THE ATOMIC WEIGHT OF VANADIUM DETERMINED FROM THE LABORATORY WORK OF EIGHTY YEARS.

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(Read April 21, 1911.)

Vanadium can no longer be considered a rare element. Ferro-vanadium is produced on a large scale for the manufacture of special vanadium steels. Strangely enough, it was in a kind of natural vanadium iron that Sefström detected this element eighty years ago.

In 1830, while technical director of the famous iron works at Taberg in Smaland, Sweden, Sefström thought it might be interesting to submit his high quality malleable iron to the Rieman Test for cold-short iron, notwithstanding the apparent absurdity of such an undertaking. Accordingly he took one of his bars. On a part of its bright metallic surface he drew the little circular ridge of tallow and poured dilute sulphuric acid into the shallow dish thus formed, expecting, of course, to see no change whatever of the bright metallic bottom of this improvised dish. But he was amazed to see that bright bottom instantly turn black while the shallow dish rapidly filled up with a black powder, exactly as it does when the iron tested is badly cold-short.

The distinguished disciple of the great Berzelius instantly realized that this striking contradiction between test and fact was a positive indication of the presence of a hitherto unknown chemical element. Accordingly he set about isolating this new element. Working up quite a number of pounds of his iron, Sefström obtained less than a decigramme of the substance from which the new element was to be separated. Hence he turned hopefully from the iron to its fresh slag and found it to yield a much larger per cent. of the black powder. He now soon succeeded in isolating the new element

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which, as a good Scandinavian, he named vanadin after Vanadiis, a designation of Freya, the greatest Goddess in Valhalla.

Sefström had promptly informed his teacher of the discovery and soon after brought his entire stock of the new element to Berzelius, requesting him to continue the research for which his own industrial work and the professorial duties at the Fahlun Montan-School left him neither the leisure nor the facilities. For a short time Sefström worked with Berzelius on the new element in that famous " Kitchen Laboratory" where Berzelius alone completed the splendid work of which he published a summary on pp. 99–110 of the " Annual Report " which he presented to the Swedish Academy of Sciences on March 31, 1831—exactly eighty years ago.

For almost forty years the element vanadin of Sefström and Berzelius remained undecomposed, but the striking isomorphism of the mineral vanadinite with the remarkable isomorphic group of apatite and pyromorphite presented the anomalous condition of the isomorphism of the element vanadin of Berzelius with the group PO of apatite and pyromorphite. This anomaly invited further attempts of the reduction of vanadin in which Roscoe was successful, 1867, proving vanadin to be really the oxide VaO, in which Va is the symbol of the present element vanadium of the atomic weight 51. This fully explains the isomorphism of vanadinite containing the oxide VaO, with pyromorphite, containing the corresponding oxide PO.

In this first research of Berzelius on vanadium, the old master already determined the atomic weight of the new element; for his value 67 for what we now know to have been VaO gives Va 51. He devised and used five distinct chemical methods for this atomic weight determination to which not one new method has been added in the eighty years elapsed since that work was done by the great chemist in his kitchen laboratory. It is a well-authenticated historic fact, Berzelius not only made atomic weight determinations for vanadium, but they were as accurate as those made forty years later by Roscoe, while some were as precise as corresponding determinations made eighty years later by Prandtl; besides, not only Roscoe and Prandtl, but all chemists have done this work by means

of the methods devised by Berzelius which he practiced in his laboratory in 1831.

It is therefore with great astonishment that I read in the first edition of the " Recalculation " of F. W. Clarke: " Roscoe's determination of the atomic weight of vanadium was the first to have any scientific value. The results obtained by Berzelius . . . were unquestionably too high, the error being probably due to the presence of phosphoric acid in the vanadic acid employed."

The same erroneous statement is repeated identically at the opening of the chapter on vanadium in the succeeding two editions of the work as may be seen by comparing: p. 183, edition 1882; p. 211, edition 1897, and p. 305, edition 1910.

The only new method, quite recently applied to the determination of the atomic weight of vanadium, is that of Edgar F. Smith.[1] This admirable method strictly conforms to the Berzelian advice " to chose such chemical methods for atomic weight determinations that the final result shall depend as little as possible on the operator's skill in manipulation." In my summary of the work of one hundred years on the determination of the atomic weight of hydrogen[2] I have given this great rule of Berzelius, in his own handwriting, from his " Sjelfbiografiska Anteckningar," published by the Kgl. Svenska Vetenskapsakademien, 1901, p. 41.

This rule requires to select such chemical reactions in which the physical and chemical characters of the substances weighed are so definitely fixed that the unavoidable errors of man and his instruments become negligible quantities. Such is the reaction no. 311 above referred to. Hence the work done by McAdam in the laboratory and under the direction of Edgar F. Smith has furnished the highest direct chemical approximation obtainable to the absolute scientific truth that Va is 51 exactly. This will appear, we think, from a careful examination of all the results actually obtained during the eighty years from 1831 to 1911 as plotted in our two diagrams no. 730 and no. 731 published with this paper.

The above reference to the presence of phosphoric acid in the

[1] See *Journal Amer. Chem. Society,* 1910, p. 1603, in the December number.
[2] In the *Révue Generale de Chimie,* 1910, Nos. 22 and 24.

vanadic acid used by Berzelius reminds us of the homely but sound scriptural advice habitually given by Berzelius to his disciples: " do not strain at a gnat while swallowing camels." The phosphoric acid in the vanadic acid used by Berzelius was detected by Roscoe in the sample which Berzelius had presented to Faraday; but the molybdic reagent necessary for the detection was not known to chemistry in the year 1831 when Berzelius did his work on vanadium.

As a matter of fact, Berzelius did not see this gnat; but his work shows that he did avoid some of the camels that stalk about the laboratories and which were deglutinated unconsciously forty and eighty years after Berzelius failed to strain that gnat. The error-shares due to the oxygen are the fattest and most numerous of these camels, up to the present day.

OUR METHOD OF REDUCTION.

In order to solve the riddle of the conflicting experimental data obtained in the chemical laboratories of the world during an entire century of painstaking work, we have, especially in the last quarter century, carried on special researches on the proper mathematical reduction of this kind of laboratory work.

The final results of this extended research are briefly summarized in five tables of which two only have thus far been published. Our work itself has been published in the following books and special papers:

"The True Atomic Weights," St. Louis, 1894, xvi + 256 pp., 8vo, with 7 plates and many illustrations. Dedicated to Berthelot.

"The Absolute Atomic Weights," St. Louis, 1901, xvi + 304 pp., 8vo, with portrait of Berzelius and three plates.

