	2.5108	20.570
.4879	2.3679	20.605
.3827	1.8577	20.601
.3603	1.7517	20.568

Mean, 20.590, ± .0049

Hence Ni = 59.03.

Cobalt.

Co.	AgCl.	Ratio.
.3458	1.6596	20.836
.3776	1.8105	20.856
.4493	2.1521	20.877

[1] Ber. Deutsch. chem. Gesell., 22, 891. 1889.
[2] Zeit. anorg. Chem., 4, 10. 1893.

.4488	2.1520	20.855
.2856	1.3683	20.873
.2648	1.2768	20.886

Mean, 20.864, ± .0050

Hence Co = 59.81.

In the volumetric determinations the neutral chloride, prepared as before, was decomposed by means of a slight excess of potassium carbonate, and in the potassium chloride solution, after removal of the nickel or cobalt, the chlorine was measured by titration by Volhard's method with a standard solution of silver. The amount of silver thus used was comparable with the metal taken.

Nickel.

Ni.	Ag.	Ratio.
.1812	.6621260	27.366
.1662	.6079206	27.339
.2129	.7775252	27.382
.2232	.8162108	27.346
.5082	1.8556645	27.386
.1453	.5315040	27.338

Mean, 27.359, ± .0059

Hence Ni = 59.03.

Cobalt.

Co.	Ag.	Ratio.
.177804	.6418284	27.702
.263538	.9514642	27.699
.245124	.8855780	27.679
.190476	.6866321	27.741
.266706	.9629146	27.696
.263538	.9503558	27.731

Mean, 27.708, ± .0064

In view of the possibility that the cobalt chloride of the foregoing experiments might contain traces of basic salt, Winkler, in a supplementary investigation,[1] checked them by another process. To the electrolytic cobalt, in a platinum dish, he added a quantity of neutral silver sulphate and then water. The cobalt gradually went into solution, and metallic silver was precipitated. The weights were as follows:

Co.	Ag.
.2549	.9187
.4069	1.4691

[1] Zeit. anorg. Chem., 4, 462. 1893.

On examination of the silver it was found that traces of cobalt were retained—less than 0.5 mg. in the first determination and less than 0.2 mg. in the second. Taking these amounts as corrections, the two experiments give for the ratio $2Ag:Co::100:x$ the subjoined values:

<div align="center">

27.706

27.687

</div>

These figures confirm those previously found, and as they fall within the limits of the preceding series, they may fairly be included in it, when all eight values give a mean of $27.705, \pm .0050$. Hence $Co = 59.78$.

Still another method, radically different from all of the foregoing processes, was adopted by Winkler in 1894.[1] The metals were thrown down electrolytically upon platinum, and so weighed. Then they were treated with a known excess of a decinormal solution of iodine in potassium iodide, which redissolved them as iodides. The excess of free iodine was then determined by titration with sodium thiosulphate, and in that way the direct ratio between metal and haloid was ascertained. The results were as follows, with the metal proportional to 100 parts of iodine given in the third column:

<div align="center">

Cobalt.

</div>

	Wt. Co.	Wt. I.	Ratio.
First series...	.4999	2.128837	23.482
	.5084	2.166750	23.463
	.5290	2.254335	23.466
	.6822	2.908399	23.456
	.6715	2.861617	23.466
Second series.	.5185	2.209694	23.465
	.5267	2.246037	23.450
	.5319	2.268736	23.445

<div align="right">

Mean, $23.462, \pm .0027$

</div>

Hence $Co = 59.56$.

<div align="center">

Nickel.

</div>

	Wt. Ni.	Wt. I.	Ratio.
First series...	.5144	2.217494	23.251
	.4983	2.148502	23.246
	.5265	2.268742	23.260
	.6889	2.970709	23.243
	.6876	2.965918	23.237
Second series.	.5120	2.205627	23.267
	.5200	2.240107	23.267
	.5246	2.259925	23.267

<div align="right">

Mean, $23.255, \pm .0091$

</div>

Hence $Ni = 59.03$.

---

[1] Zeitsch. anorg. Chem., 8, 1. 1894.

In these experiments, as well as in some previous series, a possible source of error is to be considered in the occlusion of hydrogen by the metals. Accordingly, in a supplementary paper, Winkler[1] gave the results of some check experiments made with iron, which, however, was not absolutely pure. The conclusion is that the error, if existent, must be very small.

In 1895 Hempel and Thiele's work on cobalt appeared.[2] First, cobalt oxide, prepared from carefully purified materials, was reduced in hydrogen. The weights of metal and oxygen are subjoined, with the percentage of cobalt in the oxide deduced from them:

Co.	O.	Percentage.
.90068	.24429	78.664
.79159	.21445	78.686
1.31558	.35716	78.648

Mean, 78.666, ± .0074

Hence Co = 58.998.

In their next series of experiments, excluding a rejected series, Hempel and Thiele weighed cobalt, converted it into anhydrous chloride, and noted the gain in weight. In four of the experiments the chloride was afterwards dissolved, precipitated with silver nitrate, and then the silver chloride was weighed. The data are as follows:

Co.	Cl taken up.	AgCl.
.7010	.8453	. . . . .
.3138	.3793	. . . . .
.2949	.3562	1.4340
.4691	.5657	2.2812
.5818	.7026	2.8303
.5763	.6947	. . . . .
.5096	.6142	2.4813

From these weights we get two ratios, thus:

$Cl_2:Co:100:x.$	$2AgCl:Co::100:x.$
82.929	20.565
82.731	20.564
82.791	20.556
82.924	20.538
82.807	
82.957	Mean, 20.556, ± .0043
82.970	

Mean, 82.873, ± .0241

Hence Co = 58.77.   Hence Co = 58.93.

[1] Zeitsch. anorg. Chem., 8, 291. 1895. See preceding section of this work, on iron, for the detailed determinations.

[2] Zeitsch. anorg. Chem., 11, 73.

The second of these ratios was also studied by Winkler, and the two series combine as follows:

$$\text{Winkler} \dots\dots\dots\dots\dots\dots\dots 20.864, \pm .0050$$
$$\text{Hempel and Thiele} \dots\dots\dots\dots 20.556, \pm .0043$$

$$\text{General mean} \dots\dots\dots\dots 20.687, \pm .0033$$

Hempel and Thiele apply to it a correction for silver chloride retained in solution, but its amount is small and not altogether certain. For present purposes the correction may be neglected.

The atomic weight of nickel was determined by Richards and Cushman [1] from analyses of nickel bromide. This salt, as first prepared, contained traces of oxide, which are to be deducted from the halide compound. In a preliminary series of experiments the following figures were obtained, representing vacuum weights:

$NiBr_2$.	$AgBr$.	Insoluble, mg.	Ratio.
2.26113	3.88769	3.22	58.161
2.80668	4.82431	7.08	58.178
1.41317	2.42880	3.05	58.184
1.71759	2.95307	.88	58.163
2.48565	4.27357	5.24	58.163
4.32997	7.44280	15.83	58.177
2.18072	3.74856	....	58.175

Mean, 58.172, ± .0023

In the second set of analyses, both ratios were determined, namely, with silver and with silver bromide, by the standard methods. The data follow:

$NiBr_2$.	$AgBr$.	Ag.	Ag ratio.	$AgBr$ ratio.
3.28039	5.63892	3.23910	101.275	58.174
2.70044	4.64208	2.66636	101.278	58.173
3.38230	5.81391	3.33990	101.270	58.176
1.33459	2.29435	1.31787	101.268	58.169
1.25054	2.14963	1.23482	101.273	58.175
1.32278	2.27384	1.30629	101.262	58.174
1.24452	2.85805	2.21652	101.263	58.177

Mean, 101.270, ± .0015   58.174, ± .0007

This value for the AgBr ratio, combined with the preliminary series, gives a general mean of 55.1738, ±.0007.

From Ag ratio, Ni = 58.661.
From AgBr ratio, Ni = 58.661.
And Ag : Br :: 100 : 74.082.

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

In a second memoir,[1] Richards and Cushman describe a series of determinations based upon the reduction of nickel bromide by heating in hydrogen. The corrected data appear in the next table:

$NiBr_2$.	Ni.	Per cent. Ni.
2.83325	.76081	26.853
3.21625	.86358	26.851
2.31241	.62094	26.853
2.87953	.77330	26.855
2.29650	.61679	26.858
2.98893	.80272	26.856
5.51291	1.48056	26.856
2.24969	.60415	26.855

Mean, 26.855, ± .0005

Hence $Ni = 58.685$.

In this series a correction was applied for traces of sodium bromide contained in the nickel salt. A similar correction, applied to the former series of determinations, would raise the atomic weight of nickel by 0.015.

The three memoirs upon cobalt, by Richards and Baxter,[2] contain data relative to the bromide, the chloride and the oxide. It is hardly necessary to state that all of the materials employed in the investigation were scrupulously purified, and that all weights were reduced to a vacuum basis. First, as in the case of nickel, the two silver ratios to the bromide were determined. A preliminary set of analyses gave results as follows:

$CoBr_2$.	$AgBr$.	Ratio.
2.25295	3.86818	58.243
2.88763	4.95732	58.250
1.88806	3.24056	58.263

Mean, 58.252, ± .0040

The second and third series of analyses gave both ratios, and may be tabulated together:

$CoBr_2$.	$AgBr$.	Ag.	Ag ratio.	$AgBr$ ratio.
1.33564	2.29296	1.31702	101.414	58.250
2.58129	4.43095	2.54585	101.392	58.256
2.84382	4.88135	2.80449	101.402	58.259
1.83722	3.15368	1.81170	101.409	58.256
2.68584	4.61046	2.64879	101.399	58.255
3.18990	5.47607	......	......	58.252

---

[1] Proc. Amer. Acad., 34, 327. 1899. This memoir contains a very full criticism of all the earlier work on nickel.

[2] Proc. Amer. Acad., 33, 115. 1897. *Ibid.*, 34, 351. 1899. *Ibid.*, 35, 61. 1899. For a criticism of Richards, Cushman and Baxter, see Winkler, Zeitsch. anorg. Chem., 17, 236. 1898.

2.88914	4.95943	2.84891	. 101.412	58.255
2.32840	3.99706	2.29593	101.414	58.253
1.91703	3.29053	1.89033	101.413	58.259

Mean, 101.407,
± .0018

58.255,
± .0007

The two series for the AgBr ratio, combined, give a weighted mean of 58.2549, ± .0007.

From Ag ratio, Co = 58.957.
From AgBr ratio, Co = 58.966.
And Ag : Br : : 100 : 74.075.

In their second memoir Richards and Baxter describe the reduction of cobalt bromide by heating in hydrogen. Three series of experiments were made, and in two of them a correction was necessary for small quantities of sodium bromide contained in the cobalt salt. In the following tables, the corrected weights of cobalt bromide and cobalt are given:

Series I.

$CoBr_2$.	Co.	Per cent. Co.
5.59023	1.50680	26.954
4.61518	1.24381	26.950
3.74498	1.00920	26.948
3.00135	.80899	26.954

Mean, 26.951, ± .0010

Series II.

$CoBr_2$.	Co.	Per cent. Co.
5.32194	1.43428	26.950
7.50786	2.02321	26.948
2.32630	.62677	26.943
7.44694	2.00736	26.956

Mean, 26.949, ± .0021

Series III.

$CoBr_2$.	Co.	Per cent. Co.
5.10891	1.37721	26.957
6.41339	1.72850	26.951
6.59805	1.77876	26.959
3.02854	.81606	26.953

Mean, 26.953, ± .0021

The general mean of the three series is 26.9508, ± .0008. Hence Co = 58.971.

The third memoir of Richards and Baxter gives analyses of cobalt chloride and oxide. First, the chloride was reduced to metal by heating in hydrogen. Hempel and Thiele worked in the opposite direction, heating cobalt in chlorine and thereby effecting the synthesis of the compound. For uniformity of statement I give Richards and Baxter's series in the same form, as the ratio $Cl_2 : Co :: 100 : x$:

$CoCl_2$.	Co.	Ratio.
4.16483	1.89243	83.279
2.30512	1.04723	83.253

Mean, 83.266, ± .0087

Hence $Co = 59.050$.

Hempel and Thiele's figures give for this ratio the figure 82.873, ± .0241. The general mean of both series is 83.220, ± .0082.

Five reductions of cobalt oxide in hydrogen are given, three in one series and two separate experiments with varied methods of manipulation. The results obtained are regarded by Richards and Baxter as unimportant, and they point out the difficulties of the process. Their data, arranged as one series, follow:

CoO.	Co.	Per cent. Co.
7.04053	5.53779	78.656
6.69104	5.26312	78.659
7.83211	6.15963	78.646
7.74240	6.09219	78.686
10.58678	8.32611	78.646

Mean, 78.659, ± .0051

Hence $Co = 58.973$.

This mean combines with former means as follows:

Russell	78.592,	± .0023
Zimmermann	78.635,	± .0002
Remmler	78.613,	± .0099
Hempel and Thiele..........	78.666,	± .0074
Richards and Baxter........	78.659,	± .0051
General mean	78.6324,	± .0002

Here Zimmermann's determinations practically appear alone. The analyses of cobalt chloride by Baxter and Coffin[1] were made by

---

[1] Journ. Amer. Chem. Soc., 28, 1580. 1906. Zeitsch. anorg. Chem., 51, 171.

the usual methods, as refined at Harvard University, and give the two silver ratios. The data, with vacuum weights, are as follows:

$CoCl_2$.	Ag.	AgCl.	Ag ratio.	AgCl ratio.
1.09959	1.82671	2.42676	60.195	45.311
1.47733	2.45398	3.26095	60.201	45.304
3.84133	6.38081	8.47735	60.201	45.313
3.64342	6.05232	......	60.199	.....
2.96315	4.92244	6.54019	60.197	45.307
3.48418	5.78815	7.69084	60.195	45.303
3.29523	5.47410	7.27284	60.197	45.309
1.57655	2.61905	3.48012	60.195	45.302

Mean, 60.1975,   45.3070,
$\pm$ .0006 $\pm$ .0001

From Ag ratio, Co = 58.965.
From AgCl ratio, Co = 58.968.
And Ag : Cl :: 100 : 32.866.

For the silver ratio, $2Ag : CoCl_2 :: 100 : x$, there are two earlier sets of determinations. The three series combine as follows:

Marignac .... 60.118, $\pm$ .0192
Dumas .... 60.228, $\pm$ .0110
Baxter and Coffin........... 60.1975, $\pm$ .0006

General mean .... 60.1975, $\pm$ .0006

In this combination the older series vanish. Their influence is apparent only in the fifth decimal place. .
For the atomic weight of nickel we now have the following ratios:

(1). Per cent. of Ni in $NiC_2O_4.3H_2O$, 29.084, $\pm$ .006
(2). Per cent. of CO_2 from $NiC_2O_4.3H_2O$, 44.098, $\pm$ .027
(3). Per cent. of Ni in $NiC_2O_4.2H_2O$, 31.408, $\pm$ .0026
(4). Per cent. of CO_2 from $NiC_2O_4.2H_2O$, 47.605, $\pm$ .053
(5). Per cent. of Ni in brucia nickelocyanide, 5.7295, $\pm$ .0034
(6). Per cent. of Ni in strychnia nickelocyanide, 6.595, $\pm$ .005
(7). Per cent. of NiO in $NiSO_4$, 48.269, $\pm$ .018
(8). Per cent. of Ni in NiO, 78.570, $\pm$ .0006
(9). $2Ag : NiCl_2 :: 100 : 60.194$, $\pm$ .0061
(10). $2AgCl : Ni :: 100 : 20.590$, $\pm$ .0049
(11). $2Ag : NiBr_2 :: 100 : 101.270$, $\pm$ .0015
(12). $2AgBr : NiBr_2 :: 100 : 58.1738$, $\pm$ .0007
(13). $NiBr_2 : Ni :: 100 : 26.855$, $\pm$ .0005
(14). $2Ag : Ni :: 100 : 27.359$, $\pm$ .0059
(15). $2Au : 3Ni :: 100 : 45.209$, $\pm$ .019
(16). $2BaSO_4 : K_2Ni(SO_4)_2.6H_2O :: 100 : 93.6505$, $\pm$ .001
(17). $Ni : H_2 :: 100 : 3.4211$, $\pm$ .001
(18). $I_2 : Ni :: 100 : 23.255$, $\pm$ .0091

The values used in reducing these ratios are—

Ag = 107.880, ± .00029	C = 12.0038, ± .0002
Cl = 35.4584, ± .0002	N = 14.0101, ± .0001
Br = 79.9197, ± .0003	K = 39.0999, ± .0002
I = 126.9204, ± .00033	Ba = 137.363, ± .0025
S = 32.0667, ± .00075	Au = 197.269, ± .0030

H = 1.00779, ± .00001

In making the computations, the oxalate ratios of Schneider are combined, in order to avoid the uncertain hydration of the compounds. That is, in each set of ratios, instead of calculating from the percentage of nickel or cobalt found, the cross ratio is taken, $2CO_2$: Ni or Co, as the case may be. So much assumed we obtain the following values for Ni:

From ratio 5 ....Ni = 58.027, ± .0345
"   "   1 and 2....................58.044, ± .0319
"   "   3 and 4....................58.064, ± .0648
"   "   6 ....58.085, ± .0441
"   " 11 ....58.661, ± .0033
"   " 12 ....58.661, ± .0028
"   "   8 ....58.662, ± .0017
"   " 13 ....58.685, ± .0009
"   "   7 ....58.708, ± .0381
"   " 16 ....58.789, ± .0068
"   " 17 ....58.917, ± .0172
"   "   9 ....58.958, ± .0131
"   " 10 ....59.027, ± .0141
"   " 14 ....59.030, ± .0127
"   " 18 ....59.031, ± .0231
"   " 15 ....59.456, ± .0250

General mean, Ni = 58.682, ± .00074

This mean lies within the limits of variation of Richards and Cushman's determinations, and must be regarded as satisfactory. Their work and Zimmermann's dominates the entire combination.

For cobalt we have twenty ratios, as follows:

(1). Per cent. of Co in $CoC_2O_4.2H_2O$, 32.5555, ± .0149
(2). Per cent. of CO_2 from $CoC_2O_4.2H_2O$, 47.7475, ± .0213
(3). Per cent. of Co in CoO, 78.6324, ± .0002
(4). Per cent. of Co in purpureocobalt chloride, 23.6045, ± .0018
(5). Per cent. of Co in phenylammonium cobalticyanide, 11.8665, ± .0124
(6). Per cent. of Co in ammonium cobalticyanide, 21.943, ± .029
(7). Per cent. of Co in brucia cobalticyanide, 3.7437, ± .0036
(8). Per cent. of Co in strychnia cobalticyanide, 4.5705, ± .005
(9). Per cent. of CoO in $CoSO_4$, 48.287, ± .0135
(10). $2Ag : CoCl_2 :: 100 : 60.1975$, ± .0006

(11). $2AgCl:CoCl_2::100:45.307, \pm .0011$
(12). $2Ag:Co::100:27.705, \pm .0050$
(13). $2AgCl:Co::100:20.687, \pm .0033$
(14). $Cl_2:Co::100:83.220, \pm .0082$
(15). $2Ag:CoBr_2::100:101.407, \pm .0018$
(16). $2AgBr:CoBr_2::100:58.2549, \pm .0007$
(17). $CoBr_2:Co::100:26.9508, \pm .0008$
(18). $2Au:3Co::100:45.151, \pm .025$
(19). $Co:H_2::100:3.4110, \pm .0009$
(20). $I_2:Co::100:23.462, \pm .0027$

Hence, for the atomic weight of cobalt.

From ratio 9	....................$Co = 58.706, \pm .0286$
" " 3	..........................58.880, $\pm$ .0006
" " 15	..........................58.957, $\pm$ .0040
" " 10	..........................58.965, $\pm$ .0014
" " 16	..........................58.966, $\pm$ .0027
" " 11	..........................58.968, $\pm$ .0032
" " 17	..........................58.971, $\pm$ .0019
" " 14	..........................59.017, $\pm$ .0059
" " 5	..........................59.042, $\pm$ .0630
" " 19	..........................59.091, $\pm$ .0156
" " 6	..........................59.093, $\pm$ .0810
" " 8	..........................59.100, $\pm$ .0647
" " 4	..........................59.183, $\pm$ .0048
" " 7	..........................59.203, $\pm$ .0570
" " 13	..........................59.305, $\pm$ .0095
" " 18	..........................59.378, $\pm$ .0330
" " 20	..........................59.556, $\pm$ .0069
" " 12	..........................59.776, $\pm$ .0108
" " 1 and 2	....................60.006, $\pm$ .0384

General mean, $Co = 58.915, \pm .0005$

It is evident that in this combination, ratio 3, representing principally the work of Zimmermann, receives excessive weight. For that reason, and also on chemical grounds, the final mean is probably too low. If, however, we arbitrarily assign to ratio 3 the " probable error " and weight of the next best ratio, No. 10, the general mean then becomes

$$Co = 58.961, \pm .0008$$

This is probably not far from the truth; but the change thus effected serves to illustrate the fact that the rigorous mathematical combination is not always conclusive. Although the mathematical method is most useful, it cannot do away with the exercise of judgment as based upon other knowledge than that shown in the mere figures.

That the atomic weight of cobalt is higher than that of nickel clearly appears from the evidence. Nevertheless, attempts have been made, and

that recently, to prove the opposite. For example, Parker and Sexton[1] assert that in fifteen electrolytic comparisons of silver and cobalt, they have obtained a mean value of Co = 57.7, which is lower than the atomic weight of nickel. Barkla and Sadler,[2] in studying the permeability of metals to the secondary Röntgen rays, have found that property to be a periodic function of the atomic weights. By interpolation in the periodic curve so obtained they find values for Ni ranging between 61.2 and 61.6, whereas the currently accepted atomic weight appears to be anomalous, at least as regards the physical property now under consideration. These conclusions, however, cannot weigh very heavily as against the clear chemical evidence. As for Parker and Sexton's work, the authors give no details which would furnish an adequate basis for discussion.

RUTHENIUM.

The atomic weight of this metal has been determined by Claus and by Joly. Although Claus[3] employed several methods, we need only consider his analyses 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 the analyses are as follows:

Ru.	2KCl.	3Cl.
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 = 103.24
From percentage of 2KCl......... " = 107.41
From percentage of 3Cl.......... " = 97.09

These results are obviously of little importance, especially since the best of them is not in accord with the position of ruthenium in the periodic system. The work of Joly is more satisfactory.[4] Several com-

---

[1] Nature, 76, 316. 1907.
[2] Phil. Mag. (6), 14, 408. 1907.
[3] Journ. prakt. Chem., 34, 435. 1845.
[4] Compt. Rend., 108, 946.

pounds of ruthenium were analyzed by reduction in a stream of hydrogen with the following results:

First, reduction of RuO_2:

RuO_2.	Ru.	Per cent. Ru.
2.1387	1.6267	76.060
2.5846	1.9658	76.058
2.3682	1.8016	76.075
2.8849	2.1939	76.046

Mean, 76.060, ± .0040

Second, reduction of the salt $RuCl_3.NO.H_2O$:

Per cent. Ru.
39.78
39.66

Mean, 39.72, ± .0405

Third, reduction of $RuCl_3.NO.2NH_4Cl$:

Per cent. Ru.
29.44
29.47

Mean, 29.455, ± .0101

To reduce these ratios we have—

$$Cl = 35.4584, \pm .0002$$
$$N = 14.0101, \pm .0001$$
$$H = 1.00779, \pm .00001$$

Hence,

From $RuCl_3.NO.2NH_4Cl$ ....Ru = 101.622, ± .0378
" RuO_2 ....101.668, ± .0178
" $RuCl_3.NO.H_2O$ ....101.739, ± .1242

General mean, Ru = 101.661, ± .0160

More data are needed in order to thoroughly establish the atomic weight of ruthenium.

