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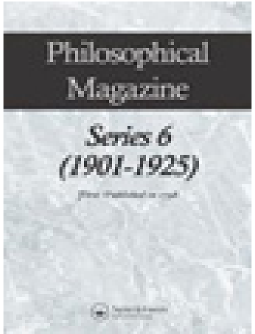

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IX. On a general numerical connexion between the atomic weights

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Finally, a well oxidized copper wire was tried in hydrogen.

Temperature	267°	287°	307°	316°
Rate of Leak	1·05	1·4	6·0	21·4

10 div. per hour at 310°.

These experiments fall into two classes.

(1) Those cases where chemical action was occurring between the electrified surface and the surrounding gas.

(2) Those cases where there was no such action.

To summarize the results: under the first head we have—

Copper in air . . .	10 div. of leak	per	hour	at 287°
Copper oxide in hydrogen	„	„	„	at 310°

under the second—

Silver in air. .	10 div. leak	per	hour	at 250°
Silver in hydrogen	„	„	„	228°
Copper oxide in air	„	„	„	266°

So far as the experiments go they suggest that chemical action is rather unfavourable than otherwise to the escape of positive electrification.

The result of most interest in the present investigation is that the discharge of positive electrification by hot metals can be detected at much lower temperature than has hitherto been supposed, becoming apparent very far below a red heat, and increasing rapidly with the temperature.

IX. *On a General Numerical Connexion between the Atomic Weights.* *By* J. H. VINCENT, *D.Sc., B.A.*[*]

[Plates I. & II.]

HISTORICAL.

MANY relationships have been made out between the atomic weights of the elements when these are considered in small groups: and there are a few formulæ which have been proposed to express the connexion between the atomic weight of an element and the order in which it stands in a list of elements of ascending atomic weights.

Mills (Phil. Mag. [5] xviii. p. 393 & xxi. p. 151) states that " it is probable that the equation

$$y = p\,.\,15 - 15(\cdot 9375)^x$$

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[*] Communicated by Prof. J. J. Thomson, F.R.S.

includes the numerics of all known elements excepting hydrogen," a numeric being an atomic weight y. He arranged all the atomic weights in ascending order of magnitude, and without altering the order, these were divided into sixteen groups by trial. The number p is the same integer for each group. The value of x was obtained by arithmetic for each element. Mills restricted himself only by having x always either an integer or infinity, and then chose its value so that the calculated atomic weight should be as near as possible to the experimental value. An example of a group is given below to illustrate the method.

Group III.

$$y=45-15(\cdot 9375)^x.$$

	x.	y.	y calc.
P …………	1	30·96	30·94
S …………	2	31·98	31·82
Cl …………	7	35·37	35·45
K …………	14	39·02	38·92
Ca …………	17	39·90	39·99
Sc …………	42	43·98	44·00

When we consider the large amount of choice involved in the compilation of such a table, it is not at all surprising that the numbers in the last two columns of the above table agree closely; indeed there seems no reason to doubt that by some such arbitrary process the numbers in the last two columns could be made to agree to any required degree of accuracy.

To find the atomic weight of an element by this method one would require to know the group in which the element had been placed, the value of x assigned to the element, as well as the constants occurring in the equation.

While regarding the work as leading to the conclusion that there might be an infinite number of elements having atomic weights less than about 240, Mills considered that this value was the upper limit.

The formulæ are subsequently derived by the contemplation of a hot nebular mass of primitive substance which, while cooling freely in space, gives birth to polymers of this primitive material. "But on account of the evolution of heat when a polymer is formed, there will ensue, as a physical consequence, the inversion of more or less of the cooling, and therefore of the polymerization." Incidentally this theory is used to explain the phenomena of variable stars.

The important point about Mills' work is that it may be considered as indicating the existence of an upper limit for atomic weights. The weak point is that the number of elements below this limit may be infinite. On this latter question Mendeléeff ('Principles of Chemistry,' English translation, 1891 ed. p. 19) expresses himself with great clearness. "The actual periodic law does not correspond with a continuous change of properties, with a continuous variation of atomic weights—in a word it does not express an uninterrupted function."

In conclusion, Mills uses his formulæ to classify the elements with some degree of success.

Stoney (Proc. Roy. Soc. 1888, p. 115, and Circular issued to members of B. A. at Bath, 1888) plots as ordinates the cube roots of the atomic weights referred to hydrogen as unit, the abscissæ being successive integers. "A curve

$$y_m = k \log (mx),$$

where

$$\log k = 0{\cdot}785,$$

and

$$\log \alpha = \bar{1}{\cdot}986,$$

threads its way through the positions plotted down from the observations."

Having obtained an expression of this form, Stoney investigated subsequent terms which should include deviations from the formula. Finally a spiral was constructed and so arranged that it not only showed the periodic classification of the elements, but also gave by inspection the atomic weights.

It should be noted that according to Stoney's formula elements of less atomic weight than hydrogen and also of greater atomic weight than uranium may exist. Three elements lighter than hydrogen and six between hydrogen and lithium were predicted; a vacant "sesqui-radius" in the spiral was left, across which the transition from electro-positive to electro-negative elements was abrupt. This "is not arbitrarily introduced into the diagram, but has a real existence in nature." This "sesqui-radius" is now occupied by the new gases, and thus the prophecy of Stoney has been fulfilled in a most remarkable way.