"The Proximate Constituents of the Chemical Elements," St. Louis, 1904, with 7 portraits, many plates, 112 pp. text, 8vo. This is an inductive treatise of the subject.

The "Cinquantenaire," 1910, gives some historical data, copies of older papers, letters in fac-simile and "Fragments inédits" with fine diagrams; 66 pp., 4to, with plates and portraits.

"Notes" published in the *Comptes Rendus* of the Academy of Sciences of Paris from 1873 to the present, almost sixty in number,

forming a volume of over 200 pp. 4to. The first, and in fact the greater number of the " Notes," were presented by Berthelot ; others were presented by Messrs. Gautier, Lemoine, Haller, Gernez, and other academicians.

In the *Moniteur Scientifique,* from 1906 to 1909 more than a dozen longer articles have appeared with many diagrams. The first two tablés above referred to are found in the November number for 1901, with discussions, pp. 731–744.

The papers were originally written in four languages : Danish, German, English and French. To these papers the reader may be referred by the Cinquantenaire and the list in the Prox. Constit. The results obtained, being in conflict with the dominant chemical school, have not been widely circulated except as adopted children.

For these reasons it is necessary here to give enough of the details of the finally worked out practical method of reduction to enable the reader to repeat all the calculations required, so that he can verify the results given.

It will then be seen that the final method is quite simple ; the difficulty was to get this method.

Let α represent *the absolute atomic weight* of any chemical element, that is the whole or round number ($\frac{1}{2}$, or even $\frac{1}{4}$) which the experiments indicate to be near the *true atomic weight A,* which exactly to determine is the object of the reduction. The *unit* adopted is exactly $\frac{1}{12}$ of carbon-diamond which is practically identical with $\frac{1}{16}$ of that of oxygen.[3]

The *departure* of the true atomic weight from the absolute atomic weight we designate by the Greek letter epsilon (ϵ) ; that is : $A = \alpha + \epsilon$. This departure, as a matter of fact, is found to be a small fraction of the unit; we invariably express it in thousandths of that unit.

This departure—in units of the third decimal—is really our new variable, the quantity to be determined. This apparently insignificant matter of form is really of the greatest importance. For this new variable all products and powers become negligible quantities

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[3] *Comptes Rendus,* 117, p. 1075, 1893.

in our necessary calculations, because the departures are small quantities; hence, *all calculations,* even involving the most complex mathematical functions, are reduced to the simple rule of three and *carried out by proportional parts.* The importance will soon be recognized by the practice of the method.

The actual *laboratory work* consists essentially in the determination of *two weights* which we denote by p and q and which represent chemically pure compounds of the formula P and Q respectively. The necessary condition is that the weight p has been completely changed into q according to the exact formulæ P and Q by means of a suitable *chemical reaction.* Of such reactions we have tabulated and examined over three hundred that have been actually used for atomic weight determinations. We designate each such reaction by a number for ready reference. This number is simply marking their place in our table above referred to; it is arbitrary but a practical necessity. We have already above referred to the remarkable chemical reaction, recently applied in the Harrison Laboratory of the University of Pennsylvania as reaction no. 311.

Substituting the absolute atomic weights α for the chemical symbols in the formulæ of the two compounds P and Q, we can readily calculate the value of the quotient P/Q which we call the *atomic ratio R* and calculate the same to five decimals, the limit of precision today. On the following pages, giving the data for the chemical reactions that have been used for the determination of the atomic weight of vanadium there will be found examples of these and of all other processes, to which we request the reader to turn as new operations are defined.

On the other hand, the weights actually taken in the laboratory and designated by the letters p and q will give the *analytical ratio r* which we calculate also to five decimal places. The analytical ratios determined by the different experiments with the same two compounds P and Q will give hardly any identical values of r; we notice their *extreme values,* that is the maximum and the minimum in any given series of determinations made in the same manner with the identical material. The difference between the greatest and the least value of the analytical ratios of a series is the range of that series. This characterizes the *concordance* of the different deter-

minations of any series without introducing any false theoretical notion, as is done by the calculation of the so-called probable error of the mean. The actual *mean value* we do calculate and use.

While the individual analytical ratios vary for the different individual determinations in a series and even the means for the different series, it is found, as a matter of fact, that they bear a close relation to the atomic ratio. We call the excess of the analytical ratio over the atomic ratio, the *analytical excess* and designate it by the symbol e. That is: $r = R + e$. The value of e is also expressed in units of the fifth decimal.

THE EQUATION OF CONDITION AND THE SOLUTION EX-ÆQUO.

In the true atomic weights of 1894 (p. 139 to p. 169, esp. p. 158) the solution of the great problem is already shown to require an application of the method of the variation of constants.

In the absolute atomic weights of 1901, the change or variation Δ of the atomic ratio for an increase of 0.1 in the atomic weight is determined for each reaction and applied for several important objects throughout the entire work. On pages 144–147 of that work the final solution is really given but implicit only, and lacking the equal distribution of the analytical excess among the elements present in the reaction.

The actual equation of condition was established in 1907 through long and difficult work, both analytical and geometrical. The general analytical deduction by means of Taylor's formula was in the hands of eminent men abroad in the form shown in fac-simile (reduced to $\frac{1}{3}$) as printed p. 61 of my " Cinquantenaire," 1910. The most general construction, which permits the establishment of a criterion for the absolute atomic weight, is printed on p. 60 of the same " Cinquantenaire."

Here we will present the final practical solution of the resulting " insoluble " indeterminate or diophantic equation in the simplest and most direct manner, suitable for common, current, practical application.

The *true atomic weight, A,* is the quantity sought, in the unit for which carbon-diamond is 12 exactly.

The *absolute atomic weight* α is indicated by the laboratory work; in case of doubt, the criterion just referred to has to be made use of.

The *departure* ϵ is expressed in units of the third decimal (thousandths) of the unit of atomic weights. Its exact determination is the main object of this paper.

The *atomic ratio R* is a function of the absolute atomic weights, expressed by the quotient P/Q above given.

If now the absolute atomic weight for any one given element in this ratio be increased by 0.1, that ratio will change or vary by an amount readily calculated from the formula of R as given; we use throughout seven place logarithms which give the precise value sought with the least trouble. This change or *variation* we denote by the Greek *capital delta* Δ for the particular element of which the atomic weight was increased by 0.1 in the atomic ratio. In 1901 we made this calculation only for one element in the ratio; now it has to be made for every element in the ratio.

In the tables here following this matter will become quite readily understood by simply repeating some of the calculations thus indicated. For the reaction no. 98 this work is quite simple, for only two elements are present, namely Va and O. In reaction 270, the work required is about double in amount, because four elements are in reaction, namely: Va, O, Cl and Ag.