RHODIUM.

Berzelius [1] 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 are as follows:

In Na_3RhCl_6.

Rh.	3NaCl.	3Cl.
26.959	45.853	27.189
27.229	45.301	27.470
.....	.....	27.616
Mean, 27.094	Mean, 45.577	Mean, 27.425

In K_2RhCl_5.

Rh.	2KCl.	3Cl.
28.989	41.450	29.561

From analyses of the sodium salt we get the following values for Rh:

From per cent. of metal................ Rh = 104.72
From per cent. of NaCl................ " = 103.08
From per cent. of 3Cl................... " = 106.10
From ratio between 3Cl and Rh.......... " = 104.85
From ratio between 3NaCl and Rh...... " = 104.27

These are discordant figures; but the last one fits in fairly well with the values calculated from the potassium compound, which are as follows:

From per cent. of metal................ Rh = 104.30
From per cent. of KCl................... " = 104.26
From per cent. of Cl................... " = 104.36
From Rh:5Cl ratio..................... " = 104.32
From Rh:2KCl ratio................... " = 104.29

Mean .... Rh = 104.37

The determinations by Jörgensen [2] seem to have been preliminary, but are good so far as they go. Rhodium pentamine chloride, $Rh(NH_3)_5Cl_3$, was ignited in hydrogen, and the residual metal was cooled in an atmosphere of carbon dioxide. The data are as follows:

Chloride.	Rhodium.	Per cent. Rh.
3.5180	1.2310	34.991
2.1507	.7517	34.951
.9091	.3182	35.002
1.9889	.6960	34.994
	Mean,	34.984, ± .0076

Hence Rh = 103.06.

[1] Poggend. Annalen, 13, 435. 1828.
[2] Journ. prakt. Chem. (2), 27, 486. 1883.

In a single analysis of the corresponding bromide, 1.2736 grammes gave 0.3065 of rhodium, or 24.065 per cent. Hence Rh = 102.97. In another experiment, 1.2675 grammes of bromide gave 1.6683 of AgBr. Hence Rh = 103.12.

Scubert and Kobbe [1] determined the atomic weight in the same way, that is, by igniting rhodium pentamine chloride in hydrogen and weighing the residual metal. Their results are given below:

$Rh(NH_3)_5Cl_3$.	Rh.	Per cent. Rh.
1.8585	.6496	34.953
1.5560	.5435	34.929
1.5202	.5310	34.930
2.0111	.7031	34.961
1.8674	.6528	34.958
2.4347	.8513	34.965
2.3849	.8338	34.962
2.5393	.8881	34.974
1.4080	.4920	34.943
1.4654	.5123	34.960
		Mean, 34.954, ± .0032

Hence Rh = 102.94.

In the sixth experiment the ammonium chloride formed was collected in a bulb tube, and estimated by weighing as silver chloride. 3.5531 grms. of AgCl were obtained. Hence Rh = 103.12.

The same process was followed by Hüttlinger,[2] who obtained almost exactly the same result. His figures are as follows:

Chloride.	Rh.	Per cent. Rh.
1.60574	.56124	34.951
1.67310	.58492	34.960
1.30182	.45507	34.956
		Mean, 34.956, ± .0020

Hence Rh = 102.93.

Another series, somewhat later, by H. Dittmar,[3] gave the subjoined figures, with vacuum weights:

Chloride.	Rh.	Per cent. Rh.
2.01526	.70465	34.967
1.83589	.64173	34.954
1.57210	.54934	34.943
2.17528	.76046	34.959
2.03911	.71271	34.952
2.20000	.76890	34.950
1.02840	.35941	34.948
		Mean, 34.953, ± .0020

Hence Rh = 102.93.

---

[1] Liebig's Annalen, 260, 318. 1890.
[2] Sitzungsb. phys. med. Soz. Erlangen, 39, 1. 1907.
[3] Sitzungsb. phys. med. Soz. Erlangen, 40, 184. 1909.

The four series of analyses of the chloride combine as follows:

Jörgensen .... 34.984, ± .0076
Seubert and Kobbe............ 34.954, ± .0032
Hüttlinger .... 34.956, ± .0020
Dittmar .... 34.953, ± .0020

General mean .... 34.955, ± .0013

The work of Hüttlinger and Dittmar was done in the laboratory at Erlangen, under the direction of Gutbier. So, too, was that of Renz,[1] who made similar analyses of rhodium pentamine bromide, $Rh(NH_3)_5Br_3$. His data, with vacuum weights, are as follows:

Bromide.	Rh.	Per cent. Rh.
.87624	.21057	24.031
1.56500	.37638	24.049
2.04033	.49069	24.049
2.00120	.48135	24.053
1.89278	.45525	24.051
2.30210	.55416	24.071
1.02065	.24555	24.058
1.31485	.31622	24.049
1.80060	.44766	24.059
1.51040	.36339	24.059

Mean, 24.053, ± .0022

Hence Rh = 102.91.

Ignoring the early work of Berzelius, and the single analysis by Jörgensen of rhodium pentamine bromide, we have two ratios from which to compute the atomic weight of rhodium:

(1). $Rh(NH_3)_5Cl_3:Rh::100:34.955$, ± .0013
(2). $Rh(NH_3)_5Br_3:Rh::100:24.053$, ± .0022

To reduce these we have—

Cl = 35.4584, ± .0002   N = 14.0101, ± .0001
Br = 79.9197, ± .0003   H = 1.00779, ± .00001

Hence,

From ratio 2 ....Rh = 102.906, ± .0099
"   "   1 ....102.934, ± .0044

General mean, Rh = 102.929, ± .0040

---

[1] Inaug. Diss., Erlangen, 1909.

PALLADIUM.

The first work upon the atomic weight of palladium seems to have been done by Berzelius. In an early paper [1] he states that 100 parts of the metal united with 28.15 of sulphur. Hence $Pd = 113.91$, a result which is clearly of no present value.

In a later paper [2] 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.	Cl₂.
32.726	46.044	21.229
32.655	45.741	21.604
Mean, 32.690	Mean, 45.892	Mean, 21.416

From these percentages, calculating directly, very discordant results are obtained:

From percentage of metal................ $Pd = 106.86$
From percentage of KCl.................. " $= 104.90$
From percentage of Cl₂ (loss)........... " $= 111.11$

Obviously, the only way to get satisfactory figures is to calculate from the ratio between the Pd and 2KCl, eliminating thus the influence of water in the salt. The two experiments give, as proportional to 100 parts of KCl, the following of Pd:

71.075
71.391

Mean, 71.233, $\pm$ .1066

Hence $Pd = 106.22$.

In 1847 Quintus Icilius [3] published a determination, which need be given only for the sake of completeness. He ignited potassium palladiochloride in hydrogen, and found the following amounts of residue. His weights are here recalculated into percentages:

---

[1] Poggend. Annalen, 8, 177. 1826.
[2] Poggend. Annalen, 13, 454. 1828.
[3] " 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.

64.708
64.965
64.781

Mean, 64.818

From this mean, Pd = 112.05. This result has no present value.

In 1889 Keiser's first determinations of this constant appeared.[1] Finding the potassium palladiochloride to contain "water of decrepitation," he abandoned its use and resorted to palladiammonium chloride, $Pd(NH_3Cl)_2$, as the most available compound for his purpose. This salt, heated in hydrogen, yields spongy palladium, which was allowed to cool in a current of dry air, in order to avoid gaseous occlusions. The salt itself was dried, previous to analysis, first over sulphuric acid, and then in an air bath at a temperature from 120° to 130°. Two series of experiments were made, the second series starting out from palladium produced by the first series. The data are as follows:

First Series.

$Pd(NH_3Cl)_2$.	Pd.	Per cent. Pd.
.83260	.41965	50.402
1.72635	.86992	50.391
1.40280	.70670	50.378
1.57940	.79562	50.375
1.89895	.95650	50.370
1.48065	.74570	50.363
1.56015	.78585	50.370
1.82658	.92003	50.369
2.40125	1.20970	50.378
1.10400	.55629	50.389
.93310	.47010	50.380

Mean, 50.379, ± .0008

Reduced to vacuum this becomes 50.360.
Hence Pd = 106.51.

Second Series.

$Pd(NH_3Cl)_2$.	Pd.	Per cent. Pd.
2.61841	1.31900	50.374
2.23420	1.12561	50.381
1.73553	.87445	50.385
1.69160	.85210	50.372
1.72403	.86825	50.362
1.12222	.56535	50.378
1.17457	.59200	50.401
2.42760	1.22280	50.371

Mean, 50.378, ± .0028

Reduced to vacuum, 50.359

Hence Pd = 106.50.

[1] Am. Chem. Journ., 11, 398. 1889.

The reductions to vacuum are neglected by Keiser himself, but are here added in order to secure uniformity with later results by the same author.

Bailey and Lamb[1] made experiments upon several compounds of palladium, but finally settled upon palladiammonium chloride, like Keiser. Two preliminary experiments, however, with potassium palladiochloride are given, in which the salt was reduced in hydrogen, and both Pd and KCl were weighed. The data are as follows, with the ratio (calculated as with Berzelius' experiments) given in a third column:

$2KCl$.	Pd.	Ratio.
1.49767	1.05627	70.528
.90484	.63738	70.441
		Mean, 70.485, $\pm$ .0290

Hence Pd = 105.11.

The palladiammonium chloride was studied by two methods. First, weighed quantities of the salt were reduced in hydrogen, the ammonium chloride so formed was collected in an absorption apparatus, and then precipitated with silver nitrate. The weights found were as follows, with the $Pd(NH_3Cl_2)$ proportional to 100 parts of silver chloride given in the third column:

$Pd(NH_3Cl)_2$.	$AgCl$.	Ratio.
1.24276	1.682249	73.879
1.08722	1.468448	74.040
1.47666	2.000164	73.828
1.34887	1.837957	73.390
1.74569	2.362320	73.898
		Mean, 73.807, $\pm$ .0742

Hence Pd = 106.60. Bailey and Lamb regard this as too high, and suspect loss of NH_4Cl during the operation.

The second series of data resemble Keiser's. The salt was reduced in hydrogen, and the spongy palladium was weighed in a Sprengel vacuum. The data are as follows:

	$Pd(NH_3Cl)_2$.	Pd.	Per cent. Pd.
A	1.890597	.947995	50.143
	1.874175	.940271	50.170
B	1.307076	.654687	50.088
	1.340045	.633207	50.238
	1.905536	.955950	50.167
	1.685582	.846472	50.218
C	1.691028	.849120	50.213
	2.112530	1.059690	50.162
	2.110653	1.057910	50.122
	1.969100	.988155	50.184
			Mean, 50.171, $\pm$ .0099

[1] Journ. Chem. Soc., 61, 745. 1892.

Hence Pd$=105.71$. Bailey and Lamb's weighings are all reduced to a vacuum.

Keller and Smith,[1] reviewing Keiser's work, find that palladiam-monium chloride, prepared as Keiser prepared it, may retain traces of foreign metals, and especially of copper. Accordingly, they prepared a quantity of the salt, after a thorough and elaborate process of purification, dried it with extreme care, and then determined the palladium by electrolysis in silver-coated platinum dishes. The precipitated palladium was dried under varying conditions, concerning which the original memoir must be consulted, and was proved to be free from occluded hydrogen. By this method two sets of experiments were made to determine the atomic weight of palladium; but for present purposes the two may fairly be treated as one. The data obtained are as follows, but the weights do not appear to have been reduced to a vacuum:

$Pd(NH_4Cl)_2$.	Pd.	Per cent. Pd.
1.29960	.65630	50.504
A 1.05430	.53253	50.510
1.92945	.97455	50.509
1.94722	.98343	50.504
1.08649	.54870	50.502
1.28423	.64858	50.503
B 1.68275	.85010	50.519
1.69113	.85431	50.517
1.80805	.91310	50.502

Mean, 50.508, $\pm$ .0014

Hence Pd$=107.14$, a result notably higher than Keiser's.

Keller and Smith account for the difference between their determinations and Keiser's partly by the assumption that the materials used by the latter were not pure, and partly by considerations based on the process. In order to clarify the latter part of the question they made three sets of experiments by Keiser's method, slightly varying the conditions. First, the chloride was not pulverized before ignition, and slight decrepitation took place, while dark stains of palladium appeared in the reduction tube, indicating loss by volatilization. Secondly, the chloride was prepared from crude palladium exactly as described by Keiser, but was pulverized before reduction. No decrepitation ensued, but traces of palladium were volatilized. The third series, also on finely pulverized material, was like the second; but the palladiammonium chloride was purified by Keller and Smith's process. The three series, here treated as one, are as follows:

---

[1] Amer. Chem. Journ., 14, 423. 1892.

	$Pd(NH_3Cl)_2.$	$Pd.$	$Per\ cent.\ Pd.$
First series..	.62955	.31743	50.422
	.77270	.38942	50.397
	.83252	.41918	50.350
	.99055	.49895	50.371
Second series..	1.02175	.51468	50.372
	1.10325	.55590	50.388
	.66690	.33590	50.367
	.86840	.43733	50.360
	1.41430	.71255	50.382
	1.15234	.58050	50.376
Third series..	.96229	.48502	50.403
	.97804	.49294	50.401
	.94253	.47517	50.414
	.86090	.43405	50.430

Mean, 50.388, ± .0043

Hence Pd = 106.63.

The three series seem to be fairly in agreement between themselves, and with Keiser's work, but diverge seriously from the electrolytic data.

Keller and Smith also attempted to determine the atomic weight of palladium by heating the palladiammonium chloride in sulphuretted hydrogen, and so converting it into the sulphide, PdS. These data were obtained:

$Pd(NH_3Cl)_2.$	$PdS.$	$Per\ cent.\ PdS.$
.71699	.47066	65.644
1.31688	.86445	65.659

Mean, 65.651, ± .0051

Hence Pd = 107.30. This result, however, is affected by the work of Petrenko-Kritschenko,[1] who has shown the existence of the sulphide PdS to be uncertain.

Joly and Leidié,[2] in their determinations of this atomic weight, returned to the potassium palladiochloride, K_2PdCl_4. In their first series of experiments the salt was dried in vacuo at ordinary temperatures. It was then electrolyzed in a solution acidulated with hydrochloric acid, both the deposited palladium and the potassium chloride being weighed. The palladium was dried, ignited in a stream of hydrogen and cooled in an atmosphere of carbon dioxide. The results were as follows, with the column added by me giving the Pd equivalent to 100 parts of KCl:

---

[1] Zeit. anorg. Chem., 4, 251. 1893.
[2] Compt. Rend., 116, 147. 1893.

K_2PdCl_4.	Pd.	2KCl.	Ratio.
1.0255	.3919	.5520	70.996
1.2178	.3937	.5551	70.924
1.2518	.4048	.5687	71.016

Mean, 70.979, ± .0188

Hence Pd = 105.84.

This series was rejected by the authors, because the salt was found to contain water—in one case 0.23 per cent. This error, however, should not invalidate the Pd:KCl ratio. In a second series the palladiochloride was dried in vacuo at 100°, giving the following data:

K_2PdCl_4.	Pd.	2KCl.	Ratio.
1.3635	.4422	.6186	71.484
3.0628	.9944	1.3929	71.391
1.4845	.4816	.6782	71.011
1.7995	.5838	.8206	71.143

Mean, 71.257, ± .0736

These experiments seem to be less concordant than the preceding set. It must be noted, however, that the authors reject the KCl determinations and compute directly from the ratio between the salt and the metal. But the ratio here chosen agrees best with the determinations made by other observers, giving for this series the mean value Pd = 106.26, and is, moreover, uniform with the data given by Berzelius and by Bailey and Lamb.

Joly and Leidié also give two experiments made by reducing the K_2PdCl_4 in hydrogen, with the subjoined results:

K_2PdCl_4.	Pd.	2KCl.	Ratio.
2.4481	.7949	1.1168	71.177
1.8250	.5930	.8360	70.933

Mean, 71.055, ± .0823

Hence Pd = 105.96.

Combining these data with previous series, we have—

Berzelius	71.233, ± .1066
Bailey and Lamb	70.485, ± .0290
Joly and Leidié, first	70.979, ± .0188
Joly and Leidié, second	71.257, ± .0736
Joly and Leidié, third	71.055, ± .0823
General mean	70.865, ± .0150

In view of the discordance among the determinations hitherto cited and because of the criticisms made by Keller and Smith, Keiser, jointly

with Miss Mary B. Breed,[1] repeated his former work, with some varia-
tions, and added precautions to ensure accuracy. His general method
was the same as before, namely. the reduction of palladiammonium
chloride by a stream of hydrogen. First, palladium was purified by
distillation as $PdCl_2$ at low red heat in a current of chlorine. From this
chloride the palladiammonium salt was then prepared. Upon heating
the compound gently in a stream of hydrogen, decomposition ensued
absolutely without decrepitation or loss of palladium by volatilization.
Neither source of error existed. The results obtained were these:

$Pd(NH_4Cl)_2$.	Pd.	Per cent. Pd.
1.60842	.80997	50.358
2.08295	1.04920	50.371
2.02440	1.01975	50.373
2.54810	1.28360	50.375
1.75505	.88410	50.375

Mean. 50.370, $\pm$ .0023
Reduced to vacuum. 50.351

Hence $Pd = 106.46$.

In a second series of experiments. palladium was purified as in the
earlier investigation, but with special care to eliminate rhodium, iron.
copper, gold, mercury, etc. The palladiammonium salt prepared from
this material gave as follows:

$Pd(NH_5Cl)_2$.	Pd.	Per cent. Pd.
1.50275	.75685	50.364
1.23672	.62286	50.365
1.34470	.67739	50.375
1.49059	.75095	50.379

Mean, 50.371, $\pm$ .0026
Reduced to vacuum. 50.352

Hence $Pd = 106.47$.

Here, again, no loss from decrepitation or volatilization occurred.
although evidence of such loss was carefully sought for.

Hardin,[2] in 1899, made three series of determinations of the atomic
weight of palladium, by reduction of three palladium salts in hydrogen.
His results, with weights reduced to a vacuum, are as follows:

---

[1] Am. Chem. Journ., 16, 20. 1894.
[2] Journ. Amer. Chem. Soc., 21, 947.

First: Reduction of diphenyl-pallad-diammonium chloride,
$$Pd(C_6H_5.NH_2Cl)_2:$$

Salt.	Pd.	Per cent. Pd.
.98480	.28953	29.400
1.10000	.32310	29.376
1.02820	.30210	29.381
1.19230	.35040	29.389
1.40550	.41300	29.385
1.26000	.37040	29.397
1.25510	.66310	29.404

Mean, 29.390, ± .0029

Hence $Pd = 107.01$.

Second: Reduction of diphenyl-pallad-diammonium bromide,

$$Pd(C_6H_5.NH_2Br)_2:$$
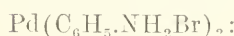
Salt.	Pd.	Per cent. Pd.
.88567	.20917	23.617
1.31280	.31000	23.614
1.50465	.35540	23.620
2.01635	.47635	23.624
2.92300	.69080	23.633

Mean, 23.622, ± .0023

Hence $Pd = 107.01$.

Third: Reduction of palladium ammonium bromide, $(NH_4)_2PdBr_4$:

Salt.	Pd.	Per cent. Pd.
.77886	.18006	23.118
1.53109	.35381	23.108
2.75168	.63614	23.118
1.88136	.43478	23.110

Mean, 23.1135, ± .0018

Hence $Pd = 106.95$.

These determinations are notably higher than those made by other methods. After reduction, the palladium was heated to redness for two hours in a stream of dry air, to remove possible carbon. It was then heated again in hydrogen, and finally cooled in a current of air. Hydrogen could hardly have been occluded in the final product.

Amberg,[1] whose determinations appeared in 1905, resorted to palladiammonium chloride as his initial substance. Three series of analyses were made, with scrupulously purified material, and all weights were reduced to a vacuum. First, the salt was reduced electrolytically. The

---

[1] Liebig's Annalen, 341, 255.

precipitated palladium was weighed, and in the rinsings from it the chlorine was determined as silver chloride. The data are subjoined, with the ratio $2AgCl : Pd(NH_3Cl)_2 :: 100 : x$ in the fifth column:

Salt.	Pd.	AgCl.	Per cent. Pd.	AgCl ratio.
1.06045	.53609	......	50.553	.....
1.00028	.50528	1.35867	50.493	73.622
1.66386	.84085	2.25437	50.541	73.807
.83195	.42092	1.12282	50.594	74.095
1.91591	.96886	2.59799	50.569	73.746

Mean, 50.550, Mean, 73.818,
± .0110   ± .0677

From the percentage of metal, Pd = 107.32.
From the AgCl ratio, Pd = 106.63.

Amberg's second series of analyses resembles the first, except that the palladium was precipitated by hydrazin sulphate. The percentage of metal is given by Amberg, but not the weights actually obtained:

Salt.	AgCl.	Per cent. Pd.	AgCl ratio.
1.32493	1.78656	50.12	74.171
1.02642	1.39247	50.29	73.712
1.30335	1.76875	50.36	73.518
1.59709	2.16641	....	73.721
1.88622	2.55028	50.49	73.961
2.59665	3.51783	50.68	73.812

Mean, 50.388, Mean, 73.814,
± .2064   ± .0614

From percentage of metal, Pd = 106.63.
From AgCl ratio, Pd = 106.62.

The silver chloride ratio combines with previous determinations as follows:

Bailey and Lamb............. 73.807, ± .0742
Amberg, first series........... 73.818, ± .0677
Amberg, second series........ 73.814, ± .0614

General mean .... 73.813, ± .0388

In his third series of analyses Amberg determined only the palladium, which was precipitated electrolytically from a sulphuric acid solution of the palladiammonium chloride with a rapidly rotating anode. This

series is excellent, but the preceding series of palladium determinations
are negligible:

Salt.	Pd.	Per cent. Pd.
.62446	.31470	50.396
.83878	.42280	50.407
1.50282	.75725	50.389
1.06704	.53763	50.385
1.98342	.99971	50.403
1.53093	.77153	50.396
1.18995	.59971	50.398
.62635	.31572	50.406
1.76110	.88739	50.388
3.79639	1.91298	50.389
3.97553	2.00333	50.392
4.62100	2.32834	50.386

Mean, 50.395, ± .0015

Hence Pd = 106.66.

The atomic weight determinations by Krell, Woernle and Haas were
all made in the laboratory of Professor Gutbier at Erlangen. Krell[1]
reduced palladiammonium (palladosamine) chloride in hydrogen, and
afterwards heated the reduced metal in a stream of carbon dioxide.
His figures, with vacuum weights, are subjoined:

Salt.	Pd.	Per cent. Pd.
1.83034	.92197	50.372
1.73474	.87433	50.401
1.92532	.96524	50.396
2.63544	1.32868	50.416
3.23840	1.63175	50.387

Mean, 50.3945, ± .0050

Hence Pd = 106.65. The first, aberrant determination in the series,
is rejected by Krell.

Woernle[2] also made analyses of palladiammonium chloride. The first
two reductions were effected in hydrogen, the other determinations were
electrolytic. His figures, with vacuum weights, are as follows:

Salt.	Pd.	Per cent. Pd.
2.94682	1.48493	50.391
1.83140	.92296	50.396
1.02683	.51479	50.397
1.22435	.61708	50.401
1.46735	.73944	50.393
.59796	.30139	50.403
2.64584	1.33329	50.392

Mean, 50.396, ± .0012

Hence Pd = 106.66.

---

[1] Inaugural Dissertation, Erlangen, 1906.
[2] Sitzungsb. phys. med. Soz., Erlangen, 38, 278. 1907.

Haas [1] analyzed palladiammonium bromide, $Pd(NH_3Br)_2$, by reduction in hydrogen. The reduced metal was subsequently heated in carbon dioxide. His data, with vacuum weights, are as follows:

Bromide.	Pd.	Per cent. Pd.
2.06470	.73274	35.488
1.73455	.61563	35.492
2.64773	.93978	35.493
1.29106	.45821	35.491
2.26758	.80490	35.495
1.90770	.67704	35.489
1.77729	.63082	35.493

Mean, 35.492, ± .0006

Hence $Pd = 106.69$.

Kemmerer [2] analyzed two palladiammonium compounds, the chloride and the cyanide, both by reduction in hydrogen, with subsequent cooling of the reduced metal in an atmosphere of nitrogen. Vacuum weights are given throughout. With the chloride, two sets of determinations were made, on two distinct preparations, but both series are here treated as one. The data are subjoined:

	Chloride.	Pd.	Per cent. Pd.
A	.89187	.44885	50.327
	.77931	.39218	50.324
	.66980	.33711	50.330
	1.08373	.54541	50.327
	.96048	.48338	50.327
B	.95615	.48129	50.336
	.94087	.47356	50.332
	.90106	.45353	50.333
	1.16994	.58908	50.351

Mean, 50.332, ± .0018

Hence $Pd = 106.39$.

With the cyanide, $Pd(NH_3CN)_2$, Kemmerer obtained the following results:

Cyanide.	Pd.	Per cent. Pd.
.85860	.47463	55.280
1.19378	.66002	55.288
1.41818	.78408	55.288
1.05254	.58206	55.301
1.39510	.77153	55.303
1.66196	.91881	55.285

Mean, 55.291, ± .0025

[1] Inaug. Dissertation, Erlangen, 1908.
[2] Thesis, University of Pennsylvania, 1908.

Hence Pd = 106.47. Why these analyses should give low values is unexplained.

The various series of figures for the percentage of palladium in palladiammonium chloride now combine thus:

Keiser, first series	50.360,	± .0008
Keiser, second series	50.359,	± .0028
Bailey and Lamb	50.171,	± .0099
Keller and Smith, electrolytic	50.508,	± .0014
Keller and Smith, hydrogen series	50.388,	± .0043
Keiser and Breed, first series	50.351,	± .0023
Keiser and Breed, second series	50.352,	± .0026
Amberg, first series	50.550,	± .0110
Amberg, second series	50.388,	± .2064
Amberg, third series	50.395,	± .0015
Krell	50.3945,	± .0050
Woernle	50.396,	± .0012
Kemmerer	50.332,	± .0025
General mean	50.3882,	± .0005

Like Haas, Gebhardt[1] also made analyses of palladiammonium bromide, and by the same method. His figures, with vacuum weights, are as follows:

Bromide.	Pd.	Per cent. Pd.
3.32462	1.17984	35.488
2.68383	.95245	35.488
1.40117	.49731	35.492
2.61673	.92877	35.494
2.64229	.93787	35.495
2.54424	.90293	35.489
2.00456	.71143	35.491

Mean, 35.491, ± .0007

Hence Pd = 106.68.

The work of Haas and Gebhardt was done under the direction of Gutbier, who has combined their material in a memoir bearing their names in joint authorship with his.[2] In this memoir ten additional analyses of the bromide are given, but six of them are rejected by Gutbier as unsatisfactory. I prefer, however, to include them in this discussion, but with low weight. The ten determinations I have divided into two sets, one containing the four preferred analyses, the other the

[1] Sitz. phys.-med. Soz., Erlangen, 40, 65. 1909.
[2] Gutbier, Haas and Gebhardt, Journ. prakt. Chem. (2), 79, 457. 1909.

six questionable ones. Their unequal value appears in the probable errors:

Bromide.	Pd.	Per cent. Pd.
3.09278	1.09783	35.496
1.98039	.70288	35.491
1.50032	.53253	35.494
2.84500	1.00992	35.498

Mean, 35.495, ± .0011

Hence Pd = 106.70.

Bromide.	Pd.	Per cent. Pd.
.54402	.19286	35.450
.80237	.28468	35.479
.91601	.32509	35.489
.42942	.15288	35.461
.76884	.27271	35.470
.62795	.22270	35.464

Mean, 35.469, ± .0038

Hence Pd = 106.58.

The four series of analyses of the bromide now combine thus:

Haas .... 35.492, ± .0006
Gebhardt .... 35.491, ± .0007
Gutbier, Haas and Gebhardt.......... 35.495, ± .0011
Gutbier, Haas and Gebhardt.......... 35.469, ± .0038

General mean .... 35.491, ± .00042

The influence of the determinations rejected by Gutbier is insignificant.

Nine ratios are now available from which to compute the atomic weight of palladium, as follows:

(1). $2KCl:Pd::100:70.865, \pm .0150$
(2). $2AgCl:Pd(NH_3Cl)_2::100:73.813, \pm .0388$
(3). $Pd(NH_3Cl)_2:Pd::100:50.3882, \pm .0005$
(4). $Pd(NH_3Br)_2:Pd::100:35.491, \pm .00042$
(5). $Pd(NH_3CN)_2:Pd::100:55.291, \pm .0025$
(6). $Pd(C_6H_5.NH_2Cl)_2:Pd::100:29.390, \pm .0029$
(7). $Pd(C_6H_5:NH_2Br)_2:Pd::100:23.622, \pm .0023$
(8). $(NH_4)_2PdBr_4:Pd::100:23.1135, \pm .0018$
(9). $Pd(NH_3Cl)_2:PdS::100:65.651, \pm .0051$

To reduce these ratios we have—

Ag = 107.880, ± .00029	C = 12.0038, ± .0002
Cl = 35.4584, ± .0002	N = 14.0101, ± .0001
Br = 79.9197, ± .0003	S = 32.0667, ± .00075
K = 39.0999, ± .0002	H = 1.00779, ± .00001

Hence.

	From ratio 1	Pd = 105.672, ± .0224
"	" 5	106.472, ± .0077
"	" 2	106.613, ± .1112
"	" 3	106.627, ± .0016
"	" 4	106.682, ± .0015
"	" 8	106.948, ± .0087
"	" 6	107.009, ± .0115
"	" 7	107.014, ± .0109
"	" 9	107.299, ± .0491

General mean, Pd = 106.662, ± .0011

The final mean is a little lower than the values found in Gutbier's laboratory. The latter, however, could not be unqualifiedly accepted without rejecting other determinations which seem to be good. The international value, Pd = 106.7, is not far from the truth.

OSMIUM.

The atomic weight of this metal has been determined by Berzelius. by Fremy, and by Seubert.

Berzelius[1] 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, the data give Os = 198.94.

Fremy's determination[2] is based upon the composition of osmium tetroxide. No details as to weighings or methods are given; barely the final result is stated, namely, Os = 199.65.

When the periodic law came into general acceptance, it became clearly evident that both of the foregoing values for osmium must be several units too high. A redetermination was therefore undertaken by Seubert.[3] who adopted methods based upon that of Berzelius. First. ammonium osmichloride was reduced by heating in a stream of hydrogen. The residual osmium was weighed, and the ammonium chloride and hydrochloric acid given off were collected in a suitable apparatus. so that the

[1] Poggend. Annalen, 13, 530. 1828.
[2] Compt. Rend., 19, 463. Journ. prakt. Chem., 31, 410. 1844.
[3] Ber. Deutsch. chem. Ges., 21, 1839. 1888.

total chlorine could be estimated as silver chloride. The weights were as follows:

Am_2OsCl_6.	Os.	$6AgCl$.
1.8403	.7996	3.5897
2.0764	.9029	4.0460
2.1501	.9344	4.1950
2.1345	.9275	4.1614

Hence we have for the percentage of osmium and for the osmichloride proportional to 100 parts of AgCl—

Per cent. Os.	AgCl : Salt.
43.446	51.266
43.484	51.320
43.458	51.254
43.453 .	51.293

Mean, 51.283, ± .0099

In a later paper [1] two more reductions are given, in which only osmium was estimated:

Salt.	Os.	Per cent. Os.
2.6687	1.1597	43.456
2.6937	1.1706	43.457

These determinations, included with the previous four as one series, give a mean percentage of Os in Am_2OsCl_6 of 43.459, ± .0036.

Secondly, potassium osmichloride was treated in the same way, but the residue weighed consisted of Os + 2KCl. From this the potassium chloride was dissolved out, recovered by evaporating the solution, and weighed separately. The volatile portion, 4HCl, was also measured by precipitation as silver chloride. In Seubert's first paper these data are given:

K_2OsCl_6.	Os.	2KCl.	4AgCl.
2.5148	. . . .	.7796	2.9837
2.1138	.8405	.6547	2.5076

Hence, with salt proportional to 100 parts of AgCl in the last column, we have—

Per cent. Os.	Per cent. KCl.	AgCl : Salt.
. . . . .	31.000	84.091
39.762	30.973	84.102

Mean. 84.097, ± .0030

---

[1] Liebig's Annalen, 261, 258.

In his second paper Seubert gives fuller data relative to the potassium osmichloride, but treats it somewhat differently. The salt was reduced by a stream of hydrogen as before, but after that the boat containing the $Os+2KCl$ was transferred to a platinum tube, in which, by prolonged heating in the gas, the potassium chloride was completely volatilized. The determinations of 4Cl as 4AgCl were omitted. Two series of data are given, as follows:

$K_2OsCl_6.$	Os.	Per cent. Os.
1.1863	.4691	39.543
.9279	.3667	39.519
1.0946	.4330	39.558
1.6055	.6351	39.558
.4495	.1778	39.555
.8646	.3417	39.521
.7024	.2781	39.593
1.2742	.5041	39.562
1.0466	.4141	39.566

Mean, 39.553, $\pm$ .0052

$K_2OsCl_6.$	2KCl.	Per cent. KCl.
2.2032	.6820	30.955
2.0394	.6312	30.950
2.7596	.8544	30.961
2.4934	.7710	30.922
2.8606	.8843	30.913
2.8668	.5768	30.898
1.2227	.3778	30.899

Mean, 30.931

Earlier set, $\begin{cases} 31.000 \\ 30.973 \end{cases}$

Mean of all nine determinations, 30.941, $\pm$ .0079

The single percentage of osmium in the earlier memoir is obviously to be rejected.

The ratios to examine are now as follows:

(1). Per cent. Os in Am_2OsCl_6, 43.459, $\pm$ .0036
(2). $6AgCl:Am_2OsCl_6::100:51.283$, $\pm$ .0099
(3). $4AgCl:K_2OsCl_6::100:84.097$, $\pm$ .0030
(4). Per cent. Os in K_2OsCl_6, 39.553, $\pm$ .0052
(5). Per cent. KCl in K_2OsCl_6, 30.951. $\pm$ .0079

To reduce these ratios we have—

$Ag = 107.880$, $\pm$ .00029 $N = 14.0101$, $\pm$ .0001
$Cl = 35.4584$, $\pm$ .0002 $K = 39.0999$, $\pm$ .0002
$H = 1.00779$, $\pm$ .00001

Hence,

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

From ratio 4 ....Os = 190.374, ± .0299
     "   " 5 ....190.832, ± .0417
     "   " 3 ....191.229, ± .0173
     "   " 1 ....191.260, ± .0200
     "   " 2 ....192.216, ± .0852

General mean, Os = 191.067, ± .0114

</div>

A modern determination of the atomic weight of osmium seems to be desirable.

IRIDIUM.

The only early determination of the atomic weight of iridium was made by Berzelius,[1] who analyzed potassium iridichloride by the same method employed with the platinum and the osmium salts. The result found from a single 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,[2] 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 results obtained were as follows:

Am_2IrCl_6.	Ir.	Per cent. Ir.
1.3164	.5755	43.725
1.7122	.7490	43.745
1.2657	.5536	43.739
1.3676	.5980	43.726
2.6496	1.1586	43.739
2.8576	1.2489	43.705
2.9088	1.2724	43.742

<div style="text-align:center">Mean, 43.732, ± .0035</div>

Hence $Ir = 193.395$.

The potassium salt was also analyzed by decomposition in hydrogen with special precautions. In the residue the iridium and the potassium

---

[1] Poggend. Annalen, 13, 435. 1828.
[2] Ber. Deutsch. chem. Gesell., 11, 1767. 1878.

chloride were separated after the usual method, and both were estimated. Eight analyses gave the following weights:

K_2IrCl_6.	$4Cl$, loss.	Ir.	KCl.
1.6316	.4779	.6507	.5030
2.2544	.6600	.8993	.6953
2.1290	.6238	.8488	.6560
1.8632	.5457	.7430	.5745
2.6898	.7878	1.0726	.8291
2.3719	.6952	.9459	.7308
2.6092	.7641	1.0406	.8040
2.5249	.7395	1.0070	.7775

Hence we have the following percentages, reckoned on the original salt:

Ir.	$2KCl$.	$4Cl$.
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, $\pm$ .0015	Mean, 30.820, $\pm$ .0037	Mean, 29.291, $\pm$ .0024
$Ir = 192.999$	192.881	193.274

Joly [1] studied derivatives of iridium trichloride. The salts were dried at 120°, and reduced in hydrogen. With $IrCl_3.3KCl.3H_2O$ he found as follows:

$Salt$.	Ir.	KCl.
1.5950	.5881	.6803
1.6386	.6037	.7000
2.6276	.9689	1.1231

These data, if the weight of the salt itself is considered, give discordant results, but the ratio $Ir : 3KCl :: 100 : x$ is satisfactory. The values of x are as follows:

115.677
115.952
115.915

Mean, 115.848, $\pm$ .0583

Hence $Ir = 193.277$.

[1] Compt. Rend., 110, 1131. 1890.

The ammonium salt. $IrCl_3.3NH_4Cl$. gave the subjoined data:

Wt. of Salt.	Wt. of Ir.	Per cent. Ir.
1.5772	.6627	42.017
1.6056	.6742	41.990

Mean, 42.003, ± .0094

Hence $Ir = 193.078$.

To sum up. the ratios available for iridium are these:

(1). Per cent. Ir in Am_2IrCl_6, 43.732. ± .0035
(2). Per cent. Ir in K_2IrCl_6, 39.880, ± .0015
(3). Per cent. KCl in K_2IrCl_6, 30.820, ± .0037
(4). Per cent. 4Cl in K_2IrCl_6, 29.291, ± .0024
(5). Per cent. Ir in Am_3IrCl_6, 42.003, ± .0094
(6). Ir : 3KCl : : 100 : 115.848, ± .0583

To reduce these ratios we have—

Cl = 35.4584, ± .0002	N = 14.0101, ± .0001
K = 39.0999, ± .0002	H = 1.00779, ± .00001

Hence,

From ratio 3	....	Ir = 192.881, ± .0189
" " 2	....	192.999, ± .0084
" " 6	....	193.078, ± .0971
" " 4	....	193.274, ± .0416
" " 5	....	193.277, ± .0534
" " 1	....	193.395, ± .0196

General mean, Ir = 193.047, ± .0070

In a preliminary note Archibald[1] states that from analyses of the salt K_2IrCl_6 he has obtained the value $Ir = 192.90$. His investigation is still in progress, and no details have yet been published.

---

[1] Chem. News, 100, 150. 1909. Paper read before the British Association for the Advancement of Science.

PLATINUM.

The earliest work upon the atomic weight of this metal was done by Berzelius,[1] who reduced platinous chloride and found it to contain 73.3 per cent. of platinum. Hence $Pt = 194.69$. In a later investigation,[2] he studied 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:

1. From loss of Cl upon ignition.......... $Pt = 198.25$
2. From weight of Pt in residue......... " $= 197.42$
3. From weight of KCl in residue........ " $= 196.63$
4. From ratio between KCl and Pt....... " $= 197.10$

The last of these values is undoubtedly the best, for it is not affected by errors due to the possible presence of moisture in the salt analyzed.

The work done by Andrews[3] is even less satisfactory than the foregoing, partly 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

Unfortunately, Andrews does not state how his calculations were made. In 1881 Seubert[4] published his determinations, basing them upon very pure chloroplatinates of potassium and ammonium. The ammonium salt, $(NH_4)_2PtCl_6$, was analyzed by heating in a stream of hydrogen, expelling 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

[1] Poggend. Annalen, 8, 177. 1826.
[2] Poggend. Annalen, 13, 468. 1828.
[3] British Assoc. Report, 1852.
[4] Ber. Deutsch. chem. Gesell., 14, 865.

estimated by precipitation as silver chloride. Three series of experiments are given, representing three distinct preparations, as follows:

Series I.

Am_2PtCl_6.	Pt.	Per cent. Pt.
2.1266	.9348	43.957
1.7880	.7858	43.948
1.8057	.7938	43.960
2.6876	1.1811	43.946
4.7674	2.0959	43.963
2.0325	.8935	43.961

Mean, 43.956, $\pm$ .002

Series II.

Am_2PtCl_6.	Pt.	Per cent. Pt.
3.0460	1.3363	43.871
2.6584	1.1663	43.876
2.3334	1.0238	43.872
1.9031	.8351	43.881
3.1476	1.3810	43.875
2.7054	1.1871	43.889

Mean, 43.876, $\pm$ .001

Another portion of this preparation, recrystallized from water, of 1.4358 grm. gave 0.6311 of platinum, or 43.955 per cent.

Series III.

Am_2PtCl_6.	Pt.	Per cent. Pt.
2.5274	1.1118	43.990
3.2758	1.4409	43.986
1.9279	.8483	44.001
2.0182	.8884	44.020
1.8873	.8303	43.994
2.2270	.9798	43.996
2.4852	1.0936	44.004
2.5362	1.1166	44.026
3.0822	1.3561	43.998

Mean, 44.001, $\pm$ .003

If these series are treated as independent and combined, giving each a weight as indicated by its probable error, and regarding the single experiment with preparation II as equal to one in the first series, we get a mean percentage of 43.907, $\pm$.0009. On the other hand, if we regard the twenty-two experiments as all of equal weight in one series, the

mean percentage of platinum becomes 43.953, ±.0078. Hence Pt = 195.14. Upon comparing the work with that done later by Halberstadt, and by Archibald, the latter mean seems the fairer one to adopt.

For the chlorine estimations in the ammonium salt, Seubert gives the subjoined data. I add in the last column the weight of salt proportional to 100 parts of silver chloride:

Am_2PtCl_6.	Pt.	$6AgCl$.	Ratio.
2.7054	1.1871	5.2226	51.802
2.2748	.9958	4.3758	51.986
3.0822	1.3561	5.9496	51.805

Mean, 51.864, ± .041

Hence Pt = 197.22.

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. The weights given are as follows:

K_2PtCl_6.	Pt.	$2KCl$.
5.0283	2.0173	1.5440
7.0922	2.8454	2.1793
3.5475	1.4217	1.0890
3.2296	1.2941	.9904
3.5834	1.4372	1.1001
4.4232	1.7746	1.3547
4.0993	1.6444	1.2589
4.4139	1.7713	1.3516

Hence we have these percentages, reckoned on the original salt:

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

Hence Pt = 194.83.   Hence Pt = 195.06.

As with the ammonium salt, three experiments were made upon the potassium compound to determine the amount of chlorine (four atoms

in this case) lost upon ignition in hydrogen. In the fourth column I add the amount of K_2PtCl_6 corresponding to 100 parts of AgCl:

K_2PtCl_6.	Pt.	$4AgCl$.	Ratio.
6.7771	2.7158	7.9725	85.006
3.5834	1.4372	4.2270	84.774
4.4139	1.7713	5.2144	84.648

Mean, 84.809, ± .071

Hence Pt = 195.31.

Halberstadt,[1] like Seubert, studied the chloroplatinates of potassium and ammonium, and also the corresponding double bromides and platinic bromide as well. The metal was estimated partly by reduction in hydrogen, as usual, and partly by electrolysis. Platinic bromide gave the following results:

I. By reduction in H.

$PtBr_4$.	Pt.	Per cent. Pt.
.6396	.2422	37.867
1.7596	.6659	37.844
.9178	.3476	37.873
1.1594	.4388	37.847
1.9608	.7420	37.842
2.0865	.7898	37.853
4.0796	1.5422	37.852
6.8673	2.5985	37.839

II. By electrolysis.

$PtBr_4$.	Pt.	Per cent. Pt.
1.2588	.4763	37.837
1.4937	.5649	37.819

Mean of all ten experiments, 37.847, ± .0033

Hence Pt = 194.66.

The ammonium platinbromide, $(NH_4)_2PtBr_6$, was prepared in two ways, and five distinct lots were studied. With this salt, as well as with those which follow, the data are given in distinct series, with from one to several experiments in each group, but for present purposes it seems best to consolidate the material and so put it in more manageable form. The percentages of platinum and weights found are as follows:

I. By reduction in H.

Am_2PtBr_6.	Pt.	Per cent. Pt.
.6272	.1719	27.408
1.0438	.2865	27.447
1.1724	.3215	27.422
1.4862	.4076	27.426
1.0811	.2966	27.435
1.3383	.3672	27.437

[1] Ber. Deutsch. chem. Gesell., 17, 2062. 1884.