The *analytical ratio r* has to be calculated for each single determination made; it is considerably simplified if the weighings are given by the chemist to the hundredth of the milligram, are rounded off to the tenth of the milligram, which is as far as the weighings can be trusted; see, for example, my demonstration of this fact for the weighings of Richards made at Harvard-Berlin.[4]

The *analytical excess e* is now obtained as it is $r-R$; it is also expressed in units of the fifth place.

Now we have in hand all the quantities required for obtaining *the departure* ϵ sought, by solving the equation of condition. While this indeterminate or diophantic equation is, of course, insoluble in general, we have nevertheless obtained two practical solutions of the same[5] of which the one properly named *ex-æquo* is the most

[4] *Moniteur Scientifique*, Juin, 1909, especially pp. 384–385.

[5] *Comptes Rendus*, T. 149, p. 1074, 1909, with a most instructive figure.

serviceable and by far the most readily understood and easiest applied.

Our general deduction (really as indicated 1894 already: a method of the variation of the constants) leads to the simple form of the *equation of condition*

$$100 \ e = \Sigma\Delta\epsilon,$$

where the constant 100 presupposes that the analytical excess e and the variation Δ are expressed in units of the fifth place while the departure ϵ is expressed in units of the third place or thousandths of the unit of atomic weights.

It may not be amiss here to insist on the fact that since in every chemical reaction there are at least two elements present, the above equation contains at least two unknown departures ϵ and is there·fore really an indeterminate or a diophantic equation.

Our practical solution ex æquo of this equation is as follows: Let m be the number of elements involved in the chemical reaction used, then the number of terms $\Delta\epsilon$ in the above sum Σ is m.

Ascribing to all elements an equal influence on the error or excess e, the part thereof due to each element will be $e' = e/m$.

Hence the actual departure ϵ for each element in the reaction will be determined by the simple relation

$$\epsilon = \frac{100 \ e'}{\Delta}.$$

If the value of Δ be above a certain limit, this determination will be sharp; the corresponding reaction therefore may also be called *sharp*.

But if the value of the variation Δ for any element is small, the *reaction* for that element *will be dull* and the determination of the atomic weight will be impossible with any high degree of precision, as we have shown in *Comptes Rendus*, T. 148, p. 484, 1909, in the attempted determination of the atomic weight of Tellurium by a reaction quite dull for that element.

This one attempt strikingly shows the real condition of the work of the dominant school to be irrational.

After having briefly explained the manner in which we have tried to solve the great problem of the deduction of the true atomic

weights from the experimental work done in the laboratories, we may proceed to the full statement of the facts obtained for the element vanadium during the past eighty years and the final results of our discussion of the same.

We shall present the facts in the most compact form of tables and finally exhibit them to the eye in the form of accurately drawn graphics, from which we shall be able to read the final result the most readily and clearly.

THE ACTUAL DETERMINATION OF THE TRUE ATOMIC WEIGHT OF VANADIUM.

I.—ABSOLUTE ATOMIC DATA.

Fundamental Constants, Calculated from the Absolute Atomic Weights.

Only seven[5a] chemical reactions have been used for the determination of the atomic weight of vanadium, thus far; they are the following:

No. 98: Pentoxide reduced by hydrogen.

No. 269: Oxychloride to silver.

No. 270: Oxychloride to silver chloride.

No. 311: Vanadate to chloride.

(*a*)—Oxychloride to pentoxide.

(*b*)—Sulphate to barium sulphate.

(*c*)—Sulphate to pentoxide.

The last three preliminary methods of Berzelius have been used by him, each once only, and by no other chemist, except that Roscoe made four determinations according to method (*a*). No. 311 has but just been introduced by Edgar F. Smith, December, 1910. All the chemical reactions used for the determination of the atomic weight of vanadium, up to that date, were devised and first used by Berzelius in 1831, eighty years ago. It seems that his work has some scientific value, after all.

In the following Table I. we have given the most important fundamental constants required by our method of reduction. They have all been calculated from the well-known absolute atomic weights: Va, 51; T, 16; Cl, 35½; Ag, 108; Na, 23; S, 32; Ba,

[5a] If we count 269 and 270 as distinct reactions.

$137\frac{1}{2}$; H, 1.008 instead of the exact value 1.00781 determined atomechanically by us (*Révue gén. de Chimie*, 1910, p. 386).

TABLE I.

Fundamental Constants for Vanadium.

No.	Formula.	Atomic Ratio, R.		Variation Δ for			
		Fraction.	Decimal.[6]	Va.	O.	Cl.	Metal.
98	$\dfrac{O_2}{Va_2O_5}$	$\dfrac{32}{182}$	0.17 582	—19	62	—	—
269	$\dfrac{VaOCl_3}{3Ag}$	$\dfrac{173.5}{324.0}$	0.53 549	31	31	93	—49(Ag)
270	$\dfrac{VaOCl_3}{3AgCl}$	$\dfrac{173.5}{430.5}$	0.40 302	23	23	42	—28(Ag)
311	$\dfrac{NaCl}{NaVaO_3}$	$\dfrac{58.5}{122.0}$	0.47 951	—39	—118	304	43(Na)
a	$\dfrac{Va_2O_5}{2VaOCl_3}$	$\dfrac{182}{347}$	0.52 450	27	113	— 91	—
b	$\dfrac{Va_2O_5}{2BaSO_4}$	$\dfrac{182}{467}$	0.38 972	43	40	— 17(S)	—17 (Ba)
c	$\dfrac{Va_2O_5}{Va\ sulphate^7}$	$\dfrac{182.00}{398.06}$	0.45 722	27	—35	— 23(S)	—140(H)

II.—General Summary of the Experimental Work Done.

In the common reviews of the experimental work done for atomic weight determinations, the amount of substance taken in each experiment is not made the subject of special consideration. This neglect is due to the erroneous estimation in which the so-called "*probable error*" of the mean is held.

This probable error has caused the most serious errors in all branches of physical science where it has been applied—in the unfortunately common way, without proper understanding. We have treated of this repeatedly, especially in our "absolute atomic weights, 1901, on the first hundred pages, to which we must refer.

In the language of Berzelius already quoted we might say the above probable error is the gnat strained at which hides from sight the camel-like systematic and constant errors which are swallowed. We have, at last, seen one admission of the fact we have always

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[6] Between the second and third decimal of the five, we always leave a space to make the constancy of the first two conspicuous.