⌈ 1.0096	.2769	27.426
⎱ 1.1935	.3269	27.390
⎰ 1.3182	.3611	27.393
⌊ 2.2476	.6159	27.402
⌈ 1.3358	.3668	27.451
⎮ 1.7859	.4899	27.431
⎮ 4.1641	1.1427	27.441
⎨ 1.1835	.3250	27.460
⎮ 2.4003	.6591	27.459
⎮ 2.5293	.6940	27.438
⌈ 1.7147	.4705	27.439
⎮ 2.3014	.6316	27.444
⎬ 3.0052	.8245	27.435
⌊ 4.8592	1.3329	27.430
⌈ 1.5337	.4210	27.449
⎨ 2.0373	.5594	27.457
⌊ 2.0939	.5751	27.465

II. By electrolysis.

Am_2PtBr_6.	Pt.	Per cent. Pt.
⌈ 1.5586	.4272	27.409
⎨ 1.6052	.4397	27.392
⎮ 3.1229	.8569	27.439
⌊ 1.1612	.3180	27.386
⌈ 2.5817	.7081	27.427
⎨ 1.0231	.2809	27.456
⌊ 1.6744	.4591	27.418
1.6744	.4591	27.418
1.6052	.4397	27.392

Mean of all thirty-two experiments, 27.429, ± .0027

Hence Pt = 194.88.

With potassium platinbromide Halberstadt found as follows:

I. By reduction in H.

K_2PtBr_6.	Pt.	2KBr.	Per cent. Pt	Per cent. KBr.
⌈ 2.5549	.6630	.8071	25.940	31.590
⎮ 2.6323	.6831	.8318	25.947	31.599
⎨ 2.9315	.7598	.9259	25.910	31.584
⎮ 3.4463	.8939	1.0895	25.938	31.613
⌊ 4.0081	1.0404	1.2653	25.957	31.568
3.9554	1.0266	1.2495	25.954	31.589
⌈ 2.0794	.5388	.6558	25.911	31.538
⎨ 2.1735	.5635	.6849	25.926	31.511
⌊ 2.3099	.5986	.7297	25.914	31.590
⌈ 1.4085	.3645	.4446	25.880	31.565
⎨ 2.6166	.6772	.8279	25.881	31.640
⌊ 2.6729	.6923	.8469	25.900	31.684

31

II. By electrolysis.

K_2PtBr_6.	Pt.	2KBr.	Per cent. Pt.	Per cent. KBr.
2.2110	.5726	.6997	25.898	31.647
3.1642	.8188	.9983	25.877	31.550
1.9080	.4947	.6025	25.927	31.577
1.6754	.4341	.5286	25.915	31.550
1.3148	.3403	.4160	25.882	31.640
1.5543	.4025	.4911	25.895	31.596

Mean of eighteen experiments, 25.915,±.0040　31.591,±.0068

Hence Pt=195.09 and 195.79.

For ammonium platinchloride Halberstadt gives the following data:

I. By reduction in H.

Am_2PtCl_6.	Pt.	Per cent. Pt.
1.0604	.4662	43.964
1.3846	.6087	43.962
1.5065	.6617	43.923
2.3266	1.0227	43.956
1.3808	.6059	43.880
1.7396	.7638	43.906
2.7420	1.2068	44.011
3.1882	1.4019	43.971
5.4644	2.4035	43.984
3.4859	1.5321	43.951

II. By electrolysis.

Am_2PtCl_6.	Pt.	Per cent. Pt.
.9474	.4161	43.920
1.1069	.4865	43.951
1.5101	.6634	43.930
.5345	.2347	43.910
1.6035	.7044	43.928
1.9271	.8459	43.894
1.1046	.4858	43.979
1.4179	.6233	43.959

Mean of eighteen experiments, 43.943, ± .0054

Hence Pt=195.01.

For potassium platinchloride Halberstadt's data are—

I. By reduction in H.

K_2PtCl_6.	Pt.	2KCl.	Per cent. Pt.	Per cent. KCl.
1.6407	.6574	.5029	40.069	30.651
1.9352	.7757	.5921	40.084	30.600
1.5793	.6334	.4836	40.106	30.621
1.6446	.6595	.5049	40.101	30.700
1.0225	.4102	.3133	40.117	30.640
2.4046	.9641	.7388	40.094	30.724
5.8344	2.3412	1.7905	40.127	30.688
7.1732	2.8776	2.1998	40.116	30.666

II. By electrolysis.

K_2PtCl_6.	Pt.	2KCl.	Per cent. Pt.	Per cent. KCl.
1.2354	.4953	.3792	40.092	30.695
2.5754	1.0318	.7898	40.063	30.667
1.0933	.4387	.3355	40.126	30.668
1.3560	.5438	.4167	40.103	30.730
1.7345	.6956	.5298	40.104	30.545
2.0054	.8038	.6147	40.081	30.652
2.0666	.8291	.6356	40.117	30.755
1.2759	.5118	.3908	40.112	30.629
1.9376	.7763	.5927	40.065	30.589
2.3972	.9608	.7355	40.080	30.681
2.7249	1.0929	.8364	40.108	30.691

Mean of nineteen experiments, 40.098,±.0031 30.663,±.0080

Seubert found, 30.682,±.0090

General mean, 30.671,±.0060

Hence Pt=194.78 and 195.36, from Halberstadt's data alone.

The work of Dittmar and M'Arthur [1] on the atomic weight of platinum is difficult to discuss and essentially unsatisfactory. They investigated potassium platinchloride, and came to the conclusion that it contains traces of hydroxyl replacing chlorine and also hydrogen replacing potassium. It is also liable, they think, to carry small quantities of potassium chloride. In their determinations, which involve corrections indicated by the foregoing considerations, they are not sufficiently explicit, and give none of their actual weighings. They attempt, however, to fix the ratio 2KCl: Pt, and after a number of discordant, generally high results, they give the following data for the atomic weight of platinum based upon the assumption that 2KCl=149.182:

195.54
195.48
195.60
195.37

Mean, 195.50, ± .0330

This ratio can also be computed from Seubert's and Halberstadt's analyses, and also the ratio 2KBr: Pt. It has not seemed necessary to do so, in view of the overwhelming weight of Archibald's more recent work.

Dittmar and M'Arthur also discuss Seubert's determinations, seeking to show that the latter also, properly treated, lead to a value nearer to 195.5 than to 195. Seubert at once replied to them,[2] pointing out that

[1] Trans. Roy. Soc. Edinburgh, 33, 561. 1887.
[2] Ber. Deutsch. chem. Gesell., 21, 2179. 1888.

the concordance between his determinations by very different methods (a concordance verified by Halberstadt's investigation) precluded the existence of errors due to impurities such as Dittmar and M'Arthur assumed.

The recent determinations by Archibald [1] of the atomic weight of platinum were based upon analyses of the platinchlorides and platin-bromides of potassium and ammonium. In these analyses every precaution was taken which modern experience had shown to be necessary. The possible presence of moisture in the several salts was carefully considered, and the potassium compounds in particular were dried at 380° to 400°. For the elaborate details of manipulation the original memoir must be consulted.

First, as to the analyses of potassium platinchloride. The salt, after thorough drying and weighing, was reduced by heating in a stream of pure hydrogen. The hydrochloric acid so formed was absorbed in water, and afterwards converted into silver chloride and weighed. Known quantities of silver were used in this operation, so that two distinct ratios were determined. From the residual mixture of potassium chloride and platinum the chloride was washed out, and its chlorine content was estimated as in the previous determinations. The metallic platinum, converted into sponge by again heating in hydrogen, was also weighed. Vacuum weights are given in all of Archibald's determinations. The weights were as follows:

K_2PtCl_6.	Pt.	$4AgCl$.	$2AgCl$.	$4Ag$.	$2Ag$.
1.43605	.57667	1.69324	.84690	1.27475	.63722
1.69914	.68226	2.00402	1.00172	1.50834	.75401
2.11830	.85062	2.49836	1.24894	1.88046	.93993
2.49734	1.00287	2.94462	1.47249	2.21626	1.10841
......	.86012	......	1.26271	......	.95030
2.20619	.88588	2.60135	1.30106	1.95842	.97909
1.70600	.68486	2.01201	1.00580	......	......
1.74397	.70018	2.05691	1.02820	1.54816	.77402
2.06137	.82789	2.43096	1.21526	1.82982	.91481
2.34095	.93991	2.76105	1.38034	2.07759	1.03868
1.54787	.62150	1.82560	.91266	1.37391	.68702
1.95944	.78694	2.31070	1.15522	1.73902	.86967
2.28366	.91697	2.69304	1.34636	2.02640	1.01338
2.27441	.91320	2.68244	1.34093	2.01870	1.00924

From these weights Archibald computes nine ratios as follows. In the first ratio I have recalculated the figures into the percentage form used for previous investigations. The other ratios are as Archibald gives them: but with the probable errors computed by myself:

---

[1] Proc. Roy. Soc. Edinburgh, 29, 721. 1909.

Per cent. Pt.	$4AgCl:Pt.$	$2AgCl:Pt.$	$4AgCl:K_2PtCl_6.$	$2AgCl:K_2PtCl_6.$
40.157	34.057	68.092	84.811	169.57
40.153	34.045	68.109	84.787	169.62
40.156	34.047	68.107	84.788	169.61
40.158	34.058	68.107	84.810	169.60
.....	.....	68.117	.....	169.61
40.154	34.055	68.089	84.810	169.57
40.144	34.039	68.091	84.791	169.62
40.149	34.040	68.098	84.786	169.61
40.162	34.056	68.125	84.797	169.62
40.151	34.042	68.093	84.785	169.59
40.152	34.044	68.098	84.787	169.60
40.161	34.056	68.120	84.799	169.62
40.154	34.050	68.107	84.799	169.62
40.151	34.045	68.102	84.789	169.62
Mean, 40.154,	34.049,	68.104,	84.795,	169.606,
± .0009	± .0013	± .0020	± .0019	± .0034
Pt = 195.21	195.22	195.24	195.23	195.20

$4Ag:Pt.$	$2Ag:Pt.$	$4Ag:K_2PtCl_6.$	$2Ag:K_2PtCl_6.$
45.238	90.498	112.65	225.36
45.233	90.484	112.65	225.35
45.235	90.498	112.65	225.37
45.251	90.478	112.68	225.31
.....	90.510	.....	225.36
45.234	90.480	112.65	225.33
45.227	90.460	112.65	225.31
45.244	90.499	112.65	225.33
45.240	90.488	112.68	225.37
45.236	90.463	112.66	225.30
45.252	90.487	112.68	225.31
45.251	90.486	112.70	225.35
45.237	90.484	112.67	225.36
Mean, 45.240,	90.486,	112.66,	225.34,
± .0016	± .0026	± .0030	± .0047
Pt = 195.22	195.23	195.20	195.24

For the first of these ratios, the percentage of Pt in K_2PtCl_6, there are previous determinations. The three series combine thus:

Seubert .... 40.107, ± .0050
Halberstadt .... 40.098, ± .0031
Archibald .... 40.154, ± .0009

General mean .... 40.1484, ± .00085

Similarly, the ratio $4AgCl:K_2PtCl_6$ as determined by Seubert, may be combined with Archibald's series. Better still the two series may be reduced to uniform type with Archibald's ratio for $2AgCl$, and given

in the form $AgCl : K_2PtCl_6 :: 100 : x$. The three series then combine as follows:

$$
\begin{array}{ll}
\text{Seubert, 4AgCl} \ldots\ldots\ldots\ldots\ldots & 339.236, \pm .2840 \\
\text{Archibald, 4AgCl} \ldots\ldots\ldots\ldots & 339.180, \pm .0076 \\
\text{Archibald, 2AgCl} \ldots\ldots\ldots\ldots & 339.212, \pm .0068 \\
\hline
\text{General mean} \ldots\ldots\ldots\ldots & 339.204, \pm .0051
\end{array}
$$

Archibald's two series of measurements of the ratios between silver and the platinchloride can also be reduced to the form $Ag : K_2PtCl_6 :: 100 : x$, and combined:

$$
\begin{array}{ll}
\text{4Ag series} \ldots\ldots\ldots\ldots\ldots & 450.64, \pm .0120 \\
\text{2Ag series} \ldots\ldots\ldots\ldots\ldots & 450.66, \pm .0094 \\
\hline
\text{General mean} \ldots\ldots\ldots\ldots & 450.654, \pm .0074
\end{array}
$$

Archibald's data for ammonium platinchloride are rather simpler than with the potassium salt, since the total chlorine was determined at once, instead of in two portions. His weights are subjoined:

Am_2PtCl_6.	Pt.	$6AgCl$.	$6Ag$.
1.75088	.76976	3.39181	2.55181
1.36500	.59997	2.64317	1.99014
1.15060	.50585	2.22810	1.67695
1.27475	.56049	2.46936	1.85794
2.54096	1.11688	4.92047	3.70420

The derived ratios are as follows:

Per cent. Pt.	$6AgCl:Pt$.	$6AgCl:Am_2PtCl_6$.	$6Ag:Pt$.	$6Ag:Am_2PtCl_6$.
43.964	22.695	51.621	30.165	68.613
43.954	22.699	51.643	30.147	68.588
43.964	22.703	51.640	30.165	68.613
43.969	22.698	51.623	30.167	68.611
43.955	22.699	51.641	30.152	68.597
Mean, 43.961,	22.699,	51.634,	30.159,	68.604,
$\pm .0061$	$\pm .0031$	$\pm .0032$	$\pm .0027$	$\pm .0034$
$Pt = 195.20$	195.22	195.24	195.21	195.23

Two of the ratios can be combined with earlier measurements, as follows:

<div align="center">Percentage Pt in Am_2PtCl_6.</div>

$$
\begin{array}{ll}
\text{Seubert} \ldots\ldots\ldots\ldots\ldots & 43.953, \pm .0078 \\
\text{Halberstadt} \ldots\ldots\ldots\ldots & 43.943, \pm .0054 \\
\text{Archibald} \ldots\ldots\ldots\ldots & 43.961, \pm .0061 \\
\hline
\text{General mean} \ldots\ldots\ldots\ldots & 43.951, \pm .0036
\end{array}
$$

Ratio $6AgCl:Am_2PtCl_6::100:x.$

Seubert .... 51.864, ± .0410
Archibald .... 51.634, ± .0032
_____
General mean .... 51.636, ± .0032

For ammonium platinbromide Archibald gives these data:

$Am_2PtBr_6.$	$Pt.$	$6AgBr.$	$6Ag.$
1.83860	.50497	2.91430	1.67448
2.31057	.63437	3.66269	2.10379
2.33965	.64272	3.70900	2.13049

Hence the following ratios:

Per cent. Pt.	$6AgBr:Pt.$	$6AgBr:Am_2PtBr_6.$	$6Ag:Pt.$	$6Ag:Am_2PtBr_6.$
27.465	17.327	63.089	30.157	109.801
27.455	17.320	63.084	30.154	109.829
27.471	17.329	63.080	30.168	109.827
___	___	___	___	___
Mean, 27.464,	17.325,	63.084,	30.160,	109.816,
± .0032	± .0018	± .0018	± .0030	± .0055
Pt = 195.22	195.22	195.23	195.22	195.22

The percentage of platinum in Am_2PtBr_6 combines with Halberstadt's figures thus:

Halberstadt .... 27.429, ± .0027
Archibald .... 27.464, ± .0032
_____
General mean .... 27.443, ± .0021

The analyses of potassium platinbromide were like those of chloride, the bromine being estimated in two portions, 2Br and 4Br. The weights are these:

$K_2PtBr_6.$	$Pt.$	$4AgBr.$	$2AgBr.$	$4Ag.$	$2Ag.$
2.19076	.56779	2.18543	1.09273	1.25544	.62770
2.42094	.62766	2.41510	1.20758	1.38761	.69378
1.78705	.46344	1.78284	.89156	1.02416	.51214
1.81840	.47156	1.81430	.90703	1.04228	.52105
2.47056	.64063	2.46507	1.23246	1.41572	.70800
2.19017	.56787	2.18525	1.09260	1.25530	.62756

From these weights nine ratios are deducible, as in the case of the platinchloride, as follows:

Per cent. Pt.	4AgBr:Pt.	2AgBr:Pt.	4AgBr:K₂PtBr₆.	2AgBr:K₂PtBr₆.
25.918	25.981	51.961	100.244	200.485
25.926	25.989	51.976	100.242	200.479
25.933	25.995	51.981	100.236	200.441
25.933	25.991	51.990	100.226	200.478
25.931	25.988	51.980	100.223	200.458
25.928	25.990	51.974	100.225	200.455
Mean, 25.928,	25.989,	51.977,	100.233,	200.466,
± .0015	± .0013	± .0027	± .0025	± .0048
Pt = 195.22	195.23	195.23	195.23	195.23

4Ag:Pt.	2Ag:Pt.	4Ag:K₂PtBr₆.	2Ag:K₂PtBr₆.
45.226	90.456	174.50	349.01
45.233	90.470	174.47	348.95
45.251	90.491	174.49	348.94
45.243	90.502	174.46	348.99
45.251	90.485	174.51	348.95
45.238	90.489	174.47	349.00
Mean, 45.240,	90.482,	174.48,	348.97,
± .0028	± .0045	± .0051	± .0085
Pt = 195.22	195.23	195.20	195.22

The percentage of platinum in the platinbromide combines with Halberstadt's figures as follows:

Halberstadt .... 25.915, ± .0040
Archibald .... 25.928, ± .0015
General mean .... 25.927, ± .0014

Several other ratios, given in diverse forms by Archibald, are also capable of consolidation. The ratio between silver bromide and potassium platinbromide, reduced to uniform type, that is, to $AgBr : K_2PtBr_6 :: 100 : x$, becomes—

2AgBr series................ 400.932, ± .0096
4AgBr series................ 400.932, ± .0100
General mean .... 400.932, ± .0069

For the ratio $Ag : K_2PtBr_6 :: 100 : x$ we have—

2Ag series.................. 697.940, ± .0170
4Ag series.................. 697.920, ± .0204
General mean .... 697.936, ± .0131

For the ratio AgBr : Pt : : 100 : x—

<div align="right">

2AgBr series................ 103.954, ± .0054
4AgBr series................ 103.956, ± .0052

General mean .... 103.955, ± .0037

</div>

For the ratio AgCl : Pt : : 100 : x—

<div align="right">

2AgCl series with K_2PtCl_6..... 136.208, ± .0046
4AgCl series with K_2PtCl_6..... 136.196, ± .0052
6AgCl series with Am_2PtCl_6... 136.194, ± .0186

General mean .... 136.203, ± .0031

</div>

For the ratio Ag : Pt : : 100 : x—

<div align="right">

2Ag series with K_2PtCl_6....... 180.972, ± .0052
4Ag series with K_2PtCl_6....... 180.960, ± .0064
6Ag series with Am_2PtCl_6..... 180.954, ± .0162
6Ag series with Am_2PtBr_6..... 180.960, ± .0180
2Ag series with K_2PtBr_6...... 180.964, ± .0090
4Ag series with K_2PtBr_6...... 180.960, ± .0112

General mean .... 180.965, ± .0034

</div>

From the last two ratios the cross ratio Ag : Cl : : 100 : 32.864, ± .0039 is deducible, which agrees closely with the measurements by Richards and Wells. From the corresponding ratios Ag : Pt and AgBr : Pt, we have the ratio Ag : Br : : 100 : 74.080, ± .0070. These agreements with the best determinations of the silver-halogen ratios is good evidence in favor of Archibald's work.

Rejecting the work of Berzelius and Andrews, the following ratios are now available from which to compute the atomic weight of platinum:

<div align="center">

(1). Am_2PtCl_6 : Pt : : 100 : 43.951, ± .0036
(2). 6Ag : Am_2PtCl_6 : : 100 : 68.604, ± .0034
(3). 6AgCl : Am_2PtCl_6 : : 100 : 51.636, ± .0032
(4). K_2PtCl_6 : Pt : : 100 : 40.1484, ± .00085
(5). Ag : K_2PtCl_6 : : 100 : 450.654, ± .0074
(6). AgCl : K_2PtCl_6 : : 100 : 339.204, ± .0051
(7). Am_2PtBr_6 : Pt : : 100 : 27.443, ± .0021
(8). 6Ag : Am_2PtBr_6 : : 100 : 109.816, ± .0055
(9). 6AgBr : Am_2PtBr_6 : : 100 : 63.084, ± .0018
(10). K_2PtBr_6 : Pt : : 100 : 25.927, ± .0014
(11). Ag : K_2PtBr_6 : : 100 : 697.936, ± .0131
(12). AgBr : K_2PtBr_6 : : 100 : 400.932, ± .0069
(13). $PtBr_4$: Pt : : 100 : 37.847, ± .0033
(14). K_2PtCl_6 : 2KCl : : 100 : 30.671, ± .0060
(15). K_2PtBr_6 : 2KBr : : 100 : 31.591, ± .0068
(16). 2KCl : Pt : : 149.182 : 195.50, ± .0330
(17). Ag : Pt : : 100 : 180.965, ± .0034
(18). AgCl : Pt : : 100 : 136.203, ± .0031
(19). AgBr : Pt : : 100 : 103.955, ± .0037

</div>

The antecedent atomic weights are—

$$Ag = 107.880, \ \pm .00029 \qquad K = 39.0999, \ \pm .0002$$
$$Cl = 35.4584, \pm .0002 \qquad N = 14.0101, \ \pm .0001$$
$$Br = 79.9197, \pm .0003 \qquad H = 1.00779, \pm .00001$$

Hence,

From ratio 13 ....Pt = 194.663, $\pm$ .0199
"   "   7 ....195.014, $\pm$ .0160
"   "   1 ....195.123, $\pm$ .0203
"   "   4 ....195.169, $\pm$ .0050
"   "   10 ....195.212, $\pm$ .0112
"   "   11 ....195.215, $\pm$ .0142
"   "   5 ....195.216, $\pm$ .0081
"   "   8 ....195.216, $\pm$ .0356
"   "   17 ....195.225, $\pm$ .0037
"   "   2 ....195.227, $\pm$ .0221
"   "   19 ....195.227, $\pm$ .0070
"   "   9 ....195.229, $\pm$ .0203
"   "   12 ....195.231, $\pm$ .0130
"   "   18 ....195.231, $\pm$ .0045
"   "   14 ....195.236, $\pm$ .0951
"   "   6 ....195.248, $\pm$ .0074
"   "   3 ....195.252, $\pm$ .0276
"   "   16 ....195.416, $\pm$ .0330
"   "   15 ....195.785, $\pm$ .1622

General mean, Pt = 195.210, $\pm$ .0020

SCANDIUM.

Cleve,[1] 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, $\pm$ .0175

Hence $Sc = 45.12$.

Later results are those of Nilson,[2] who converted scandium oxide into the sulphate. I give in a third column the percentage of oxide in sulphate:

.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 $Sc = 44.09$.

Combining the two series, we have—

Cleve .... 36.530, $\pm$ .0175
Nilson .... 36.181, $\pm$ .0040

General mean .... 36.190, $\pm$ .0039

Hence, if $S = 32.0667, \pm .00075$, $Sc = 44.115, \pm .0085$.

[1] Compt. Rend., 89, 419.
[2] Compt. Rend., 91, 118.

YTTRIUM.

Nearly all the regular determinations of the atomic weight of yttrium depend upon analyses or syntheses of the sulphate. A series of analyses of the oxalate, however, by Berlin,[1] is sometimes cited, and the data are as follows. In three experiments upon the salt $Yt_2(C_2O_4)_3.3H_2O$ the subjoined percentages of oxide were found:

<div align="center">

45.70
45.65
45.72
_____

Mean, 45.69, $\pm$ .0141
</div>

Hence $Yt = 89.55$.