[7] The crystallized sulphate is $[VaO]_2S_2O_8 + 4H_2O$.

accentuated, that large constant and systematic errors may exist though the value found for the probable error of the mean is insignificant. In Clarke's third edition (1910, pp. 93–98) the probable error of the mean amounts to only one unit in the fifth decimal of the analytical ratio while the constant error of that ratio amounts to 120 such units, according to the famous analyses of Stas and Baxter.

To detect the constant and systematic errors we have always plotted the results of the individual experimental determinations as ordinates to the weight taken as abscissæ. In these diagrams the scale selected for the atomic weights or the ratios must be very great while that for the weight taken has to be small. In my diagram representing in this manner all the atomic weight determinations of hydrogen made in a century (*Révue gén. de Chimie*, 1910, p. 380) the unit of atomic weights is 30 meters (about 100 feet) while a decagram of water produced is represented by three centimeters (or a little over one inch).

To permit this *search for the really important constant and systematic errors,* we give the weight taken (to the decigram) in all our tables. For a series of determinations, we give the total weight taken for all the determinations of the series, and the mean weight taken for each determination—which is obtained from the total by dividing this latter by the number of determinations made.

Table II. thus shows that 50 determinations have actually been made for the determination of the atomic weight of vanadium on 4 grams each of the substance taken, not counting the seven preliminary determinations on 1 gram of matter each.

It is also seen at a glance that by reaction 98 the work of Roscoe ought to be the most reliable, while for 270 the work of Prandtl should be the best and that the work done by one chemist for 311 has been carried out under equally as favorable condition in regard to the weight operated upon.

By means of the reference letter specified in the last column the corresponding line on the diagrams can be instantly identified. We may here already remark, that the length of this line, extending to the right or to the left from the vertical in the middle, marks the magnitude of the departures for the elements as indicated by the chemical symbol added.

Thus the least deviation or departure has resulted from the use of the Method 311 recently introduced by Edgar F. Smith. The preliminary work of Berzelius, done eighty years ago, according to methods a and b as represented by lines D and T on the diagram, showed departures for sulphur and barium extending beyond the limit of our diagram: 470 to the left (negative) in line D and 776 to the right (positive) in line T; the former is almost half a unit, the latter three quarters of a unit of atomic weight.

TABLE II.

SUMMARY OF THE EXPERIMENTAL DETERMINATION.

Reaction.	Number of Determ.	Weight Taken, Grammes.		Chemist.	Letter on Diagram.
		Mean.	Total.		
98	3	1.6	4.7	Berzelius	B
	1	0.6	0.6	Berzelius	B*
	5	6.0	30.0	Roscoe	F
	4	2.5	10.0	Prandtl	C
	13	3.4	45.3		
269	9	2.7	24.3	Roscoe	N(M, R)
270	1	1.6	1.6	Berzelius	G
	6	1.2	7.4	Roscoe (A)	H } I.
	2	2.4	4.7	Roscoe (B)	K }
	5	4.7	23.5	Prandtl, I.	L
	6	4.8	28.8	" II.	P
	4	8.1	32.4	" III.	O
	24	4.1	98.4		
311	5	6.0	30.2	Smith-McAdam	Q
Total or say :	51 50	3.9 4	198.2 200		

PRELIMINARY REACTIONS :

(a) Oxychloride	1	1.6	1.6	Berzelius, 1831	A
to Pentoxide	4	1.0	4.0	Roscoe, 1868	E
(b) Va Sulphate to Ba Sulphate	1	0.8	0.8	Berzelius, 1831	D
(c) Va Sulphate to Pentoxide	1	0.8	0.8	Berzelius, 1831	T
Mean	7	1.0	7.2		

III.—The Analytical Results.

The chemical work, beginning with the determination of the weight p and ending with the determination of the weight q (or the inverse) gives directly the atomic ratio r, by a simple division carried to five decimal places. A simple substraction now will give the analytical excess e by using the atomic ratio calculated once for all for the reaction. The results obtained in this way are given in Table III.

We will here only call attention to the following peculiarly interesting circumstances:

"Analyst B" working under Roscoe makes three determinations under reaction 269, and takes almost the same weight of the oxychloride for each one of these determinations; notwithstanding the fact that he really only repeats one and the same determination three times, his results range over 501 units in the fifth place—an enormous range under so favorable conditions.

In the language of Berzelius, this enormous range is quite a big camel which was swallowed without an effort in the laboratory of Roscoe, who strained laboriously at the tiny gnat of phosphoric acid which a test of high delicacy, that was not yet known in the days when Berzelius did his splendid pioneer work on vanadium and courteously presented to Faraday a sample of the vanadic acid he had received from his disciple who discovered the element vanadium and which acid Berzelius had purified himself as far as the science of his time permitted. These facts I gather from Becker, Smithson. Misc. Collections, 358, Washington, 1880, p. 132, quoting from *Liebig's Annalen*, 93, p. 6, 1868.

TABLE III.

The Analytical Ratios Determined.

Reaction 98.—Atomic Ratio, $R = 0.17582$.

Berzelius, 1831.—Meyer-Seubert, "Atomgew.," 1883, p. 28.

Determ.	Sums of Weights. Pentoxide.	Oxygen.	r.	e.
3	4.6995	0.8120	0.17 278	— 304
1	0.6499	0.1124	294	— 288

Diagram. Lines B and B^x.

Roscoe, 1868.—Jour. Chem. Soc., 6, p. 330, 1868.

No.	1.	2.	3.	4	5.	Mean
Weight Oxide	7.7	6.6	5.2	5.1	5.4	6.0
$r = 0.17$	533	507	489	515	501	509
$e =$	— 49	— 75	— 93	— 67	— 81	— 73

Range 44.—Diagram, Line F.

Prandtl, 1910.—Jour. Am. Chem. Soc., 1911, pp. 266–7, from *Ztsch. anorg. Chem.,* 67, 257.

No.	1.	2.	3.	4.	Mean.
Weight Oxide	9.1	9.9	8.7	12.3	10.0
$r = 0.17$	261	376	395	394	356
$e =$	— 321	— 206	— 187	— 188	— 225

Range 133.—Diagram, Line C.

REACTION *269.*—Atomic Ratio, $R = 0.53549$.

Roscoe, 1868; Analyst A.—*Jour. Chem. Soc.,* Vol. 6.

No.	1.	2.	3.	4.	5.	6.	Mean.
Oxychlor.	2.4	4.7	4.2	4.0	0.9	1.4	2.9
$r = 0.53$	425	528	533	510	530	532	510
$e =$	— 124	— 21	— 16	— 39	— 19	— 17	— 39

Range: 108.—Diagram: Line M.