The early work of Berzelius[2] may be ignored. The first determinations of the atomic weight of yttrium to be considered are those of Popp,[3] who 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

Hence $Yt = 102.05$ from A, 102.27 from B.

[1] Forhandlingar ved de Skandinaviske Naturforskeres, 8, 452. 1860.
[2] Lehrbuch, 5 Aufl., 3, 1225.
[3] Ann. Chem. Pharm., 131, 179. 1864.

In 1865 Delafontaine[1] 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, ± .081

Hence $Yt = 96.09$.

In another paper[2] 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, ± .055

Hence $Yt = 87.89$.

Bahr and Bunsen,[3] 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, ± .0233

Hence $Yt = 92.64$.

Cleve's first results are published in a joint memoir by Cleve and Hoeglund,[4] and are as follows:

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

Hence $Yt = 89.58$.

[1] Ann. Chem. Pharm., 134, 108. 1865.
[2] Arch. Sci. Phys. Nat. (2), 25, 119. 1866.
[3] Ann. Chem. Pharm., 137, 21. 1866.
[4] K. Svenska Vet. Akad. Handlingar, Bd. 1, No. 8. 1873.

In a later paper Cleve [1] gives syntheses of yttrium sulphate made with yttria which was carefully freed from terbia. The weights and percentages are as follows:

Yt_2O_3.	$Yt_2(SO_4)_3$.	Per cent. Yt_2O_3.
.8786	1.8113	48.507
.8363	1.7234	48.526
.8906	1.8364	48.497
.7102	1.4645	48.494
.7372	1.5194	48.519
.9724	2.0047	48.506
.9308	1.9197	48.487
.8341	1.7204	48.483
1.0224	2.1073	48.517
.9384	1.9341	48.519
.9744	2.0093	48.494
1.5314	3.1586	48.484

Mean, 48.503, $\pm$ .0029

Hence Yt $= 89.12$.

The yttria studied by Jones [2] had been purified by Rowland's method—that is, by precipitation with potassium ferrocyanide—and certainly contained less than one-half of one per cent. of other rare earths as possible impurities. Two series of determinations were made—one by ignition of the sulphate, the other by its synthesis. The results were as follows, with the usual percentage column added:

First series.   Syntheses.

Yt_2O_3.	$Yt_2(SO_4)_3$.	Per cent. Yt_2O_3.
.2415	.4984	48.455
.4112	.8485	48.462
.2238	.4617	48.473
.3334	.6879	48.466
.3408	.7033	48.457
.3418	.7049	48.489
.2810	.5798	48.465
.3781	.7803	48.456
.4379	.9032	48.483
.4798	.9901	48.460

Mean, 48.467, $\pm$ .0025

---

[1] K. Svenska Vet. Akad. Handlingar, No. 9, 1882. See also Bull. Soc. Chim., 39, 120. 1883.
[2] Amer. Chem. Journ., 17, 154. 1895.

Second series. Analyses.

$Yt_2(SO_4)_3$.	Yt_2O_3.	Per cent. Yt_2O_3.
.5906	.2862	48.459
.4918	.2383	48.455
.5579	.2705	48.485
.6430	.3117	48.478
.6953	.3369	48.454
1.4192	.6880	48.478
.8307	.4027	48.477
.7980	.3869	48.484
.8538	.4139	48.477
1.1890	.5763	48.469

Mean, 48.472, ± .0024

From syntheses .... $Yt = 88.96$
From analyses .... " $= 88.98$

These data of Jones were briefly criticised by Delafontaine,[1] who regards a lower value as more probable. In a brief rejoinder[2] Jones defended his own work: but neither the attack nor the reply needs farther consideration here. They are referred to merely as part of the record.

By Muthmann and Böhm[3] there is a single determination. 2.46505 grammes $Yt_2(SO_4)_3$ gave 1.19511 Yt_2O_3. Per cent. Yt_2O_3, 48.482, and $Yt = 89.00$.

In a preliminary note, G. and E. Urbain[4] state that $Yt = 88.6$, but they give no details. Three determinations by Bodman[5] are as follows:

Yt_2O_3.	$Yt_2(SO_4)_3$.	Per cent. Yt_2O_3.
.4381	.8928	49.070
.5929	1.2093	49.028
.4062	.8286	49.022

Mean, 49.040, ± .0102

Hence $Yt = 91.57$.

There are also two determinations by Brill,[6] made with the microbalance. The percentages of Yt_2O_3 in the sulphate are

48.647
48.617

Mean, 48.632, ± .0100

Hence $Yt = 89.70$.

[1] Chem. News, 71, 243.
[2] Chem. News, 71, 305.
[3] Ber. Deutsch. chem. Ges., 33, 42. 1900.
[4] Compt. Rend., 132, 136. 1901.
[5] Bihang Svensk. Vet. Akad. Handl., 26 (2), No. 3. 1901.
[6] Zeitsch. anorg. Chem., 47, 464. 1905.

For the percentage of yttria in the sulphate we now have the following data, to be combined in the usual way. The one determination by Muthmann and Böhm is arbitrarily given equal weight with the figure assigned to Brill:

Popp .... 51.208, ± .0110
Delafontaine, first .... 49.998, ± .0810
Delafontaine, second .... 48.230, ± .0550
Bahr and Bunsen........... 49.2695, ± .0233
Cleve and Hoeglund......... 48.605, ± .0096
Cleve, later .... 48.503, ± .0029
Jones, syntheses .... 48.467, ± .0025
Jones, analyses .... 48.472, ± .0024
Muthmann and Böhm........ 48.482, ± .0100
Bodman .... 49.040, ± .0102
Brill .... 48.632, ± .0100

General mean .... 48.543, ± .0014

If we reject the first four of the values in this combination, the mean becomes 48.495, ± .0014. Hence $Yt = 89.040, ± .0047$, as compared with $Yt = 89.299$, derived from the mean of all. The determinations, previous to those of Cleve and Hoeglund, are of no present value.

The determinations made by Feit and Przibylla,[1] by their volumetric method, are as follows:

Yt_2O_3.	O.	Atomic weight.
.3677	.07781	89.415
.4928	.10438	89.309
.3660	.07749	89.356
.3660	.07751	89.328
.3704	.07840	89.387
.3635	.07701	89.284

Mean, 89.346, ± .0135

From the sulphate, when $S = 32.0667, ± .00075$, $Yt = 89.040, ± .0047$. Combined with Feit and Przibylla's value the general mean becomes

$$Yt = 89.094, ± .0044$$

This is probably too high, by at least 0.1. But it would be unwise to reject any of the values included in the final combination.

---

[1] Zeitsch. anorg. Chem., 50, 262. 1906. For the process, see under lanthanum.

LANTHANUM.

If we leave out of account the work of Mosander, and some worthless experiments of Choubine, our discussion of the atomic weight of lanthanum must begin with a single analysis by Rammelsberg [1] published in 1842. From 0.700 gramme of lanthanum sulphate he obtained 0.883 of barium sulphate. Hence 100 parts of $BaSO_4$ are equivalent to 79.276 of $La_2(SO_4)_3$, and $La = 133.48$.

Marignac,[2] 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 = 139.44
From B .... " = 148.17

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

[1] Poggend. Annalen, 55, 65.
[2] Arch. Sci. Phys. Nat. (1), 11, 29. 1849. Oeuvres Complètes, 1, 230.

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:

$La_2(SO_4)_3$.	$BaCl_2$.	Ratio.
11.644	12.765 — 12.825	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 $= 141.21$.

Although not next in chronological order, some still more recent work of Marignac's [1] 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 data follow:

$La_2(SO_4)_3$.	La_2O_3.	Per cent. La_2O_3.
2.0988	1.2082	57.566
2.3504	1.3532	57.573
2.8113	1.6165	57.500
3.3385	1.9215	57.556

Mean, 57.549, $\pm$ .0112

Hence La $= 138.81$.

The atomic weight determinations of Holzmann [2] 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:

Sulphate.	La_2O_3.	$BaSO_4$.
.9663	.5157	1.1093
.6226	.3323	.7123
.8669	.4626	.9869

[1] Ann. Chim. Phys. (4), 30, 68. 1873. Oeuvres Complètes, 2, 566.
[2] Journ. 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 estimated 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	.1569	.0417	.1131
.5931	.1734	.0467	.1262
.5662	.1647	.0442	.1197
.3757	. . . .	.0297	.0813
.3263	. . . .	.0256	.0693

These weighings give the subjoined perecentages 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 atomic weight of La as follows:

From sulphate .... La $= 139.42$
From iodate .... " $= 137.65$
From magnesian nitrate........ " $= 138.65$

Czudnowicz[1] based his determination of the atomic weight of lantha-

---

[1] Journ. prakt. Chem., 80, 33. 1860.

num upon one analysis of the air-dried sulphate. The salt contained 22.741 per cent. of water.

<div align="center">.598 grm. gave .272 grm. La$_2$O$_3$ and .586 grm. BaSO$_4$</div>

The La$_2$O$_3$ 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$_2$O$_3$ in the anhydrous sulphate the figure 58.668. 79.117 parts of the salt are proportional to 100 parts of BaSO$_4$. Hence La = 146.43 and 132.93.

Hermann [1] studied both the sulphate and the carbonate of lanthanum. From the anhydrous sulphate, by precipitation as oxalate and ignition, the following percentages of La$_2$O$_3$ were obtained:

<div align="center">

57.690
57.663
57.610
</div>

<div align="center">Mean, 57.654, ± .016</div>

Hence La = 139.51.

The carbonate, dried at 100°, gave the following percentages:

<div align="center">

68.47 La$_2$O$_3$
27.67 CO$_2$
3.86 H$_2$O
</div>

Reckoning from the ratio between CO$_2$ and La$_2$O$_3$, the molecular weight of the latter becomes 326.66.

Zschiesche's [2] 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$_2$O$_3$ in the *anhydrous* salt:

H$_2$O.	SO$_3$.	La$_2$O$_3$.	La$_2$O$_3$ 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
22.570	33.333	44.090	56.947
22.610	33.160	44.240	57.150
22.630	33.051	44.310	57.277

<div align="right">Mean, 57.021, ± .051</div>

Hence La = 135.34.

Erk [3] found that .474 grm. of La$_2$(SO$_4$)$_3$, by precipitation as oxalate and

---

[1] Journ. prakt. Chem., 82, 396, 1861.
[2] Journ. prakt. Chem., 104, 174.
[3] Jenaisches Zeitschrift, 6, 306, 1871.

ignition, gave .2705 grm. of La_2O_3, or 57.068 per cent. Hence La = 135.64. .7045 grm. of the sulphate also gave .8815 grm. of $BaSO_4$. Hence 100 parts of $BaSO_4$ are equivalent to 79.921 of $La_2(SO_4)_3$, and La = 135.74.

From Cleve we have two separate investigations relative to the atomic weight of lanthanum. In his first series[1] 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

Hence La = 139.28.

In his second paper,[2] published nine years later, Cleve gives results similarly obtained, but with lanthanum oxide much more completely freed from other earths. The data are as follows, lettered to correspond to different fractions of the material studied:

B	.8390 grm. La_2O_3 gave 1.4600 sulphate.		57.466 per cent.	
	1.1861	"	2.0643 "	57.458 "
C	.8993	"	1.5645 "	57.482 "
	.8685	"	1.5108 "	57.486 "
	.8515	"	1.4817 "	57.468 "
D	.6486	"	1.1282 "	57.490 "
	.7329	"	1.2746 "	57.500 "
E	1.2477	"	2.1703 "	57.490 "
F	1.1621	"	2.0217 "	57.481 "
	1.5749	"	2.7407 "	57.463 "
G	1.3367	"	2.3248 "	57.497 "
	1.4455	"	2.5146 "	57.484 "

Mean, 57.480, ± .0040

Hence La = 138.35.

Brauner, in 1882, published two sets of determinations, both based upon the conversion of pure La_2O_3 into $La_2(SO_4)_3$.

In his first paper, Brauner[3] gives only two syntheses, as follows:

1.75933 grm. La_2O_3	gave 3.05707 $La_2(SO_4)_3$.	57.566 per cent.	
.92417	"	1.60589 "	57.549 "

Mean, 57.5575, ± .0057

Hence La = 138.87.

---

[1] K. Svensk. Vet. Akad. Handlingar, Bd. 2, No. 7. 1874.
[2] K. Svensk. Vet. Akad. Handlingar, No. 2, 1883.
[3] Monats. Chem., 3, 1.

In Brauner's second [1] paper six determinations are given, one being affected by a misprint, which is corrected by a citation in Abegg's Handbuch: [2]

.7850 grm. La_2O_3 gave	1.3658	$La_2(SO_4)_3$.		57.476 per cent.	
2.3500	"	4.0917	"	57.433	"
2.1052	"	3.6633	"	57.467	"
1.0010	"	1.7411	"	57.525	"
1.3807	"	2.4021	"	57.479	"
1.5275	"	2.6588	"	57.451	"

Mean, 57.472, $\pm$ .0086

Hence $La = 138.30$.

Brauner's weighings are all reduced to a vacuum.

Both Bauer and Bettendorff made their determinations of the atomic weight of lanthanum by the same general method. Bauer's data [3] are as follows:

.6431 grm. La_2O_3 gave	1.1171	sulphate.		57.569 per cent.	
.7825	"	1.3613	"	57.482	"
1.0112	"	1.7571	"	57.549	"
.7325	"	1.2725	"	57.564	"

Mean, 57.541, $\pm$ .0136

Hence $La = 138.76$.

Bettendorff found [4]—

.9146 grm. La_2O_3 gave	1.5900	sulphate.		57.522 per cent.	
.9395	"	1.6332	"	57.525	"
.9133	"	1.5877	"	57.523	"
1.0651	"	1.8515	"	57.526	"

Mean, 57.524, $\pm$ .0006

Hence $La = 138.65$.

The few determinations by Wolcott Gibbs [5] were made by the oxalate method, which is described in the chapter on cerium. Their purpose, however, was rather to test the method than to definitely fix an atomic weight. The data given are as follows, with the ratio $3C_2O_3 : La_2O_3$ added:

La_2O_3.	C_2O_3.	Ratio.
45.61	30.15	151.327
45.64	30.07	151.729
———	30.08	151.679
Mean, 45.625	30.11	151.528

Mean, 151.566, $\pm$ .0607

Hence $La = 139.71$.

[1] Monats. Chem., 3, 486.
[2] Band 3, Abth. 1, p. 240. Brauner's discussion of the atomic weight.
[3] Inaugural Dissertation, Freiburg, 1884.
[4] Liebig's Annalen, 256, 168. 1890.
[5] Proc. Amer. Acad., 28, 260. 1893.

Gibbs cites three determinations, by the same method, made by Shapleigh, who found La=139.75, 139.72 and 139.67. The weighings, however, are not given, and the data are unavailable for present purposes.

In 1901 Bodman [1] published three determinations, based on syntheses of lanthanum sulphate. The figures are:

La_2O_3.	$La_2(SO_4)_3$.	Per cent. La_2O_3.
.4038	.7013	57.579
.4408	.7660	57.546
.4467	.7758	57.579

Mean, 57.568, ± .0070

Hence La=138.94.

In 1902 Jones [2] published his elaborate series of determinations, based upon scrupulously purified materials. He effected twelve syntheses of lanthanum sulphate from the oxide, and examined his product carefully for acid sulphate, whose presence would tend to lower the apparent atomic weight of the metal. This source of error Jones regards as excluded from his determinations. His results are as follows:

La_2O_3.	$La_2(SO_4)_3$.	Per cent. La_2O_3.
1.0122	1.7592	57.538
1.1268	1.9581	57.546
.94585	1.6437	57.543
1.0675	1.8553	57.538
.9030	1.5692	57.545
1.1273	1.9589	57.548
.9407	1.6347	57.546
1.0455	1.8168	57.546
1.1271	1.9586	57.546
1.3074	2.2720	57.544
1.3389	2.3267	57.545
1.2012	2.0874	57.545

Mean, 57.544, ± .0006

Hence La=138.78.

The atomic weight determinations by Brauner and Pavlíček [3] included a study of both the sulphate and the oxalate methods. In lanthanum sulphate the acid salt was always found to be present, and its amount was determined by titration, with sodium hydroxide, using ethyl-orange as an indicator. The excess of acid thus measured tends to lower the apparent atomic weight of lanthanum, and Brauner argues very forcibly that all previous determinations of atomic weights among the rare earths

[1] Bihang Svensk. Vet. Akad. Handl., 26 (2), No. 3. 1901.
[2] Amer. Chem. Journ., 28, 23. 1902.
[3] Journ. Chem. Soc., 81, 1243. 1902. Preliminary notice in Proc. Chem. Soc., 17, 63. 1901.

are vitiated by this error. The authors give three series of syntheses of the sulphate, in which corrections for the acid salt are applied. First, there is a preliminary series, with weights in air. The data, with the acid correction, are as follows, representing eight different fractions of the oxide:

La_2O_3.	$La_2(SO_4)_3$.	Per cent. La_2O_3.
.93205	1.6198	57.541
.8416	1.46234	57.552
.85993	1.49440	57.543
.7847	1.3635	57.550
.80645	1.40145	57.544
1.0760	1.86913	57.567
*1.0683	*1.51479	57.572
.8721	1.51449	57.584
.9755	1.69381	57.592
.9188	1.5955	57.587
.9507	1.65040	57.604
.9677	1.68062	57.580
.8570	1.48736	57.619

Mean, 57.572, ± .0047

Corrected to a vacuum this mean becomes 57.564, ±.0047. Hence La = 138.91. Its significance, however, is diminished by the fact that the fractions show a progressive change in composition, which appears in the percentage column. The later fractions are higher in La_2O_3 than the earlier ones.

The next set of syntheses, representing a different series of lanthanum preparations, gave the subjoined results, corrected for acid sulphate, but with weights in air:

La_2O_3.	$La_2(SO_4)_3$.	Per cent. La_2O_3.
.8262	1.4353	57.563
.95652	1.66133	57.576
.45780	.79574	57.538
1.34754	2.34074	57.569
1.17280	2.03804	57.545

Mean, 57.558, ± .0048

Corrected for weighing in air this becomes 57.550. La = 138.82.

This series, like the preceding one, is given by Brauner and Pavlíček as preliminary to more exact work, which seems to have been continued by Brauner alone. His final series of figures, determined with extreme

---

* These weights are erroneous, either through misprinting in the original or because of copying. The percentage given is that calculated by Brauner and Pavlíček.

care, and with all corrections applied, including the reduction to a vacuum, follows:

La_2O_3.	$La_2(SO_4)_3$.	Per cent. La_2O_3.
1.06562	1.85054	57.5843
1.00694	1.74856	57.5868
1.12553	1.95457	57.5845
1.70276	2.95707	57.5827
1.02460	1.77943	57.5802
1.28650	2.23419	57.5824
1.06488	1.84910	57.5891

Mean, 57.5843, ± .00075

Hence La = 139.05.

The oxalate series of determinations by Brauner and Pavlíček is less satisfactory than this sulphate series, although it leads to sensibly the same value for the atomic weight of lanthanum. Rejecting one experiment in their series, which is thrown out as abnormal by the authors, their percentages are as given in the next table, together with the usual ratios:

Per cent. C_2O_3.	Per cent. La_2O_3.	Ratio.
31.041	46.884	151.039
	46.876	151.013
	44.722	150.716
	44.711	150.679
29.673	44.694	150.622
	44.719	150.706
	44.746	150.797
29.755	44.879	150.828
	44.845	150.714
31.920	48.197	150.993
29.689	44.751	150.733
30.883	46.719	151.277
	46.678	151.145
	48.129	151.530
31.762	48.118	151.495
	48.133	151.543

Mean, 150.989, ± .0543

Hence La = 139.08.

The Gibbs value for the same ratio is 151.566, ±.0607. The general mean of both series is 151.246, ±.0400.

In a criticism of Jones' determinations by the sulphate method Brauner[1] reiterates his statements concerning the acid salt, and also suggests other sources of error, such as contamination of the lanthanum

---

[1] Zeitsch. anorg. Chem., 33, 317. 1903.

preparations by cerium, and losses by spattering. To this criticism
Jones [1] promptly replied, giving a new series of determinations as follows:

La_2O_3.	$La_2(SO_4)_3$.	Per cent. La_2O_3.
1.2161	2.1132	57.548
1.6311	2.8342	57.551
1.7804	3.0938	57.547
1.4168	2.4619	57.549
1.9702	3.4235	57.549

Mean, 57.549, ± .0010

Hence La = 138.81.

The material was spectroscopically pure, and the sulphate was neutral
and soluble. The operations were performed in porcelain crucibles, and
the oxide was perfectly white. Brauner used platinum crucibles, and
Jones found that lanthanum oxide, heated in platinum, became per-
ceptibly discolored. Two determinations made in platinum gave the
following results:

La_2O_3.	$La_2(SO_4)_3$.	Per cent. La_2O_3.
1.2820	2.2264	57.582
1.3885	2.4110	57.590

Mean, 57.586, ± .0027

Hence La = 139.06, a value in accord with Brauner's. According to
Jones the discoloration and variation in atomic weight suggest the
presence of some other oxide than the normal compound in Brauner's
preparations. The controversy, however, remains unsettled, and addi-
tional investigations are needed to determine the truth.

The two determinations by Brill [2] are of slight value, and hardly worth
considering. Small quantities of lanthanum sulphate were calcined to
oxide, and the weighings were made with the Nernst microbalance, in
order to test its applicability to work of this kind. The percentages of
oxide in sulphate are given below, more for the sake of completeness
than for any real significance in them:

57.664
57.726

Mean, 57.695, ± .0207

Hence La = 139.79., a very high value.