Roscoe, 1868; Analyst B.

No.	7.	8.	9.	Mean.	Mean of All 9.
Oxychlor.	2.9	2.1	1.4	2.1	2.7
$r = 0.53$	980	755	479	738	586
$e =$	431	206	— 70	189	37

Range: 501.—Diagram: Line R.   Range: 555.

REACTION *270.*—Atomic Ratio, $R = 0.40302$.

Berzelius, 1831.—1 determ.: 1.6385 oxychlor. gave 4.0515 Ag, hence $r = 0.40442$ and e 140. Meyer-Seubert, " Atomgew.," 1882, pp. 90–91.
Diagram: Line G.
Roscoe, 1868; Analyst A:

No.	1.	2.	3.	4.	5.	6.	Mean.
Oxychlor.	1.9	0.7	0.8	1.4	1.0	1.6	1.2
$r = 0.40$	323	531	537	337	399	174	383
$e =$	21	229	235	35	97	— 128	81

Range: 363.—Diagram: Line H.

ANALYST B:

No.	7.	8.	Mean.	Mean of A and B.
Oxychlor.	2.2	2.5	2.4	1.5
$r = 0.40$	391	333	362	378
$e =$	89	31	60	76

Range: 58.—Diagram Line K.   Diagram: I.

Prandtl and Bleyer.[8] Series I., 1909.

No.	1.	2.	3.	4.	5.	Mean.
Oxychlor.	5.5	5.9	3.2	5.3	3.6	4.7
$r = 0.40$	393	346	365	322	367	359
$e =$	91	44	63	20	65	57

Range: 71.—Diagram: Line L.

[8] Clarke, "Recalc.," 1910, p. 307 for I. and II.; *Journ. Am. Chem. Soc.,* 1911, p. 266, for III.

SERIES II., 1909.

No.	1.	2.	3.	4.	5.	6.	Mean.
Oxychlor.	4.9	3.7	5.0	6.5	4.3	4.1	4.8
$r = 0.40$	331	286	318	315	308	325	314
$e =$	29	— 16	16	13	6	23	12

Range: 45.—Diagram: Line P.

SERIES III., 1910.

No.	1.	2.	3.	4.	Mean.
Oxychlor.	7.8	8.4	10.7	5.5	8.1
$r = 0.40$	301	311	321	333	317
$e =$	— 1	9	19	31	14

Range: 32.—Diagram: Line O.

REACTION No. 311.—Atomic Ratio, $R = 0.47951$.

Edgar F. Smith and *McAdam, Jour. Am. Chem. Soc.,* 1910, p. 1614.

No.	1.	2.	3.	4.	5.	Mean.
Vanadate	4.9	5.6	4.4	5.8	9.5	6.04
$r = 0.47$	931	927	941	937	921	931
$e =$	— 20	— 24	— 10	— 14	— 30	— 20

Range: 20.—Diagram: Line Q.

Strictly this series consists of 3 determinations only, two of which have been made twice, as follows:

No.	1.3.	2.4.	5.	Mean.
Vanadate	4.6	5.7	9.5	6.0
$r = 0.47$	936	932	921	931
$e =$	— 15	— 19	— 30	— 20

Range: 15.

This shows how even within narrow limits of weights taken (here from 4½ to 9½ grammes) *the systematic error* becomes evident as a function of the weight taken. Within the actual range, the analytical excess approaches zero with diminishing amount operated upon.

PRELIMINARY WORK.

Line.	Reac-tion.			Analytical Ratio. r.	Excess. e.	
A. a	1 det.	1.6385 oxychl. gave	0.874 oxide	0.53342	892	Berzelius.
E.	4 det.	4.0418	2.1258	0.52608	158	Roscoe.
D. b	1 det.	0.351 pentoxide	0.913 Ba sulphate	0.38445	— 527	Berzelius.
T. c	1 det.	0.351 pentoxide from	0.775 Va sulphate	0.45290	+ 432	Berzelius.

IV. The Analytical Excess.

The analytical excess e is only comparable in work carried out according to the same chemical reaction by different chemists. This condition has determined the form of Table IV., in which the capital letter marks the line on our final diagram representing the work, while the numbers below the letter represent: the first, the number of determinations made, the second giving the analytical excess obtained. This excess will naturally be found the greatest for all preliminary (or pioneer) work such as that done by Berzelius in his single trials of reactions (a), (b), (c).

This table makes it very apparent that each succeeding chemist benefited by the work and experience of his predecessor. This shows best under reaction 270 where Berzelius (1 determination) gives the excess 140, Roscoe (8 determinations) only 76 and Prandtl (15 determinations) brings it down to an average of 28 only.

For Reaction 98 this relation holds good for the work of Berzelius and Roscoe only, while that of Prandtl, done as recently as 1909, reaches almost the excess of Berzelius single first trial of eighty years ago, although Prandtl used the mean weight of 2.5 grams while Berzelius had only half a gram for his work.

TABLE IV.

The Resulting Analytical Excess.

Reaction.	98	269	270	311	a	b	c
Chemist :							
Berzelius, 1831	B 3 —304 / B′ 1 —288		G 1 140		A 1 892	I 1 —527	D 1 432
Roscoe, 1868	F 5 — 73	R 3 189 / N 9 37 / M 1 —39	H 6 81 / I 8 76 / K 2 60		E 4 158		
I							
Prandtl, 1909	C 4 —255		L 5 57 / O 4 14 / P 6 12				
Smith-McAdam, 1910	—			Q 5 —20			

V. The Final Departures.

In this table (IV.) we have finally given all the departures for all the elements taking part in the different reactions used for the determination of the atomic weight of vanadium during the last eighty years—from Berzelius in Stockholm to Edgar F. Smith in Philadelphia. We have fully explained the manner of calculating these departures; every reader can verify any of these values for himself by the methods stated. Since the element most concerned is vanadium, we have arranged the record of departures in the order of the magnitude of the departures of vanadium, for which the extreme values are 1062 and minus 307, giving a total range of 1369, say one and one third units of atomic weight; that is, from Va 52.06 to 50.69.

If we omit the pioneer and preliminary work done by Berzelius in trying reactions (*a*) and (*b*), the extreme departures will be 800 and — 31, a total range of 831 only. The atomic weights will run from 51.80 to 50.69, which is a remarkably fine showing for so long a series of very difficult work on the rare element.

To realize the generally excellent work of the early days of Berzelius and of Roscoe—when the element was decidedly rare and difficult to purify—we need only compare the limits of the determinations by Prandtl of today with the range of the entire series (excluding only, as we have done already, the reactions (*a*) and (*b*)); these extremes of Prandtl are 594 with reaction 98 and 13 in Series II. with reaction 270; a total range of 581 thousandths. The corresponding atomic weights of vanadium are 51.59 and 51.01 differing 58 hundredths.