In 1906 Feit and Przibylla [3] determined the atomic weights of several
rare earth metals by a special volumetric process, which, however, seems

---

[1] Zeitsch. anorg. Chem., 36, 92. 1903. Chem. News, 88, 13.
[2] Zeitsch. anorg. Chem., 47, 464. 1905.
[3] Zeitsch. anorg. Chem., 50, 248. 1906. See also an earlier paper in Vol. 43, p. 213. 1905.

to be approximate rather than exact. In each case the weighed oxide was dissolved in an excess of half-normal sulphuric acid, the excess being afterwards measured by titration with tenth-normal sodium hydroxide solution. From the data thus obtained, by a process which is not clearly explained, the authors compute the proportion of oxygen in the oxides, and thence deduce the atomic weights of the several methods. It would have been better to have given the H_2SO_4 equivalent to the oxide, and then to have made a more direct calculation. However, I cite the determinations for what they may be worth, their value being essentially corroborative. For lanthanum the authors give the following determinations:

La_2O_3.	O.	Atomic weight.
.5125	.07544	139.05
.5256	.07731	139.11
.4835	.07116	139.08
.5235	.07706	139.04
.4815	.07088	139.03
.5156	.07585	139.15
.5348	.07867	139.15

Mean, 139.09, $\pm$ .0430

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 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, $\pm$ .027
Erk	57.068, $\pm$ .027
Hermann	57.654, $\pm$ .016
Zschiesche	57.021, $\pm$ .051
Marignac	57.549, $\pm$ .0112
Cleve, earlier series	57.619, $\pm$ .0085
Cleve, later series	57.480, $\pm$ .0040
Brauner, 1882, first series	57.5575, $\pm$ .0057
Brauner, 1882, second series	57.472, $\pm$ .0086
Bauer	57.541, $\pm$ .0136
Bettendorff	57.524, $\pm$ .0006
Bodman	57.568, $\pm$ .0070
Jones, 1902	57.544, $\pm$ .0006
Brauner and Pavliček, first	57.564, $\pm$ .0047
Brauner and Pavliček, second	57.550, $\pm$ .0048
Brauner and Pavliček, third	57.5843, $\pm$ .00075
Jones, 1903, porcelain series	57.549, $\pm$ .0010
Jones, 1903, platinum series	57.586, $\pm$ .0027
Brill	57.695, $\pm$ .0207

General mean | 57.5469, $\pm$ .00034

This mean agrees very closely with the figures given by Jones. The early determinations, previous to Marignac, might be properly rejected altogether, as their influence upon the combination is imperceptible.

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
Marignac	80.934
Rammelsberg	79.276
Czudnowicz	79.117
Erk	79.921

Mean, 80.054, ± .270

In all there are eight ratios from which to calculate the atomic weight of lanthanum:

(1). Percentage of La_2O_3 in $La_2(SO_4)_3$, 57.5469, ± .00034
(2). $3BaCl_2 : La_2(SO_4)_3 :: 100 : 91.322$, ± .048—Marignac
(3). $3BaSO_4 : La_2(SO_4)_3 :: 100 : 80.054$, ± .270
(4). $3BaSO_4 : La_2O_3 :: 100 : 46.671$, ± .075—Holzmann
(5). Percentage of La_2O_3 in iodate, 23.447, ± .0216—Holzmann
(6). Percentage of La_2O_3 in magnesian nitrate, 21.3056, ± .058—Holzmann
(7). $3C_2O_3 : La_2O_3 :: 100 : 151.246$, ± .0400
(8). $O : La :: 16 : 139.09$, ± .0430—Feit and Przibylla

Hermann's single experiment on the carbonate is omitted from this scheme as being of no value.

The antecedent atomic weights are—

Ba $=$ 137.363, ± .0025		Cl $=$ 35.4584, ± .0002
Mg $=$ 24.304, ± .0006		I $=$ 126.9204, ± .00033
S $=$ 32.0667, ± .00075		N $=$ 14.0101, ± .0001
C $=$ 12.0038, ± .0002		H $=$ 1.00779, ± .00001

Hence,

From ratio 3	La $=$ 136.205, ± .6875
" " 5	137.652, ± .1557
" " 6	138.637, ± .4587
" " 1	138.801, ± .0020
" " 8	139.090, ± .0430
" " 7	139.363, ± .0303
" " 4	139.416, ± .2626
" " 2	141.208, ± .1500

It is evidently unnecessary to combine these values into a general mean, for only one of them, that from ratio 1, carries any appreciable weight. The other values could not modify it to any noteworthy extent.

The value La = 138.8 is essentially that found by Jones, whose work is entitled to high credit. Brauner, however, by two distinct methods, found La = 139, with much to be said in favor of his determinations. The question as to the true atomic weight of lanthanum is therefore not closed; and it should be taken up anew by means of other methods than those heretofore employed.

CERIUM.

Although cerium was discovered almost at the beginning of the nineteenth 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,[1] 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 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.	1.119 grm.	40.557
.6715 "	1.6595 "	40.464
1.1300 "	2.786 "	40.560
.5366 "	1.3316 "	40.297

Mean, 40.469, ± .0415

Hence Ce = 142.02.

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 $BaSO_4$:

Sulphate.	CeO_2.	$BaSO_4$.	Ratio.
1.379	.8495	1.711	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

Hence Ce = 142.44.

Beringer also gives a single analysis of the formate and the results of

---

[1] Ann. Chem. Pharm., 42, 134. 1842.

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. Obviously, the presence of didymium in the salts analyzed tends to raise the apparent atomic weight of cerium.

Shortly after Beringer, Hermann[1] 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 $BaSO_4$, and $Ce = 138.44$.

In 1848 similar figures were published by Marignac,[2] who found the following amounts of $BaSO_4$ proportional to 100 of dry cerium sulphate:

<div align="center">

122.68
122.00
122.51
_____

Mean, 122.40, $\pm$ .138

</div>

Hence $Ce = 141.97$.

If we give Hermann's single result the weight of one experiment in this series, and combine, we get a mean value of $122.856, \pm .130$.

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	11.990 — 12.050	91.606
First crystallization...	13.194	14.365 — 14.425	91.657
Second crystallization.	13.961	15.225 — 15.285	91.518
Second crystallization.	12.627	13.761 — 13.821	91.559
Second crystallization.	11.915	12.970 — 13.030	91.654
Third crystallization...	14.888	16.223 — 16.283	91.602
Third crystallization...	14.113	15.383 — 15.423	91.755
Fourth crystallization.	13.111	14.270 — 14.330	91.685
Fourth crystallization.	13.970	15.223 — 15.283	91.588

<div align="right">

Mean, 91.625, $\pm$ .016

</div>

Hence $Ce = 141.33$.

---

[1] Journ. prakt. Chem., 30, 185. 1843.
[2] Arch. Sci. Phys. Nat. (1), 8, 273. 1848. Oeuvres Complètes, 1, 215.

Omitting the valueless experiments of Kjerulf,[1] we come next to the figures published by Bunsen and Jegel[2] 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, ± .077

Hence Ce = 138.48.
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.

In each sample of CeO_2 the excess of oxygen over Ce_2O_3 was estimated by an iodometric titration; but the data thus obtained need not be further considered.

In two papers by Rammelsberg[3] data are given for the atomic weight of cerium, as follows. In the earlier paper cerium sulphate was 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's and Rammelsberg's cerium salts were undoubtedly freer from didymium than the material studied by Beringer.

[1] Ann. Chem. Pharm., 87, 12.
[2] Ann. Chem. Pharm., 105, 45. 1858.
[3] Poggend. Annalen, 55, 65; 108, 44.

In his later paper Rammelsberg gives these figures concerning cerium oxalate. One hundred 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 $Ce =$ 138.18.

In all of the foregoing experiments the 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 color remained, which was supposed to be characteristic of the oxide itself. In 1868, however, some experiments of Dr. C. Wolf[1] 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 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.	CeO_2.	Per cent. CeO_2.
1.4542	.19419	.76305	60.559
1.4104	.1898	.7377	60.437
1.35027	.1820	.70665	60.487
			Mean, 60.494

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.	CeO_2.	Per cent. CeO_2.
1.4327	.2733	.69925	60.311
1.5056	.2775	.7405	60.296
1.44045	.2710	.7052	60.300
			Mean, 60.302

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.

[1] Amer. Journ. Science (2), 46, 53.

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 account. The death of Dr. Wolf interrupted the investigation, the results of which were edited and published by Professor F. A. Genth.

. In the light of more recent evidence, little weight can be given to these observations. All the experiments, taken equally, give a mean percentage of CeO_2 from $Ce_2(SO_4)_3$ of 60.366, ±.0308. This mean has obviously little or no real significance. It gives $Ce = 138.74$.

The experiments of Wolf attracted little attention, except from Wing,[1] who partially verified certain aspects of them. This chemist, incidentally to other researches, purified 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	.1707	.6732	60.225
1.4090	.1857	.7372	60.263
			Mean, 60.244

Hence $Ce = 137.88$.

The ceric oxide in this case was perfectly white. The cerium oxalate which yielded it was precipitated boiling by a boiling concentrated solution of oxalic acid. The precipitate stood twenty-four hours before filtering.

In 1875 Buehrig's[2] paper upon the atomic weight of cerium was issued. He first studied the sulphate, which, after eight crystallizations, still retained traces of free sulphuric 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. 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 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

[1] Am. Journ. Sci. (2), 49, 358. 1870.
[2] Journ. prakt. Chem., 120, 222. 1875.

acid and water were collected after the usual method. Ten determinations were made; in all of them the above-named products were estimated, and in five analyses the resulting 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	2.1897	3.6942	.....
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
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	.....
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	Mean, 63.4316, $\pm$ .0032

Hence $Ce = 141.56$.   Hence $Ce = 141.48$.

These results could not be appreciably affected by combination with the single oxalate experiments of Jegel and of Rammelsberg, and the latter may therefore be ignored.

Robinson's work, published in 1884,[1] was based upon pure cerium chloride, prepared by heating dry cerium oxalate in a stream of dry, gaseous hydrochloric acid. This compound was titrated with standard solutions of pure silver, prepared according to Stas, and these were

---

[1] Chemical News, 50, 251, 1884. Proc. Roy. Soc., 37, 150.

weighed, not measured. In the third column I give the ratio between $CeCl_3$ and 100 parts of silver:

$CeCl_3$.	Ag.	Ratio.
5.5361	7.26630	76.189
6.0791	7.98077	76.172
6.4761	8.50626	76.133
6.98825	9.18029	76.122
6.6873	8.78015	76.164
7.0077	9.20156	76.158
6.9600	9.13930	76.150

Mean, 76.155, $\pm$ .0065

Reduced to a vacuum this becomes 76.167. Hence Ce = 140.13.

In a later paper,[1] Robinson discusses the color of ceric oxide, and criticises the work of Wolf. He shows that the pure oxide is not white, and makes it appear probable that Wolf's materials were contaminated with compounds of lanthanum. He also urges that Wolf's cerium sulphate could not have been absolutely definite, because of defects in the method by which it was dehydrated.

Brauner,[2] in 1885, investigated cerium sulphate with extreme care, and appears to have obtained material free from all other earths and absolutely homogeneous. The anhydrous salt was calcined with all necessary precautions, and the data obtained, reduced to a vacuum, were as follows:

$Ce_2(SO_4)_3$.	CeO_2.	Per cent. CeO_2.
2.16769	1.31296	60.5693
2.43030	1.47205	60.5707
2.07820	1.25860	60.5620
2.21206	1.33989	60.5721
1.28448	.77845	60.6043
1.95540	1.18436	60.5687
2.46486	1.49290	60.5673
2.04181	1.23733	60.5997
2.17714	1.31878	60.5739
2.09138	1.26654	60.5605
2.21401	1.34139	60.5863
2.44947	1.48367	60.5711
2.22977	1.35073	60.5771
2.73662	1.65699	60.5486
2.62614	1.59050	60.5642
1.67544	1.01470	60.5632
1.57655	.95540	60.6007
2.72882	1.65256	60.5600

[1] Chemical News, 54, 229. 1886.
[2] Sitzungsb. Wien. Akad., Bd. 92. July, 1885.

2.10455	1.27476	60.5716
2.10735	1.27698	60.5965
2.43557	1.47517	60.5692
3.01369	1.82524	60.5649
4.97694	3.01372	60.5537

Mean, 60.5729, ± .0021

Hence $Ce = 140.22$.

In 1895 several papers upon the cerite earths were published by Schutzenberger.[1] In the first of these a single determination of atomic weight is given. Pure CeO_2, of a yellowish-white color, was converted into sulphate, which was dried in a current of dry air at 440°. This salt, dissolved in water, was poured into a hot solution of caustic soda, made from sodium, and, after filtration and washing, the filtrate, acidulated with hydrochloric acid, was precipitated with barium chloride. The trace of sulphuric acid retained by the cerium hydroxide was recovered by re-solution and a second precipitation, and added to the main amount. 100 parts of $Ce_2(SO_4)_3$ gave 123.30 of $BaSO_4$. This may be assigned equal weight with one experiment in Marignac's series, giving the following combination:

Hermann	123.926, ± .238
Marignac	122.40, ± .138
Schutzenberger	123.30, ± .238
General mean	122.958, ± .1139

Schutzenberger, criticising Brauner's work, claims that the latter was affected by a loss of oxygen during the calcination of the cerium dioxide.

In his second and third papers Schutzenberger describes the results obtained upon the fractional crystallization of cerium sulphate. Preparations were thus made yielding oxides of various colors—canary-yellow, rose, yellowish-rose, reddish and brownish-red. These oxides, by synthesis of sulphates, the barium-sulphate method, etc., gave varying values for the atomic weight of cerium, ranging from 135.7 to 143.3. Schutzenberger therefore infers that cerium oxide from cerite contains small quantities of another earth of lower molecular weight; but the results as given are not conclusive. The third paper is essentially a continuation of the second, with reference to the didymiums.[2]

Schutzenberger's papers were promptly followed by one from Brauner,[3] who claimed priority in the matter of fractionation, and gave some new

---

[1] Compt. Rend., 120, pp. 663, 962, and 1143. 1895.

[2] Similar results were also obtained by Boudouard (Compt. Rend., 125, 772. 1897). The correctness of these conclusions is questionable.

[3] Chem. News, 71, 283.

data, the latter tending to show that cerium oxide is a mixture of at least two earths. One of these, of a dark salmon color, he ascribed to a new element, "meta-cerium." The other he called cerium, and gave for it a preliminary atomic weight determination. The pure oxalate, by Gibbs' method, gave 46.934 per cent. of CeO_2, and, on titration with potassium permanganate, 29.503 and 29.506 per cent. of C_2O_3. Hence $Ce = 139.62$. In mean, this ratio may be written—

$$3C_2O_3 : 2CeO_2 : : 100 : 159.074$$

which will be combined with other corresponding expressions later.

Wyrouboff and Verneuil [1] determined the atomic weight of cerium by analyses of the sulphate, $Ce_2(SO_4)_3.8H_2O$. The salt was prepared from three different sources, two samples from monazite, and one from cerite. It was dehydrated at 250°, and reduced to CeO_2 at 1500°. The latter was perfectly white. The weights were as follows:

Hydrous sulphate.	Anhydrous sulphate.	CeO_2.
1.2385	.9875	.5977
1.2730	1.0148	.6138
1.2030	.9590	.5794
1.5420	1.2295	.7430
.9642	.7685	.4642
1.3260	1.0571	.6389
1.1429	.9112	.5512
.9072	.7232	.4372
1.2114	.9658	.5840
1.2411	.9894	.5984

Hence the following percentages:

H_2O.	CeO_2 in hydrate.	CeO_2 in $Ce_2(SO_4)_3$.
20.267	48.259	60.526
20.282	48.216	60.484
20.282	48.162	60.417
20.265	48.184	60.431
20.296	48.143	60.403
20.279	48.182	60.438
20.273	48.280	60.557
20.282	48.192	60.453
20.274	48.208	60.468
20.280	48.215	60.481
Mean, 20.278, ± .0019	48.204, ± .0095	60.466, ± .0103
Hence Ce = 139.21	139.39	139.45

[1] Bull. Soc. Chim. (3), 17, 679. 1897. Also Ann Chim. Phys. (8), 9, 349. Moissan, Compt. Rend., 124, 1233, also describes white ceric oxide.

Kölle [1] studied anhydrous cerium sulphate, which he reduced by calcination to CeO_2. His figures are as follows:

$Ce_2(SO_4)_3$.	CeO_2.	Per cent. CeO_2.
1.84760	1.11648	60.429
1.16074	.70078	60.331
1.53599	.92722	60.366
.97196	.58661	60.353
1.40374	.84760	60.384
1.75492	1.05956	60.377
1.53784	.92853	60.379
1.64233	.99150	60.372

Mean, 60.374, $\pm$ .0067

Hence Ce = 138.80, an unusually low and improbable value.

The very careful investigation by Brauner and Batĕk [2] involved the study of two cerium salts, the sulphate and the oxalate. The sulphate was dehydrated at 440°, and then calcined to oxide. The figures given in the next table represent a number of different samples of the salt, but I have here combined the data into one series:

$Ce_2(SO_4)_3$.	CeO_2.	Per cent. CeO_2.
1.5074	.9130	60.568
1.7979	1.08945	60.596
1.5937	.9665	60.645
2.6240	1.5895	60.575
1.2161	.7370	60.604
1.5074	.9130	60.568
1.2192	.7386	60.581

Mean, 60.591, $\pm$ .0070

Reduced to a vacuum basis this becomes 60.584.

Hence Ce = 140.30.

Combining this series with others, we have

Wolf	60.366, $\pm$ .0308
Wing	60.244, $\pm$ .0308
Brauner	60.5729, $\pm$ .0021
Wyrouboff and Verneuil	60.466, $\pm$ .0103
Kölle	60.374, $\pm$ .0067
Brauner and Batĕk	60.584, $\pm$ .0070
General mean	60.5528, $\pm$ .0019

Wing's mean is here arbitrarily given equal weight with that of Wolf, but both series practically vanish.

[1] Beiträge zur Kenntnis des Cers. Inaugural Dissertation, Zürich, 1898.
[2] Zeitsch. anorg. Chem., 34, 103. 1903.

Cerium oxalate contains water, in proportions which are not absolutely constant; at least not constant enough for good atomic weight determinations. In Buehrig's analyses the water was estimated, but it is doubtful whether the estimations can be made with adequate sharpness. Cerium oxalate, therefore, is best handled by the method of Stolba and Gibbs; which consists in determining the amount of ceric oxide left after calcination; and in another portion of the same sample, estimating the radicle C_2O_3 by titration with potassium permanganate. From the ratio $3C_2O_3 : 2CeO_2$ the atomic weight of cerium can be calculated.

This method was followed by Brauner, in a single determination which has already been cited. It was also adopted by Brauner and Batěk, who give five sets of determinations, with vacuum weights, as follows. I cite now only the percentages of CeO_2 and C_2O_3, as computed from the weighings, together with the required ratio:

Sample I.

Per cent. CeO_2.	Per cent. C_2O_3.	Ratio.
46.949	29.423	150.503
46.939	29.391	159.685
46.913	29.393	159.664
46.920	29.442	159.398
————	29.422	159.507
Mean, 46.930	29.397	159.642
	29.406	159.593
	29.459	159.306
	29.414	159.540
	29.459	159.306
	29.459	159.306
	29.436	159.431

The ratio here is computed from the individual figures for C_2O_3 and the mean for CeO_2.

Sample II.

Per cent. CeO_2.	Per cent. C_2O_3.	Ratio.
47.197	29.601	159.353
47.089	29.564	159.552
47.225	29.559	159.579

Mean, 47.170

Samples III, IV, V.

	Per cent. CeO_2.	Per cent. C_2O_3.	Ratio.
III	47.161 ⎱ 47.160 ⎰	29.512	159.718
IV	46.926 ⎱ 46.922 ⎰	29.391	159.654
V	47.039	29.531	159.287

The mean of the 18 values for the ratio is 159.501.±.0285.   Hence
Ce = 140.28.

In a later memoir, Brauner [1] gives additional analyses of cerium oxalate
and sulphate.   The oxalate figures are as follows:

Per cent. CeO₂.	Per cent. C₂O₃.	Ratio.
47.070	29.548	159.304
47.067	29.544	159.325
47.077	29.478	159.682
47.070	29.486	159.638
47.074		

Mean, 47.071

Mean, 159.487, ± .0677

Hence Ce = 140.26.

If we give to Brauner's earliest, single determination, the weight of
one experiment in the Brauner and Batĕk series, the values for this
ratio combine thus:

Brauner, early .... 159.074, ± .0990
Brauner and Batĕk........... 159.501, ± .0285
Brauner, latest .... 159.487, ± .0677

General mean .... 159.471, ± .0254

In the memoir last cited Brauner also gives a series of determinations
based on the calcination of the octohydrated cerium sulphate.   In the
subjoined table I include two separate determinations given near the
beginning of the paper.   All weights were reduced to a vacuum standard:

Sulphate.	CeO₂.	Per cent. CeO₂.
1.98989	.96175	48.332
1.99154	.96251	48.330
2.33919	1.13027	48.319
1.95882	.94679	48.335
1.20961	.58453	48.324
1.54162	.74504	48.329
1.67748	.81074	48.331
2.02736	.97985	48.331

Mean, 48.329, ± .0011

Brauner rejects the third determination, a procedure which changes
the mean to 48.330, ±.0009.   We may adopt the latter and combine it
with another series, thus:

Wyrouboff and Verneuil....... 48.204, ± .0095
Brauner .... 48.330, ± .0009

General mean .... 48.329, ± .0009

[1] Zeitsch. anorg. Chem., 34, 207. 1903.

From Brauner's series Ce = 140.26.

Brauner discusses at some length the color of ceric oxide, and describes it as nearly white, but with a faint tinge of brownish-yellow.

The ratios, good and bad, for cerium now are—

(1). $Ce_2(SO_4)_3:3BaSO_4::100:122.958, \pm .1139$
(2). $3BaSO_4:2CeO_2::100:49.360, \pm .035$
(3). $3BaCl_2:Ce_2(SO_4)_3::100:91.625, \pm .016$
(4). $3AgCl:CeO_2::100:40.469, \pm .0415$
(5). Percentage CeO_2 from $Ce_2(SO_4)_3$, 60.5528, $\pm .0019$
(6). Percentage CeO_2 in $Ce_2(SO_4)_3.8H_2O$, 48.329, $\pm .0009$
(7). Percentage H_2O in $Ce_2(SO_4)_3.8H_2O$, 20.278, $\pm .0019$
(8). Percentage CeO_2 from $Ce_2(C_2O_4)_3$, 63.4316, $\pm .0032$
(9). Percentage CO_2 from $Ce_2(C_2O_4)_3$, 48.2546, $\pm .001$
(10). $3Ag:CeCl_3::100:76.167, \pm .0065$
(11). $3C_2O_3:2CeO_2::100:159.471, \pm .0254$

The antecedent atomic weights are—

Ag = 107.880,	± .00029	C = 12.0038,	± .0002
Cl = 35.4584,	± .0002	Ba = 137.363,	± .0025
S = 32.0667,	± .00075	H = 1.00779,	± .00001

Hence,

From ratio 7 ....Ce = 139.210, ± .0276
"   " 5 ....140.079, ± .0100
"   " 10 ....140.132, ± .0105
"   " 11 ....140.247, ± .0275
"   " 6 ....140.251, ± .0045
"   " 1 ....140.663, ± .2638
"   " 2 ....140.832, ± .1225
"   " 3 ....141.330, ± .0500
"   " 8 ....141.483, ± .0176
"   " 9 ....141.559, ± .0064
"   " 4 ....142.023, ± .1785

General mean, Ce = 140.583, ± .0032

This mean appears to be, on chemical grounds, too high, because of the evident overweighting of ratio 9. If we reject all values in excess of 141, the general mean of the remaining seven values is

Ce = 140.197, ± .0038

This represents mainly the work of Brauner and Robinson.

PRASEODYMIUM.