We are greatly tempted to point out a number of interesting features on this table, but fear that the paper will assume undue length and trust the reader will help himself.

We only remind the reader that the letter in the first column of this table permits the ready identification of the experimental result expressed in numbers in this table with the graphical representation on our two diagrams.

TABLE V.

The Departure. Determined from Eighty Years of Work.

Line in Diagram.	Chemist.	Reaction.	No. of Determ.	Analyt. Excess. e.	Departure, ε, in Thousandths.				True Atomic Weight	
					Va	O	Cl	Metal.	Va.	O.
A	Berzelius	a	1	892	1062	263	—326		52.06	16.26
B	"	98	3	—304	800	—245			51.80	15.75
B*	"	98	1	—288	784	—241			.78	.76
C	Prandtl	98	4	—225	594	—183			.59	.82
D	Berzelius	c	1	432	400	—310	—470[9]	— 77[10]	.40	.69
E	Roscoe	a	4	158	195	47	— 58		.20	16.47
F	"	98	5	— 73	192	— 59			.19	15.41
								Ag :		
G	Berzelius	270	1	140	153	153	83	—125	.15	16.15
M	Roscoe (B)	269	3	189	150	150	50	— 95	.15	.15
H	" (A)	270	6	81	87	87	47	— 71	.09	.09
I	" (A, B)	270	8	76	83	83	45	— 68	.08	.08
K	" (B)	270	2	60	65	65	36	— 54	.07	.07
L	Prandtl, I	270	5	57	62	62	34	— 51	.06	.06
N	Roscoe (M, R)	269	9	37	30	30	10	— 19	.03	.03
O	Prandtl, III	270	4	14	15	15	7	— 12	.01	.01
P	" II	270	6	12	13	13	7	— 11	.01	.01
								Na :		
Q	Smith-McAdams	311	5	— 20	13	4	— 2	— 12	51.01	16.00
								Ag :		
R	Roscoe (A)	269	6	— 39	— 31	— 31	— 10	20	50.97	15.97
T	Berzelius	b	1	—527	—307	—330	776[9]	776[11]	.69	15.67

[9] S.   [10] H.   [11] Ba.

VI. Our Graphics.

The values of all departures given in Table V. are represented to the eye in our two graphics.

Fig. 1 gives all the larger departures and as many of the smaller ones as space would permit. The scale used is 200 thousandths of the unit of atomic weights to the inch; or, what amounts to the same, the unit of the atomic weights is represented by five inches in length.

Fig. 2 gives all the departures of the central region on a scale which is five times the one used in the construction of the first figure. Hence in Fig. 2 the unit is represented by a line of twenty-five inches; or, in other words, it shows forty thousandths to the inch.

The vertical of the ordinate represents the departures of vanadium, while the departures of the elements combined with vanadium are set off on the horizontal as abscissæ.