In 1885 Auer von Welsbach[1] succeeded in proving that the old
" didymia " was a mixture of two earths, one yielding green, and the
other rose-colored salts. To the corresponding metals, praseodymium and
neodymium, he assigned the atomic weights $Pr = 143.6$ and $Nd = 140.8$,
respectively, values which were curiously reversed, either in printing or
by the error of a copyist. The true values are now known to be nearly
$Pr = 141$ and $Nd = 144$, in round numbers. For " didymium," many dis-
cordant atomic weight determinations had been made, which now have
only historical interest, and need, therefore, no consideration now. They
are thoroughly summed up in the first edition of this work, which was
published about three years before Welsbach's brilliant discovery.

In 1898 Brauner[2] published a preliminary notice upon praseodymium.
Thirteen determinations of the atomic weight, by both the sulphate and
the oxalate methods, gave values from 140.84 to 141.19, in mean 140.95,
but the details of the work were not given. These early data, therefore,
are not now available for discussion. The first fully described series of
determinations was made by Jones,[3] who published his results a little
later than Brauner.

Jones effected the synthesis of praseodymium sulphate from the oxide,
the latter having been first reduced from Pr_4O_7 to Pr_2O_3 by heating in
hydrogen. The material, after purification, still contained minute traces
of lanthanum and neodymium, but these were too small to seriously
affect the atomic weight determination. The weights and percentages
appear in the following table:

Pr_2O_3.	$Pr_2(SO_4)_3$.	Per cent. Pr_2O_3.
.5250	.9085	57.789
.6436	1.1135	57.800
.7967	1.3788	57.782
.7522	1.3018	57.782
.7788	1.3473	57.805
.6458	1.1172	57.805
.6972	1.2062	57.801
.7204	1.2464	57.798
.8665	1.4990	57.805
.6717	1.1624	57.796
.7439	1.2873	57.788
.6487	1.1224	57.796

Mean, 57.796. ± .0016

Hence $Pr = 140.47$.

---

[1] Monatsh. Chem., 6, 477. 1885.
[2] Proc. Chem. Soc., 14, 70. 1898.
[3] Amer. Chem. Journ., 20, 345. 1898.

C. von Schéele,[1] also in 1898, gave three series of determinations. First, by the synthesis of praseodymium sulphate, which, however, contained a little lanthanum sulphate, as follows:

Pr_2O_3.	$Pr_2(SO_4)_3$.	Per cent. Pr_2O_3.
1.6738	2.8926	57.865
1.4327	2.4788	57.798
1.1105	1.9221	57.775
1.0072	1.7431	57.782

Mean, 57.805, $\pm$ .0139

Hence $Pr = 140.53$.

The second series by von Schéele is somewhat obscure, being a combination of the oxalate and sulphate methods. A part of the oxalate was converted into sulphate, and in another part the C_2O_3 radicle was determined by titration with permanganate solution. The proportion of oxide in sulphate was also found. I give below the several percentages, and also the ratio $3C_2O_3 : Pr_2(SO_4)_3$:

Sulphate from oxalate.	Per cent. C_2O_3.	Pr_2O_3 in sulphate.	Ratio.
81.682	31.07	57.73	
81.638	31.06	57.71	
———	31.11		
Mean, 81.665	———		
	Mean, 31.08		262.515
77.828	29.60	57.77	262.845
	29.58		
	29.64		
	———	———	———
	Mean, 29.61	57.737	262.680
		$\pm$ .0117	$\pm$ .1113
		$Pr = 140.07$	139.62

These two series have small claims to consideration, and may be regarded as preliminary. The third series, by the sulphate method, is far better:

Pr_2O_3.	$Pr_2(SO_4)_3$.	Per cent. Pr_2O_3.
.6872	1.1890	57.796
.7834	1.3550	57.815
.6510	1.1260	57.815
.7640	1.3216	57.809
.5183	.8967	57.801

Mean, 57.807, $\pm$ .0026

Hence $Pr = 140.54$.

---

[1] Zeitsch. anorg. Chem., 17, 310, 1898.

In 1901 Brauner[1] gave a preliminary notice of an investigation upon the atomic weight of praseodymium, but without details. He has since published his data in Abegg's Handbuch der anorganischen Chemie,[2] as follows:

First, the octohydrated sulphate was dehydrated at 500°, then calcined to oxide, and the latter finally analyzed iodometrically to determine the true proportions of Pr_2O_3. Percentage A in the next table is that of Pr_2O_3 in the hydrous sulphate, and B refers to the anhydrous salt:

$Pr_2(SO_4)_3.8H_2O.$	$Pr_2(SO_3)_4.$	$Pr_2O_3.$	Per cent. A.	Per cent. B.
1.29269	1.03242	.59747	46.219	57.871
1.27990	1.02193	.59137	46.204	57.868
			Mean, 46.211,	57.8695
			± .0050	
			Pr = 141.09	

Secondly, four samples of praseodymium oxalate were analyzed by the method already described under cerium and lanthanum. I give the ratio computed from the percentages, in the form $3C_2O_3 : Pr_2O_3 :: 100 : x$:

Sample.	Per cent. $Pr_2O_3.$	Per cent. $C_2O_3.$	Ratio.	Weight.
A	45.183 	29.581 29.581	152.743	2
B	45.142 45.098 45.095 45.102 45.063	29.499 29.593 29.532 29.511	152.671	4
C	45.032 45.123	29.503 29.483	152.840	2
D	45 136 	29.565 29.562	152.677	2

Each value for the ratio is here weighted according to the number of the C_2O_3 determinations. The mean of all, thus weighted, is 152.720, ± .0148.

Hence Pr = 140.95.

Finally, Brauner affected the synthesis of the anhydrous sulphate. Praseodymium oxalate was calcined, and the composition of the oxide produced was ascertained by iodometric titration. It was then converted into sulphate, with the correction, described under lanthanum, for excess of sulphuric acid. The corrected data are these:

[1] Proc. Chem. Soc., 17, 65.
[2] Bd. 3, Abth. 1, pp. 263-265.

Pr_2O_3.	$Pr_2(SO_4)_3$.	Per cent. Pr_2O_3.
.73359	1.26782	57.863
.64871	1.12059	57.890
.74103	1.28051	57.870
.72894	1.25972	57.865
.36559	.63350	57.867
.82769	1.43024	57.871

In his first series Brauner found, for the same percentage, 57.871 and 57.868. Including these, the eight determinations, taken as one series, give a mean of $57.871, \pm .0021$.

Hence $Pr = 140.97$.

Combining this mean with other means for the same ratio we have—

Jones	57.796,	$\pm$ .0016
Schéele, first	57.805,	$\pm$ .0139
" second	57.737,	$\pm$ .0117
" third	57.807,	$\pm$ .0026
Brauner	57.871,	$\pm$ .0021
General mean	57.8194,	$\pm$ .0010

Three other determinations by Welsbach[1] were published in 1903. He used the sulphate method and found $Pr = 140.64$, 140.50 and 140.56 when $O = 16$. Unfortunately, he gave no weighings, nor did he state what value he used for the atomic weight of sulphur. His figures, therefore, are unavailable for discussion now.

There are also three determinations by Feit and Przibylla,[2] who used the peculiar volumetric method already described under lanthanum. Their results are as follows:

Pr_2O_3.	O.	Atomic weight.
.54010	.07879	140.518
.53420	.07789	140.601
.50054	.07302	140.516

Mean, $140.545, \pm .0189$

The ratios for praseodymium now are—

(1). $Pr_2(SO_4)_3.8H_2O : Pr_2O_3 :: 100 : 46.211, \pm .0050$
(2). $Pr_2(SO_4)_3 : Pr_2O_3 :: 100 : 57.8194, \pm .0010$
(3). $3C_2O_3 : Pr_2(SO_4)_3 :: 100 : 262.680, \pm .1113$
(4). $3C_2O_3 : Pr_2O_3 :: 100 : 152.720, \pm .0148$
(5). $O : Pr :: 16 : 140.545, \pm .0189$

---

[1] Sitzungsb. Wien. Akad., 112, 1037. 1903.
[2] Zeitsch. anorg. Chem., 50, 258. 1906.

To reduce these ratios we have $S = 32.0667, \pm .00075$; $C = 12.0038, \pm .0002$; and $H = 1.00779, \pm .00001$.

Hence,

From ratio 3 ....Pr $= 139.623, \pm .1200$

"   "   5 ....140.545, $\pm .0189$

"   "   2 ....140.628, $\pm .0035$

"   "   4 ....140.954, $\pm .0160$

"   "   1 ....141.090, $\pm .0236$

General mean, Pr $= 140.619, \pm .0033$

Brauner's determinations make Pr $= 141$, very nearly, and must be taken into consideration in criticizing the foregoing combination. His value may be nearer the truth, but the work of Jones and of Scheele cannot yet be rejected. There is still an uncertainty of half a unit in the atomic weight of praseodymium. The later determinations by Welsbach are in harmony with the general mean of all the other estimations.

NEODYMIUM.

Our knowledge of the atomic weight of neodymium is almost entirely based upon a study of the sulphate. Welsbach's first determination was cited under praseodymium, and needs no farther consideration. So also Brauner's [1] first, preliminary figure, Nd $= 143.63$, given without analytical details, may be dismissed here. The first important series of determinations is that by Jones,[2] published in 1898. The synthesis of the sulphate was effected in the usual way, with the following results:

Nd_2O_3.	$Nd_2(SO_4)_3$.	Per cent. Nd_2O_3.
.8910	1.5296	58.251
.7880	1.3530	58.241
.9034	1.5509	58.250
.7668	1.3166	58.241
.8908	1.5296	58.237
.8848	1.5194	58.234
.8681	1.4903	58.250
.8216	1.4103	58.257
.8531	1.4646	58.248
.8711	1.4957	58.240
.8932	1.5332	58.257
.8893	1.5268	58.246

Mean, 58.246, $\pm .0015$

Hence Nd $= 143.54$.

[1] Proc. Chem. Soc., 14, 72. 1898.

[2] Amer. Chem. Journ., 20, 345. 1898. See additional note in Zeitsch. anorg. Chem., 19, 339. 1899.

One determination, by Boudouard,[1] was made by calcination of the sulphate. 2.758 grammes of $Nd_2(SO_4)_3$ gave 1.605 of Nd_2O_3, or 58.194 per cent. Hence $Nd = 143.18$.

Brill,[2] in 1905, made two analyses of neodymium sulphate, with the aid of the microbalance. His percentages of Nd_2O_3 are

58.000
58.180
_____

Mean, 58.090, $\pm$ .0600

Hence $Nd = 142.46$.

In Abegg's Handbuch, Brauner[3] gives the details of a synthesis of neodymium sulphate, with corrections for excess of acid. 0.93788 gramme Nd_2O_3 gave 1.60873 $Nd_2(SO_4)_3$. Per cent. Nd_2O_3, 58.299, whence $Nd = 143.90$.

Holmberg,[4] who employed the usual synthetic method, found no serious difficulty in obtaining a neutral sulphate. In his series of determinations, therefore, a correction for excess of sulphuric acid was not needed. His six syntheses are as follows:

Nd_2O_3.	$Nd_2(SO_4)_3$.	Per cent. Nd_2O_3.
.9692	1.6618	58.322
.6584	1.1287	58.333
1.0292	1.7643	58.335
1.0118	1.7346	58.330
.5518	.9462	58.317
.5345	.9164	58.326

Mean, 58.327, $\pm$ .0019

Hence $Nd = 144.10$.

In combining these various determinations of the oxide-sulphate ratio, the single experiments by Boudouard and Brauner are each given the probable error of one experiment in Jones' series:

Jones .... 58.246, $\pm$ .0015
Boudouard .... 58.194, $\pm$ .0067
Brill .... 58.090, $\pm$ .0600
Brauner .... 58.299, $\pm$ .0067
Holmberg .... 58.327, $\pm$ .0019
_____

General mean .... 58.2831, $\pm$ .0011

[1] Compt. Rend., 126, 900. 1898.
[2] Zeitsch. anorg. Chem., 47, 464. 1905.
[3] Abegg's Handbuch, Bd. 3, Abth. 1, p. 276. Preliminary note in Proc. Chem. Soc., 17, 66. 1901.
[4] Zeitsch. anorg. Chem., 53, 124. 1907.

In this combination only the series by Jones and Holmberg are important. The other figures count for little or nothing. Welsbach's[1] determinations, also by the sulphate method, cannot be safely utilized, for lack of details. He found $Nd = 144.55$, 144.52 and 144.57; in mean, $144.547, \pm .0103$.

Feit and Przibylla[2] give the following data for neodymium, obtained by their volumetric method:

Nd_2O_3.	O.	Atomic weight.
.5380	.07661	144.542
.5388	.07675	144.485
.5358	.07632	144.491
.5265	.07497	144.547
		Mean, 144.516, $\pm$ .0111

Calculating with $S = 32.0667, \pm .00075$, we now have two distinct values for neodymium, as follows:

From the sulphate......$Nd = 143.752, \pm .0057$
From the oxide................$144.516, \pm .0111$

General mean, $Nd = 143.910, \pm .0051$

If we assume that Welsbach's latest determinations were based upon essentially the same value for sulphur as that given above, his mean, $144.547, \pm .0103$, may be combined with the other values. In that case the general mean becomes $Nd = 144.037$. The round number, $Nd = 144$, is as near the truth as the present evidence will permit us to approach. It is possibly some tenths of a unit too low.

[1] Sitzungsb. Wien. Akad., 112, 1037. 1903.
[2] Zeitsch. anorg. Chem., 50, 259. 1906. For the process, see under lanthanum.

SAMARIUM.

According to Marignac,[1] the atomic weight of samarium is 149.4. He gives, however, one analysis of the octohydrated sulphate, as follows: 1.8515 grammes gave 0.365 of water, and on calcination lost 0.607 SO_3. Hence the percentage of Sa_2O_3 in the hydrous salt is 47.502, and in the anhydrous sulphate 59.166. From these data $Sa = 149.87$ and 150.02. Brauner,[2] with purer material, made $Sa = 150.7$, but gave no details. The first regular series of atomic weight determinations was by Cleve,[3] who effected the synthesis of the sulphate from the oxide. Data as follows:

Sa_2O_3.	$Sa_2(SO_4)_3$.	Per cent. Sa_2O_3.
1.6735	2.8278	59.180
1.9706	3.3301	59.175
1.1122	1.8787	59.201
1.0634	1.7966	59.190
.8547	1.4440	59.190
.7447	1.2583	59.183

Mean, 59.1865, ± .0025

Hence $Sa = 150.17$.

Another set of determinations by Bettendorff,[4] after the same general method, gave as follows:

Sa_2O_3.	$Sa_2(SO_4)_3$.	Per cent. Sa_2O_3.
1.0467	1.7675	59.219
1.0555	1.7818	59.238
1.0195	1.7210	59.225

Mean, 59.227, ± .0038

Hence $Sa = 150.46$.

In a single analysis of the hydrous sulphate, Brauner[5] obtained the following figures: 1.36567 grammes $Sa_2(SO_4)_3.8H_2O$ gave 1.09770 $Sa_2(SO_4)_3$ and 0.65046 Sa_2O_3. Per cent. Sa_2O_3 in hydrate, 47.629; in anhydrous salt, 59.257. Hence $Sa = 150.76$ and 150.67.

Käppel,[6] cited by Muthmann and Weiss, from 4.12673 grammes $Sa_2(SO_4)_3$ obtained 2.45028 Sa_2O_3, or 59.376 per cent. Hence $Sa = 151.59$.

[1] Arch. Sci. Phys. Nat. (3), 3, 435. 1880. Oeuvres Complètes, 2, 709.
[2] Journ. Chem. Soc., 43, 287. 1883.
[3] Journ. Chem. Soc., 43, 362. 1883
[4] Am. Chem. Pharm., 263, 164. 1891.
[5] Abegg's Handbuch, Bd. 3, Abth. 1, p. 284.
[6] Liebig's Annalen, 331, 16. 1904.

Brill's [1] analyses of samarium sulphate, with the aid of the microbalance, need not be considered, for his two experiments, as recorded, are widely discordant. The most thorough investigation is that by Urbain and Lacombe,[2] whose material was scrupulously freed from other rare earths, an impurity to be discussed more fully a little later. The samarium preparations of Urbain and Lacombe were derived from different sources, gadolinite, monazite sand, etc., and the octohydrated sulphate was analyzed by dehydration and calcination in the ordinary way. In the next table I give their weights, and also three percentage columns, as follows: A, percentage of $Sa_2(SO_4)_3$, in $Sa_2(SO_4)_3.8H_2O$. B, Sa_2O_3 in the hydrous sulphate. C, Sa_2O_3 in the anhydrous sulphate. The different samples of material are indicated by brackets:

$Sa_2(SO_4)_3.8H_2O.$	$Sa_2(SO_4)_3.$	$Sa_2O_3.$	A.	B.	C.
1.0499	.8435	.4996	80.341	47.585	59.229
1.2898	1.0362	.6137	80.338	47.580	59.225
1.3650	1.0969	.6497	80.359	47.597	59.230
1.7992	1.4453	.8557	80.330	47.560	59.206
1.8636	1.4977	.8873	80.366	47.605	59.244
.8407	.6749	.4001	80.277	47.591	59.283
2.5107	2.0172	1.1948	80.344	47.588	59.228
3.1171	2.5045	1.4840	80.347	47.608	59.253
2.9425	2.3635	1.4004	80.323	47.592	59.251
3.2200	2.5872	1.5324	80.348	47.590	59.230
2.8382	2.2804	1.3508	80.347	47.594	59.237
		Mean,	80.338,	47.590,	59.238,
			± .0048	± .0026	± .0040

From A, Sa = 150.34.
From B, Sa = 150.49.
From C, Sa = 150.54.

Two of the ratios given by Urbain and Lacombe's experiments may now be combined with former series of determinations. First, for the percentage of Sa_2O_3 in the anhydrous sulphate, giving the single determinations of Marignac, Brauner and Käppel the weight of one experiment in Urbain and Lacombe's series:

Marignac .... 59.166, ± .0199
Cleve .... 59.1865, ± .0025
Bettendorff .... 59.227, ± .0038
Brauner .... 59.257, ± .0199
Käppel .... 59.376, ± .0199
Urbain and Lacombe........ 59.238, ± .0040

General mean .... 59.2074, ± .0018

[1] Zeitsch. anorg. Chem., 47, 464, 1905.
[2] Compt. Rend., 138, 1166, 1904.

Secondly, for the percentage of Sa_2O_3 in the hydrous sulphate, giving, arbitrarily, the single determinations of Marignac and Brauner the same weight as in the anhydrous series:

Marignac .... 47.502, $\pm$ .0199
Brauner .... 47.629, $\pm$ .0199
Urbain and Lacombe.......... 47.590, $\pm$ .0026

General mean .... 47.589, $\pm$ .0025

The value of these combinations is perhaps questionable. The earlier work on the atomic weight of samarium is affected by the discovery of europium, which was made by Demarçay.[1] According to this chemist, the original samaria contained admixtures of europia, which tended to raise its apparent molecular weight. For samarium itself, by the sulphate method, he found $Sa = 147.2$ to 148, and for europium, $Eu = 151$. The material studied by Urbain and Lacombe, however, was free from europium, and still gave a higher percentage of oxide in sulphate than the substances examined by the earlier investigators. Their material, therefore, was either free from europium, or else contained compensating impurities. At all events, the general means are close to Urbain and Lacombe's figures, and may be allowed to stand unchanged.

Still another method for measuring the atomic weight of samarium has been proposed by Matignon,[2] who found that the normal sulphate, heated to between 500° and 1000°, yielded a stable basic salt, Sa_2SO_6. In one determination, 0.7325 gramme $Sa_2(SO_4)_3$ gave 0.5335 of Sa_2SO_6. Hence $Sa = 150.67$.

There are also the determinations by Feit and Przibylla,[3] with their special volumetric method, as follows:

Sa_2O_3.	O.	Atomic weight.
.5576	.07668	150.522
.5576	.07670	150.477
.5583	.07684	150.378
.5633	.07747	150.514

Mean, 150.473, $\pm$ .0221

In all, there are five ratios relative to the atomic weight of samarium:

(1). $Sa_2(SO_4)_3.8H_2O : Sa_2(SO_4)_3 : : 100 : 80.338$, $\pm$ .0048
(2). $Sa_2(SO_4)_3.8H_2O : Sa_2O_3 : : 100 : 47.589$, $\pm$ .0025
(3). $Sa_2(SO_4)_3 : Sa_2O_3 : : 100 : 59.2074$, $\pm$ .0018
(4). $Sa_2(SO_4)_3 : Sa_2SO_6 : : 100 : 72.883$
(5). $O : Sa : : 16 : 150.473$, $\pm$ .0221

[1] Compt. Rend., 122, 728. 1900. Ibid., 130, 1185, 1469. 1900. Ibid., 132, 1484.
[2] Compt. Rend., 141, 1230.
[3] Zeitsch. anorg. Chem., 50, 259. 1906.

To reduce these we have $S = 32.0667, \pm .00075$, and $H = 1.00779, \pm .0001$. Hence, giving to the value from ratio 4 the arbitrary weight represented by $\pm .075$—

From ratio 3	....	$Sa = 150.316, \pm .0095$
" " 1	....	$150.344, \pm .0740$
" " 5	....	$150.473, \pm .0221$
" " 2	....	$150.483, \pm .0124$
" " 4	....	$150.666, \pm .0750$

General mean, $Sa = 150.390, \pm .0071$

The average from the determinations by Urbain and Lacombe is $Sa = 150.46$. The rounded-off figure 150.4 is probably near the truth, with an actual uncertainty as large as 0.1.

EUROPIUM.

Demarçay,[1] the discoverer of europium, found for its atomic weight the approximate number 151. The first detailed determinations, however, were those of Urbain and Lacombe,[2] who analyzed the octohydrated sulphate. I give their weights, and three percentage columns, as follows: A, $Eu_2(SO_4)_3$ in $Eu_2(SO_4)_3.8H_2O$. B, Eu_2O_3 in $Eu_2(SO_4)_3.8H_2O$. C, Eu_2O_3 in $Eu_2(SO_4)_3$.

$Eu_2(SO_4)_3.8H_2O.$	$Eu_2(SO_4)_3.$	$Eu_2O_3.$	A.	B.	C.
1.7787	1.4303	.8500	80.413	47.788	59.428
2.4785	1.9935	1.1848	80.432	47.803	59.433
2.4177	1.9449	1.1554	80.444	47.789	59.407
2.4831	1.9968	1.1870	80.416	47.803	59.445
2.2988	1.8488	1.0990	80.425	47.807	59.444
		Mean,	80.426,	47.798,	59.431,
			$\pm .0038$	$\pm .0027$	$\pm .0047$
		Hence $Eu =$	151.99	151.95	152.01

Jantsch[3] determined the atomic weight of europium by calcination of the hydrous sulphate:

[1] Compt. Rend., 132, 1484. 1900.
[2] Compt. Rend., 138, 627. 1904.
[3] Compt. Rend., 146, 473. 1908.

Sulphate.	Eu_2O_3.	Per cent. Eu_2O_3.
1.3501	.6455	47.811
1.5054	.7197	47.808
1.5213	.7274	47.814
1.2881	.6159	47.815

Mean, 47.812, ± .0010

Hence $Eu = 152.05$.