The results for a complete analysis of any given compound are therefore set off on the horizontal line drawn through the point on the vertical determined by the departure for vanadium.
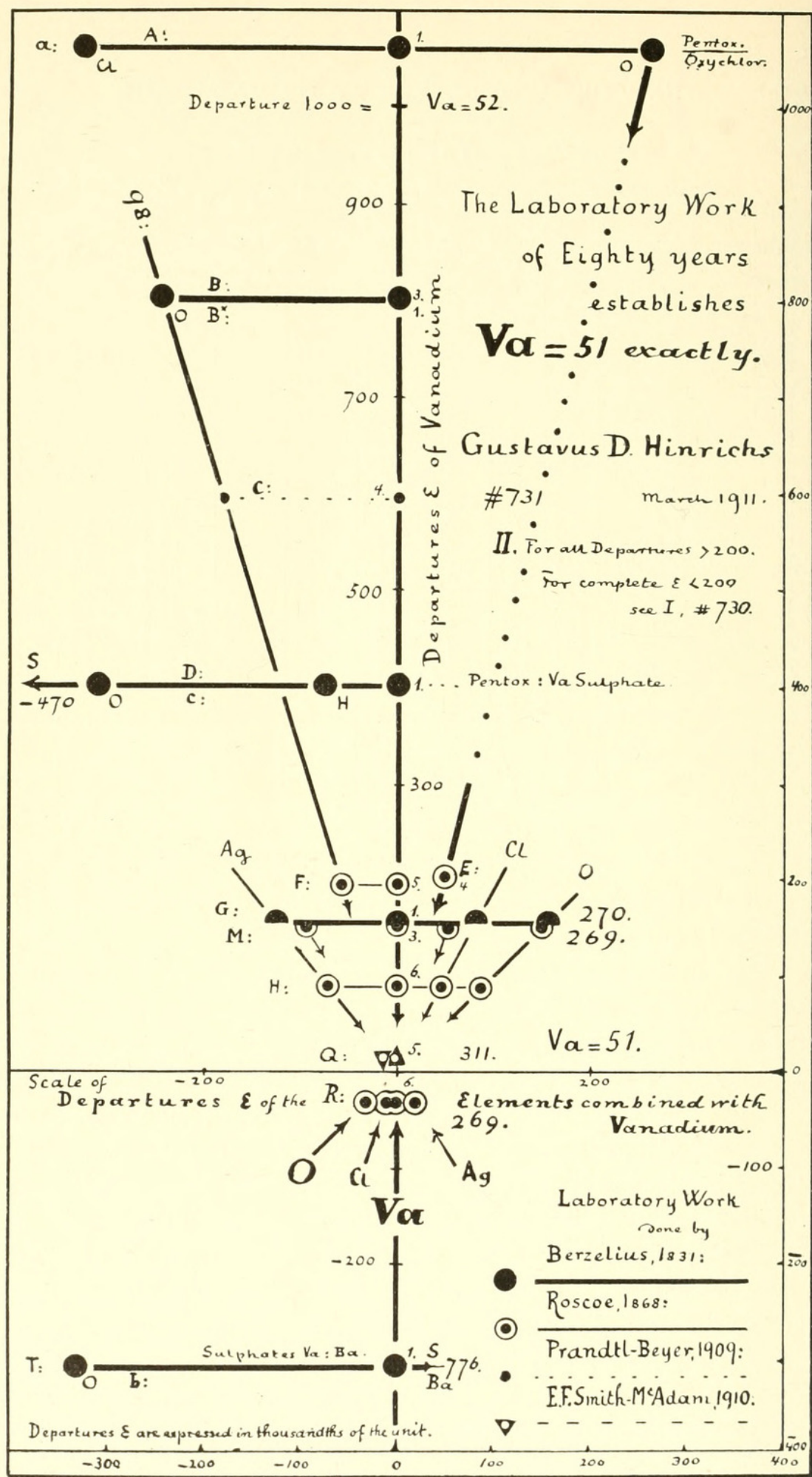
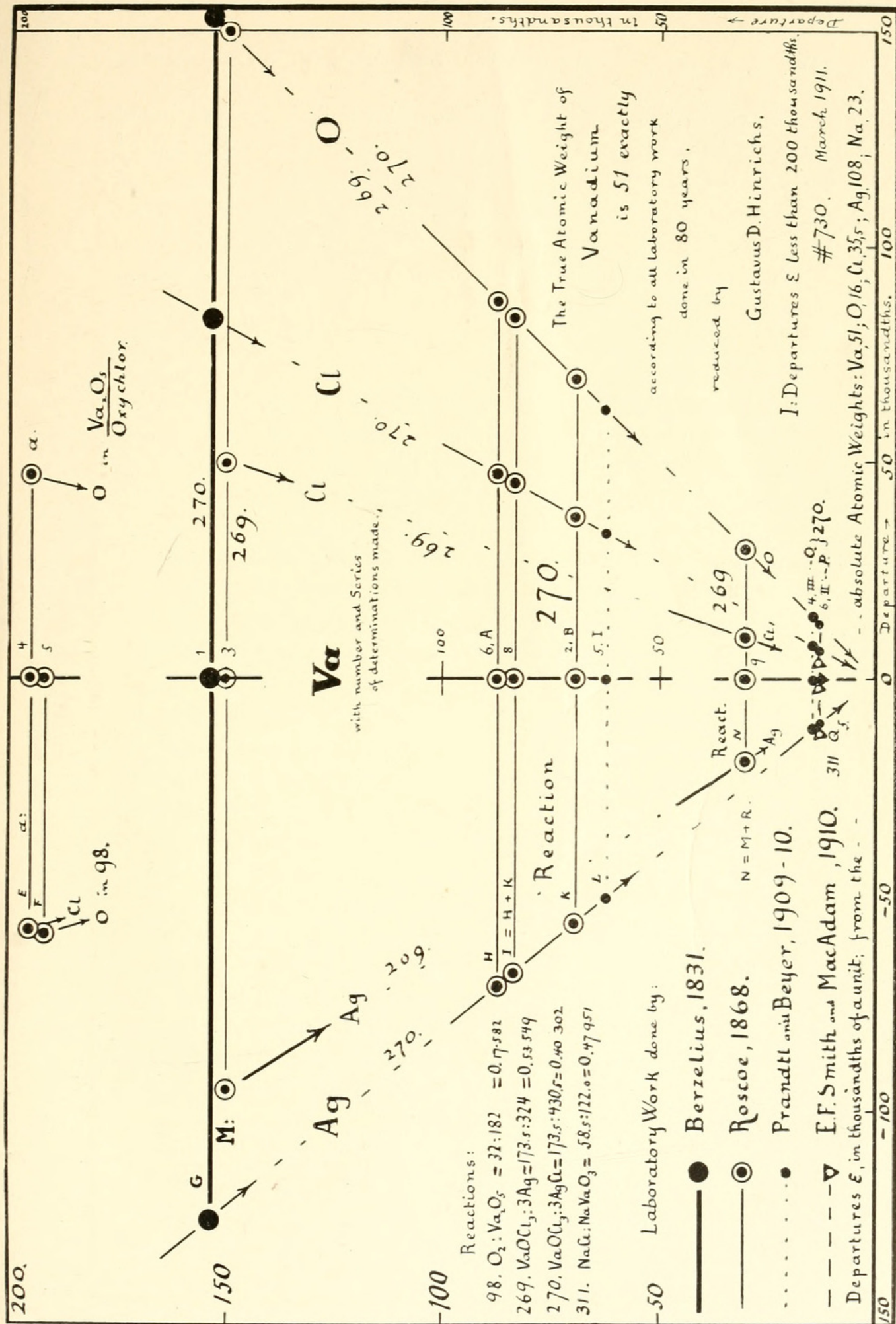FIG. 1. Departures. Scale 200 thousandths to the inch.

Fig. 2. Departures, E. Scale: 40-thousandths to the inch.

The chemist whose work is represented is indicated by the special mark used to designate the point, as shown in the explanation of signs on the diagram.

The small figure near the vanadium sign on the vertical indicates the number of determinations made represented in that line.

The line itself is marked by a letter, used in the tables for the purpose of ready identification.

For each reaction, the geometrical place (or locus) is a straight line passing through the center or the origin; the angle under which it cuts the axes is determined by the ratio of the variation of the element concerned and that of vanadium. These lines can therefore be drawn before any laboratory work is done, depending entirely on the chemical formulæ of the compounds taken and obtained in the reaction used.

For further particulars, some of which are very interesting as well as useful, we may refer to page 60 of our " Cinquantenaire," where also a remarkable criterion is given, permitting to detect any error in the assumed absolute atomic weight. The example there taken is copper.

Our two figures here inserted bring into clearest possible view the fundamental fact that all these departures are co-related; that the experimental error is not thrown on the vanadium for which the atomic weight is sought, but is distributed ex-æquo to all elements partaking in the reaction, as we have shown in formulæ, but which is here presented to the eye directly.

We do not recognize or find the slightest pretext for the assumption that any one element is immaculate and cannot be conceived to partake in any error of whatever cause or origin; but we have found that all elements in a chemical reaction are affected by the same cause of error according to the ties that bind them and which we have read in the chemical formula and in the mathematical relations first studied by Lagrange under the name of the Variation of arbitrary constants.[12]

We know that it is absurd to suppose that oxygen is always found to be 16, absolutely unaffected by any error, physical or chemical, in practice; that next some other atomic weight of some other element

[12] " True Atomic Weights," 1894, p. 158.

can be determined and that this value also will remain unaffected in all reactions; and so forth. That errors rapidly accumulate in such an irrational process, we have shown as far back as 1893, almost twenty years ago. That paper was presented by Berthelot to the Academy of Sciences of Paris and published in its *Comptes Rendus*.[13]

After having completed a thorough examination of all the atomic weight determinations made, we have, by a sort of crucial test, demonstrated that the present value Ag 107.88, implying a departure of 120 thousandths, is impossible; that O 16 requires Ag 108 exactly, according to all determinations made during an entire century in all the laboratories of the world.[14]

It is this same principle that is demonstrated by the diagrams here printed and this demonstration is made visible to the eye: It is not vanadium alone that causes the error affecting the laboratory work, but all elements in the reaction contribute to the error recognized in the final result of the analytical work.

Instead of the common notion that the work of the different chemists conflicts in the different values they have presented as the results of their determination of the atomic weight of vanadium our figures here inserted show to the eye that *all determinations made agree in the common result of Va 51 exactly*. While no experimental work of any kind, done by man, with instruments and by chemical reactions, all of which are but approximations to a mathematical perfection, can be expected to give perfectly exact results, we have proved that the final error cannot be ascribed to vanadium alone, as continues to be done by the dominant school, but that on the contrary, all the elements present in a reaction contribute, each one its share, to the excess or deficiency resulting. It was therefore necessary to find the laws regulating this participation of the different elements in the errors of the reactions and of the entire experimental work. Having discovered these laws, we have applied them here, to the atomic weight determinations made for vanadium and present in the two graphics (Figs. 1 and 2) the final results thus obtained.

These figures show plainly that all the departures from the abso-

[13] T. 116, p. 695.

[14] See paper read December 2, 1910, before the American Philosophical Society; *Proceedings*, 1910, pp. 359–363.

lute values are converging to zero along each of the lines of work pursued in the eighty years by the different chemists; there is but one insignificant exception, which we shall consider, when we take up the recent work of Prandtl.

Our Figs. 1 and 2 proclaim that the atomic weight of vanadium is exactly 51 in all these determinations, just as sure as oxygen has the atomic weight 16 exactly and silver 108 exactly, chlorine $35\frac{1}{2}$ exactly, sodium 23 exactly; in fact, all the elements have as atomic weights exactly the absolute values given in our publications of the last twenty years.

Even the very first determinations made by Berzelius, with only a fraction of a gramme of material at service, and only in one single determination, by the reactions designated (*a*), (*b*) and (*c*), do confirm the value Va 51; for the deviation noted for Va affects all the other elements present as well, and therefore it would be absurd to suppose that the atomic weight of vanadium could be obtained from a reaction which fails to give an exact determination for the other elements present. Thus reaction (*c*) represented by line D in Fig. 1, gives by the single determination made by Berzelius on 8 decigrams of the rather complex hydrated vanadium sulphate, a departure of 400 thousandths from 51 for the atomic weight of vanadium; but the same determination gave the atomic weight of oxygen 310 thousandths low as marked on the figure; it also gave the atomic weight of sulphur 470 thousandths low as indicated near the edge of the diagram and by the arrowpoint: for the real circular mark falls far beyond the limit of the diagram.

Is it so hard to understand that a reaction that fails to give precise determinations for all the elements it involves cannot necessarily be expected to furnish a value of precision for vanadium? Is it not about time for each individual chemist to begin to consider these simple facts for himself, as was the practice in former days?

It would be interesting to trace the gradual approach to the center where all departures are zero, as exemplified in the actual work of the successive chemists. This will be found to hold good for all, with the single exception already mentioned. We will only point to a few special instances, expecting the reader to go over the entire ground by himself.

The preliminary analysis, represented in the line A at the top of Fig. 1, gave not only the greatest departure for Va, but also for O, in the only determination made by Berzelius. When Roscoe, forty years after, made a series of four determinations the result entered at E in our figure (both 1 and 2) he cut the departure from 1062 to 195 for Va and from 263 to 47 for oxygen. If this determination were repeated with the benefit of all the progress made in laboratory work, the resulting mark would undoubtedly find its place much nearer the zero departure on the line (mainly dotted) on our figure (1).

Let us also look at the results obtained by the use of reaction 270, best seen on Fig. 2, lines G, H, I, K, L, O, P. Of these lines, G is the most distant, representing the largest departures: it marks the one determination made by the old master in 1831. Then we meet, in going toward the center of perfection or zero departure, the lines H, I and K bearing the mark of Roscoe and only about half as far from the zero as the line G of 1831. The total number of determinations made by Roscoe in 1868 was 8, represented by line I; 6 of these eight were "done by Analyst A" and are represented by line H; the other two were "done by Analyst B" and are represented by line K. Finally we have three series (I., II. and III., represented by lines L, P and O, respectively) made by Prandtl quite recently; of these, the last two series come quite close to the center, the departure for Va being 14 only for the mean of the two series (see Table V.). Since on our diagram the departures for O, Cl and Ag are set off as abscissæ to that of Va taken as ordinate, *the gradual diminution of all the departures is strikingly shown in the lines for these elements converging to the point of zero departure.* At the same time we here have the positive evidence that Prandtl has produced two very concordant series (his II. and III.) with a very small departure (mean 14 for Va and O) and one series (his first, I.) represented by line L for which the departure is 62, that is more than four times as large.

Now we may consider the results obtained by the reduction test, reaction No. 98, represented on our Fig. 1 by the lines B, C and F. Here we meet that one exception before referred to; for the greatest departure (line B) of Berzelius is but slightly diminished by Prandtl's

quite recent work (line C) and far surpassed by the small departures of the much older work of Roscoe (line F). It is to be hoped that Prandtl will also make one or two additional series under reaction 98, as he has done under 270; we dare say that, with due care, he may repeat the experience he has reported for reaction 270 and greatly reduce the departure, at least to that of Roscoe in 1868.

It will hardly be necessary to state that the numerical data we have quoted in the discussion of our Figs. 1 and 2 are taken from tables II. and V. especially.

CONCLUSION.

We think that the reader will have no trouble now in completing his study of the facts placed before him in our tables and in our figures which both comprise much more than their size would seem to indicate.

We therefore think that the reader will fully understand the utter fallacy of throwing all the errors of all kinds on the one element, the atomic weight of which the modern chemist tries to determine " in the chemical laboratory and by experiment exclusively."

The reader will, we believe, now fully comprehend the situation—both of the chemist and of his intended victim, the element. The victim—if it were conscious—would shiver in anticipation of being made responsible for every error and mishap that may befall any of the elements present in the reactions, the apparatus used and even the chemist at work; for all these errors and shortcomings the modern chemical school *de facto* charges up to the element the atomic weight of which it undertakes to determine. The only new step—other than what the general progress of practical laboratory work may favor him with—will be the straining out a few more innocent gnats without in the least disturbing the ever attendant herd of the old camels.

It sometimes does seem strange that in twenty years this Berzelian picture from Saint Matthew (XXIII., 24) has remained so true to Nature. It is not the fault of the individual chemists, except in so far as they have surrendered a fundamental part of their rightful domain to the International Atomic Weight Committee.