Urbain and Lacombe, for the same ratio, found $47.798, \pm.0027$. The two series combined give $47.810, \pm.00094$.

Feit and Przibylla [1] have also applied their volumetric method to the determination of this atomic weight, with the following results:

Eu_2O_3.	O.	Atomic weight.
.3961	.05385	152.535
.4096	.05566	152.615
.4115	.05594	152.546

Mean, 152.565, ± .0170

The four ratios for Eu now are—

(1). $Eu_2(SO_4)_3.8H_2O : Eu_2(SO_4)_3 :: 100 : 80.426, \pm .0038$
(2). $Eu_2(SO_4)_3.8H_2O : Eu_2O_3 :: 100 : 47.810, \pm .00094$
(3). $Eu_2(SO_4)_3 : Eu_2O_3 :: 100 : 59.431, \pm .0047$
(4). $O : Eu :: 16 : 152.565, \pm .0170$

Reducing these ratios with $S = 32.0667, \pm.00075$ and $H = 1.00779, \pm .00001$ we have —

From ratio 1 .... $Eu = 151.991, \pm .0542$
" " 3 ....152.012, ± .0247
" " 2 ....152.035, ± .0048
" " 4 ....152.265, ± .0170

General mean, $Eu = 152.072, \pm .0045$

In round numbers the atomic weight of europium is 152.

---

[1] Zeitsch. anorg. Chem., 50, 260. 1906.

GADOLINIUM.

Marignac,[1] the discoverer of gadolinium, assigned to its oxide the "equivalent" 120.5, whence $Gd = 156.75$. Boisbaudran[2] found $Gd = 155.33$, 156.06, 155.76 and 156.12, with preference for the last figure. Cleve, quoted by Boisbaudran, found $Gd = 154.15$, 155.28, 155.1 and 154.77. For these determinations there are no details, and all, probably, are referred to $SO_3 = 80$.

The first chemist to publish his determinations with individual data was Bettendorff.[3] He effected the synthesis of the sulphate from the oxide, and his weights were as follows. The percentage of Gd_2O_3 in $Gd_2(SO_4)_3$ is given in the third column:

Gd_2O_3.	$Gd_2(SO_4)_3$.	Per cent. Gd_2O_3.
1.0682	1.7779	60.082
1.0580	1.7611	60.076
1.0796	1.7969	60.081

Mean, 60.080, $\pm$ .0013

Hence $Gd = 156.75$.

Benedicks'[4] series of determinations were also by the synthetic process, as follows:

Gd_2O_3.	$Gd_2(SO_4)_3$.	Per cent. Gd_2O_3.
.4308	.7171	60.075
.5675	.9451	60.047
.5726	.9534	60.059
.6785	1.1301	60.039
.7399	1.2329	60.013
1.3253	2.2063	60.069

Mean, 60.050, $\pm$ .0020

Hence $Gd = 156.52$.

The two determinations by Marc[5] are unimportant, but cannot be overlooked. The data are—

Gd_2O_3.	$Gd_2(SO_4)_3$.	Per cent. Gd_2O_3.
.2201	.3666	60.014
.2444	.4070	60.049

Mean, 60.032, $\pm$ .0120

Hence $Gd = 156.39$.

---

[1] Oeuvres Complètes, 2, 704.
[2] Compt. Rend., 111, 409. 1890.
[3] Ann. Chem. Pharm., 270, 376. 1892.
[4] Zeitsch. anorg. Chem., 22, 393. 1899.
[5] Zeitsch. anorg. Chem., 38, 121. 1904.

Brauner,[1] in a single experiment, found $0.88884Gd_2O_3 = 1.4825$ $Gd_2(SO_4)_3 = 1.83903$ $Gd_2(SO_4)_3.8H_2O$. Per cent. Gd_2O_3 in hydrous sulphate, 48.332; in anhydrous salt, 59.951. Hence $Gd = 155.725$ and 155.78.

The material studied by Brauner was received from Cleve, and was not perfectly pure. The atomic weight found is too low. In combining the figures for the percentage of Gd_2O_3 in $Gd_2(SO_4)_3$, Brauner's determination may be given equal weight with that of Marc. We have then—

Bettendorff	60.080, ± .0013
Benedicks	60.050, ± .0020
Marc	60.032, ± .0120
Brauner	59.951, ± .0120
General mean	60.070, ± .0011

The purest gadolinium preparations were probably those studied by Urbain,[2] who calcined the octohydrated sulphate to oxide. Two series of determinations are given, representing different groups of fractions obtained in the purification of his material. The data are as follows:

Series I.

$Gd_2(SO_4)_3.8H_2O.$	$Gd_2O_3.$	Per cent. $Gd_2O_3.$
1.9256	.9350	48.557
1.9749	.9589	48.555
1.9975	.9698	48.551
2.1083	1.0231	48.528
1.8993	.9214	48.514
2.2065	1.0707	48.525
1.9535	.9479	48.524
2.2008	1.0685	48.551
2.2482	1.0914	48.546
2.1932	1.0646	48.541

Mean, 48.539, ± .0033

Series II.

$Gd_2(SO_4)_3.8H_2O.$	$Gd_2O_3.$	Per cent. $Gd_2O_3.$
2.0551	.9974	48.534
2.1555	1.0469	48.570
2.2277	1.0867	48.512
2.2559	1.0946	48.529
2.2523	1.0939	48.569

Mean, 48.543, ± .0077

[1] Abegg's Handbuch, Bd. 3, Abth. 1, p. 304.
[2] Compt. Rend., 140, 583, 1905.

The weighted mean of both series is nearly 48.540, ±.0030. Hence Gd = 157.24. Brauner's single determination may be neglected.

There are also two determinations made by Feit and Przibylla[1] with their volumetric method:

Gd_2O_3.	O.	Atomic weight.
.3852	.05097	157.377
.3956	.05234	157.398
		Mean, 157.388, ± .0067

The three ratios for gadolinium are—

(1). $Gd_2(SO_4)_3.8H_2O:Gd_2O_3::100:48.540, \pm .0030$
(2). $Gd_2(SO_4)_3:Gd_2O_3::100:60.070, \pm .0011$
(3). $O:Gd::16:157.388, \pm .0067$

Reducing these ratios with $S = 32.0667, \pm .00075$, and $H = 1.00774, \pm .0001$, we have—

From ratio 2 ....Gd = 156.677, ± .0117
    "   " 1 ....157.258, ± .0154
    "   " 3 ....157.388, ± .0067

General mean, Gd = 157.218, ± .0055

This final value is near Urbain's determination, which, upon chemical grounds, is probably the best.

---

[1] Zeitsch. anorg. Chem., 50, 260. 1906.

TERBIUM.

The older determinations of atomic weight, made upon terbium preparations of doubtful character, may well be ignored. Boisbaudran[1] has published two estimates of this constant. First, for two preparations, one with a lighter and one with a darker earth, he gives Tb = 161.4 and 163.1. In his second paper he makes Tb = 159.01 to 159.95; probably with $SO_3 = 80$. According to Feit[2] Tb = 158.6. Emma Potratz,[3] by various methods, found Tb = 154, approximately. For all of these determinations the essential details are lacking.

The series of determinations by Urbain[4] is more satisfactory. The octohydrated sulphate was converted into the anhydrous salt by careful heating, with the following results:

$Tb_2(SO_4)_3.8H_2O.$	$Tb_2(SO_4)_3.$	Per cent. $H_2O.$
2.0407	1.6489	19.199
1.9626	1.5859	19.194
2.2580	1.8245	19.198
2.2385	1.8087	19.201
2.0037	1.6190	19.200

Mean, 19.198, ± .0008

Hence Tb = 159.201, ± .0130.

DYSPROSIUM.

The atomic weight of dysprosium has been well determined by Urbain and Demenitroux.[5] They reduced the octohydrated sulphate to oxide, by calcination, with the following results, taking all their data as one series:

$Dy_2(SO_4)_3.8H_2O.$	$Dy_2O_3.$	Per cent. $Dy_2O_4.$
1.6966	.8359	49.269
2.0926	1.0301	49.226
1.8415	.9069	49.248
1.5519	.7649	49.288
2.4955	1.2296	49.273
1.8130	.8927	49.238

[1] Compt. Rend., 102, 396, and 111, 474. 1886-1890.
[2] Zeitsch. anorg. Chem., 43, 280. 1905.
[3] Chem. News, 92, 3. 1905.
[4] Compt. Rend., 142, 957. Preliminary papers by Urbain are in C. R. 141, 521; ibid., 142, 727; Bull. Soc. Chim. (3), 33, 403. See also Journ. Chim. Phys., 4, 321.
[5] Compt. Rend., 143, 598. 1906.

1.8817	.9271	49.269
1.1164	.5500	49.266
1.7308	.8528	49.272
2.6038	1.2820	49.236
1.6942	.8346	49.262
2.1776	1.0726	49.256

Mean, 49.259, $\pm$ .0036

Hence $Dy = 162.550, \pm .0190$.

ERBIUM, HOLMIUM, THULIUM.

Since the earth which was formerly regarded as the oxide of erbium 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, if only for the sake of completeness.

First, Delafontaine's [1] 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	.353	.177	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

Hence $Er = 118.75$.

Bahr and Bunsen [2] 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.

Hence $Er = 169.59$.

Hoeglund,[3] following the method of Bahr and Bunsen, gives these figures:

---

[1] Ann. Chem. Pharm., 134, 108. 1865.
[2] Ann. Chem. Pharm., 137, 21. 1866.
[3] K. Svensk. Vet. Akad. Handlingar, Bd. 1, No. 6.

Er_2O_3.	$Er_2(SO_4)_3$.	Per cent. Er_2O_3.
1.8760	3.0360	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, ± .0063

Hence Er = 170.61.

According to Thalén,[1] spectroscopic evidence shows that the " erbia " studied by Hoeglund was largely ytterbia.

Humpidge and Burney[2] 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, ± .0074

Hence Er = 171.75.

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 several earths, to one of which, a rose-colored body, the name erbia is now restricted. For the atomic weight of the supposedly true erbium Cleve[3] gives three determinations, based on syntheses of the sulphate after the usual method. His weights were as follows, with the percentage ratio added:

Er_2O_3.	$Er_2(SO_4)_3$.	Per cent. Er_2O_3.
1.0692	1.7436	61.321
1.2153	1.9820	61.317
.7850	1.2808	61.290

Mean, 61.309, ± .0068

Hence Er = 166.31.

The discussion over the complexity of erbia, however, did not stop with the work of Cleve. Krüss,[4] assisted by K. Hofmann, made a long series of fractionations of erbium material, and gave crude atomic weight determinations of them, which varied widely. The figures need not be

[1] Wiedemann's Beiblätter, 5, 122. 1881.
[2] Journ. Chem. Soc., 35, 116. 1879.
[3] K. Svensk. Vet. Akad. Handlingar, No. 7. 1880.
[4] Zeitsch. anorg. Chem., 3, 353. 1893.

reproduced here. L. Hermann[1] also has studied the subject, and states that the old erbia is separable into two earths, one giving red and the other yellow salts.

More recent determinations of the atomic weight of erbium are as follows. First, two unimportant analyses made by Brill[2] with the aid of the microbalance:

$Er_2(SO_4)_3$.	Er_2O_3.	Per cent. Er_2O_3.
92.35	56.55	61.234
36.75	22.68	61.496

Mean, 61.365, ± .0873

Hence Er = 166.76.

Under the name " neo-erbium " Hofmann and Burger[3] describe carefully purified material, which gave a sharp and distinct spectrum. Four syntheses of the sulphate gave the subjoined figures:

Er_2O_3.	$Er_2(SO_4)_3$.	Per cent. Er_2O_3.
.9048	1.4724	61.451
.4666	.7594	61.443
1.4181	2.3077	61.451
1.0789	1.7563	61.436

Mean, 61.445, ± .0031

Hence Er = 167.40.

It is not necessary to combine these data. The latest, by Hofmann and Burger, is the most probable, and should be accepted.

The atomic weight of thulium has not yet been carefully determined. Cleve[4] assigned to it the atomic weight 170.7, but without details as to weighings. According to Urbain,[5] the atomic weight is below 168.5. Urbain[6] also states that the value for holmium is near 140.

---

[1] Dissertation, Technische Hochschule, München. 1906.

[2] Zeitsch. anorg. Chem., 47, 464. 1905.

[3] Ber. Deutsch. chem. Ges., 41, 308. 1908.

[4] Compt. Rend., 91, 329. 1880.

[5] Compt. Rend., 145, 759. 1907. According to Auer von Welsbach (Anzeiger Wien. Akad., 45, 529), thulium is really complex. The atomic weight assigned to it has little significance.

[6] Bull. Soc. Chim. (3), 33, 493. 1905.

YTTERBIUM AND LUTECIUM.

Although ytterbium was long supposed to be a definite element, it has recently been shown to be complex, and its oxide is a mixture of at least two distinct earths. Nevertheless, the data relative to the atomic weight of the old ytterbium are worth assembling, if only for historical reference.

The first good series of determinations was by Nilson,[1] who effected the synthesis of the sulphate from the oxide in the usual manner. His figures are as follows:

Yb_2O_3.	$Yb_2(SO_4)_3$.	Per cent. Yb_2O_3.
1.0063	1.6186	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

Hence Yb = 173.18.

Astrid Cleve,[2] by the same method, obtained the subjoined results:

Yb_2O_3.	$Yb_2(SO_4)_3$.	Per cent. Yb_2O_3.
.7791	1.2535	62.154
.5190	.8353	62.133
.4905	.7894	62.136

Mean, 62.141, ± .0044

Hence Yb = 173.13.

Brill,[3] who used the microbalance, gives the following figures:

$Yb_2(SO_4)_3$.	Yb_2O_3.	Per cent. Yb_2O_3.
106.00	65.90	62.170
92.35	57.30	62.047

Mean, 62.108, ± .0407

Hence Yb = 172.85.

Brauner,[4] from 1.67279 grammes Yb_2O_3, obtained 2.69209 of $Yb_2(SO_4)_3$. Percentage Yb_2O_3, 62.137, and Yb = 173.10. There is also a preliminary note by G. and E. Urbain,[5] who found Yb = 172.6, but who give no details of the determination.

[1] Compt. Rend., 91, 56. 1880. Ber. Deutsch. chem. Ges., 13, 1430.
[2] Zeitsch. anorg. Chem., 32, 129. 1902.
[3] Zeitsch. anorg. Chem., 47, 464. 1905.
[4] Abegg's Handbuch, 3 (1), 335.
[5] Compt. Rend., 132, 136.

Feit and Przibylla,[1] by their volumetric method, obtained the following figures:

Yb_2O_3.	O.	Atomic weight Yb.
.6424	.07808	173.459
.6408	.07783	173.600
.6403	.07779	173.547
.6466	.07858	173.485

Mean, 173.523, $\pm$ .0214

The complexity of the old ytterbium was proved almost simultaneously by Auer von Welsbach and Urbain. Urbain,[2] by a long series of fractionations, obtained from it two end products, one, *neo-ytterbium*, with an atomic weight near 170; the other, *lutecium*, approximately 174. Welsbach,[3] whose work was published a little later, proposed for his earths the names *aldebaranium* and *cassiopeium*, and gave more explicit figures as to their atomic weights. His data are as follows:

Ad_2O_3.	$Ad_2(SO_4)_3$.	Per cent. Ad_2O_3.
.4181	.6730	62.125
.5984	.9634	62.113
.6173	.9939	62.109

Mean, 62.116, $\pm$ .0011

Hence Ad $= 172.92$.

Cp_2O_3.	$Cp_2(SO_4)_3$.	Per cent. Cp_2O_3.
.3716	.5967	62.276
.3086	.4956	62.268
.4026	.6465	62.274

Mean, 62.273, $\pm$ .0017

Hence Cp $= 174.24$.

It is not necessary to enter here into the general controversy between Welsbach and Urbain relative to priority. In the matter of nomenclature alone, the priority of Urbain is clear.[4]

His name lutecium is therefore accepted, with Lu $= 174.24$. For the other component of the mixed earths the original name ytterbium would seem to be preferable to neoytterbium, and Yb $= 172.92$. The round numbers 174 and 173 are perhaps equally probable, for the determinations by Welsbach are certainly not final.

[1] Zeitsch. anorg. Chem., 50, 261. 1906.
[2] Compt. Rend., 145, 759, 1907; and 146, 406. 1908.
[3] Monatsh. Chem., 29, 192. 1908.
[4] For a reclamation of priority, see Welsbach, Monatsh. Chem., 33, 695.

THE HELIUM-ARGON GROUP.

The five inert gases, helium, neon, argon, krypton and xenon are apparently incapable of forming compounds. Their atomic weights, therefore, can only be inferred from their densities, for which the following data are available.

For helium the earliest determinations by Ramsay[1] are too high. He obtained values ranging from 3.89 to 4.84, and later figures above 2.13, when the density of oxygen, as the standard is put at 16. Langlet,[2] a little later, assigned to helium the density 2.00. Ramsay and Travers,[3] after the discovery of neon, krypton and xenon, with purer helium, found its density to be 1.98, which is the best value now assignable to it.

The density of argon has been more carefully determined, both by Ramsay[4] and by Rayleigh.[5]

Compared with an equal volume of oxygen weighing 2.62760 grammes, Rayleigh found for argon the following weights:

3.2710
3.2617
3.2727
3.2652
3.2750
3.2748
3.2741

Rayleigh accepts the last three determinations, which give 3.27463 in mean. With $O = 16$, the density of argon becomes $19.9399, \pm .0012$.

Ramsay's figures, also referred to $O = 16$, are as follows:

19.904
19.823
19.816
19.959
19.969
19.932

Rejecting the second and third of these determinations the four remaining values give in mean a density of $19.941, \pm .0099$. Correcting the figures for argon by the method of limiting densities, D. Berthelot[6] assigns to argon the density 19.941.

[1] Proc. Roy. Soc., 58, 81. 1895. Journ. Chem. Soc., 57, 684. 1895.
[2] Zeitsch. anorg. Chem., 10, 289. 1895.
[3] Proc. Roy. Soc., 67, 329. 1900. Phil. Trans., 197, A, 47. 1900.
[4] Phil. Trans., 186, 238. 1905.
[5] Proc. Roy. Soc., 53, 201. 1896.
[6] Compt. Rend., 126, 1501.

The densities of the three other inert gases were first determined by Ramsay and Travers.[1] Referred to $O = 16$, the figures become

Ne	9.99	9.94
Kr	40.88	40.78
Xe	64.00	63.64

They also assign to argon the densities 19.93 and 19.96.

Ladenburg and Krügel,[2] in their determinations of the density of krypton, obtained erroneous values, namely, 29.335 and 29.405. Ramsay,[3] in still later experiments, found for Kr the densities 40.81, 40.82 and 40.73, in agreement with the figures given by Ramsay and Travers.

More conclusive data for krypton and xenon are given by Moore,[4] who worked with residues separated by fractionation from 120 tons of liquid air. For krypton the densities found were 41.504 and 41.509, or 41.506 in mean. For xenon Moore found the densities 65.380 and 65.328, in mean, 65.354.

Since these gases are all monatomic, their atomic weights are double their densities as given in the foregoing paragraphs. They are then to be taken as follows:

$$
\begin{aligned}
\text{He} &= 3.96 \\
\text{Ne} &= 19.93 \\
\text{A} &= 39.882 \\
\text{Kr} &= 83.013 \\
\text{Xe} &= 130.704
\end{aligned}
$$

Moore's figures are preferred for krypton and xenon, and Berthelot's for argon.

[1] Proc. Roy. Soc., 67, 329. Phil. Trans., 197A, 47. 1900.
[2] Chem. News, 81, 205. From Sitzungsb. Berlin. Akad., 1900, 212.
[3] Proc. Roy. Soc., 71, 421. 1903.
[4] Journ. Chem. Soc., 93, 2181. 1908.

TABLE OF ATOMIC WEIGHTS.

In the following table the results of the foregoing calculations are brought together, each atomic weight being rounded off to five significant figures, or sometimes fewer. For convenience, the values are given in two columns, referring to the two ultimate standards, $O = 16$ and $H = 1$. Many chemists prefer the latter, and their wishes are, in a work like this, entitled to respectful consideration:

	$O = 16$.	$H = 1$.		$O = 16$.	$H = 1$.
Aluminum	27.040	26.831	Molybdenum	96.029	95.287
Antimony	120.05	119.11	Neodymium	143.91	142.80
Argon	39.882	39.574	Neon	19.93	19.776
Arsenic	74.957	74.378	Nickel	58.682	58.228
Barium	137.36	136.30	Nitrogen	14.010	13.908
Bismuth	208.06	206.45	Osmium	191.07	189.59
Boron	10.980	10.896	Oxygen	16.000	15.876
Bromine	79.920	79.302	Palladium	106.66	105.84
Cadmium	112.40	111.53	Phosphorus	31.041	30.872
Cæsium	132.81	131.78	Platinum	195.21	193.70
Calcium	40.132	40.006	Potassium	39.100	38.798
Carbon	12.004	11.911	Praseodymium	140.62	139.53
Cerium	140.20	139.11	Radium	226.37	224.62
Chlorine	35.458	35.184	Rhodium	102.93	102.13
Chromium	52.019	51.617	Rubidium	85.436	84.776
Cobalt	58.961	58.505	Ruthenium	101.66	100.87
Columbium	93.528	92.805	Samarium	150.39	149.23
Copper	63.555	63.064	Scandium	44.115	43.774
Dysprosium	162.55	161.30	Selenium	79.176	78.564
Erbium	167.40	166.10	Silicon	28.246	28.028
Europium	152.07	150.90	Silver	107.88	107.05
Fluorine	19.041	18.894	Sodium	23.011	22.833
Gadolinium	157.22	156.00	Strontium	87.616	86.938
Gallium	69.91	69.385	Sulphur	32.067	31.819
Germanium	72.50	71.95	Tantalum	181.02	179.62
Glucinum	9.0945	9.0242	Tellurium	127.52	126.53
Gold	197.27	195.74	Terbium	159.20	157.97
Helium	3.96	3.93	Thallium	204.04	202.74
Hydrogen	1.0078	1.0000	Thorium	232.60	230.80
Indium	114.86	113.97	Thulium	168.5	167.2
Iodine	126.92	125.94	Tin	119.06	118.14
Iridium	193.05	191.55	Titanium	48.099	47.727
Iron	55.880	55.448	Tungsten	184.09	182.67
Krypton	83.013	82.371	Uranium	238.98	237.13
Lanthanum	138.80	137.73	Vanadium	51.037	50.642
Lead	206.97	205.37	Xenon	130.71	129.70
Lithium	6.9379	6.8843	Ytterbium	172.92	171.58
Lutecium	174.24	172.90	Yttrium	89.094	88.405
Magnesium	24.304	24.116	Zinc	65.418	64.912
Manganese	54.947	54.522	Zirconium	90.483	89.784
Mercury	200.05	198.51			