This is a very strong argument in favour of the formula with which Stoney worked, but it is perhaps a stronger argument in favour of the treatment of the periodic law by graphic methods. The prejudice against such methods entertained by Mendeléeff is very surprising. In his book already referred to, he says he has never expressed, "and will never express, the periodic relations of the elements by any geometrical figures."

Carnelley (Phil. Mag. [5] xxix. p. 97) founded his method of computing the atomic weights on the periodic law. He mentions that he had made frequent attempts to find a simple numerical expression for the periodic law during seventeen years previous to the publication of this paper, but without marked success.

The atomic weight A is given by the formula

$$A = 6{\cdot}6(m + \sqrt{v}),$$

where m is a constant for each of Mendeléeff's "series," while v is equal to the order of each element in its series. The values chosen for m were 0, $2\frac{1}{2}$, 5, $8\frac{1}{2}$, and thence by differences of $3\frac{1}{2}$ to 33, for the successive series II., III.,...XII. Thus "for any element in series IV. or upwards

$$A = 6{\cdot}6(3{\cdot}5a - 9 + \sqrt{v}),$$

where a = the number of series to which the element belongs, and v the numerical order of the element in its own series." A table of determined and computed atomic weights with their differences is given, from which it is at once evident that the rule is capable of calculating the atomic weights with a considerable degree of accuracy. The greatest variation is for iodine, in which the computed atomic weight falls short of the real atomic weight by 6·7 units. The difference in the same direction for tellurium is given as 6·5; but if we substitute the value now accepted for the atomic weight of tellurium, the difference becomes greater. The mean difference for the 54 elements considered is only 1·9.

If, on the other hand, we examine the results from a percentage point of view, they do not appear so satisfactory. Thus the computed value for the atomic weight of carbon is 10 per cent. too high, that of selenium is 8·2 per cent. too low, that of lithium is 5·7 per cent. too low, and that of nitrogen is 5·7 per cent. too high.

The nearness of the constant 6·6 to the 6·4 of Dulong and

Petit's law suggested to Carnelley the trial of the rule

$$\text{Specific heat} = \frac{1}{m + \sqrt{v}};$$

and he found "that in almost all cases the numbers agree very closely with the experimental specific heats."

A NEW RULE FOR COMPUTING ATOMIC WEIGHTS.

If a list of all the atomic weights in ascending order of magnitude be taken and the order in this list be called n, then the nth atomic weight, from $n=3$ to $n=60$, is given by the equation

$$W = (n+2)^{1 \cdot 21}.$$

In the table (p. 108) headed "Augmented List of the Elements," the numbers standing under n give the actual order of the elements in such a list as the above. The determined atomic weights are given under w, the computed atomic weights under W.

The atomic weights are Clarke's with hydrogen as unit (Journ. Am. Chem. Soc. March 1902).

The difference between the determined and the calculated atomic weight is given in another column. Confining our attention for the present to that part of the table from lithium to samarium inclosed by the large bracket, we see that for the 58 elements considered, the difference between the experimentally determined atomic weight and that calculated by the rule is less than unity in 36 cases. It is greater than 1 and less than 2 in 13 cases; is between 2 and 3 in 7 cases; while in only two cases does the computed value differ from the determined value by more than three units, in both of which the difference is less than 4. The mean difference for the whole of the 58 elements with which we are now dealing is about 1·01.

The percentage differences are given also in the table. In 19 instances the difference is less than 1 per cent., in 19 it is either 1 per cent. or greater than 1 per cent. and less than 2 per cent.; in 11 cases it is greater than 2 but less than 3, and in 6 it is either equal to or greater than 3 and less than 4, in two instances the percentage difference exceeds 4, and in one case the error is 5·8 per cent. The mean percentage error for the 58 elements is about 1·6.

AUGMENTED LIST OF THE ELEMENTS.

n.		N.	w.	W.	$w-\mathrm{W}$.	$\frac{(w-\mathrm{W})}{w}\times 100$.
1. Hydrogen		1	1 (by definition)	1	0·00	0·0
		2	……	2·313	……	…
2. Helium		3	3·93	3·780	+0·15	+3·8
		4	……	5·352	……	…
3. Lithium		5	6·97	7·012	−0·04	−0·6
4. Glucinum		6	9·0	8·746	+0·25	+2·8
5. Boron		7	10·9	10·54	+0·36	+3·3
6. Carbon		8	11·9	12·38	−0·48	−4·0
7. Nitrogen		9	13·93	14·28	−0·35	−2·5
8. Oxygen		10	15·88	16·22	−0·34	−2·1
9. Fluorine		11	18·9	18·20	+0·70	+3·7
10. Neon		12	19·8	20·24	−0·44	−2·2
11. Sodium		13	22·88	22·28	+0·60	+2·6
12. Magnesium		14	24·1	24·37	−0·27	−1·1
13. Aluminium		15	26·9	26·49	+0·41	+1·5
14. Silicon		16	28·2	28·64	−0·44	−1·6
15. Phosphorus		17	30·75	30·82	−0·07	−0·2
16. Sulphur		18	31·83	33·03	−1·20	−3·8
17. Chlorine		19	35·18	35·26	−0·08	−0·2
18. Potassium		20	38·82	37·53	+1·29	+3·3
19. Argon		21	39·6	39·80	−0·20	−0·5
20. Calcium		22	39·8	42·10	−2·30	−5·8
21. Scandium		23	43·8	44·43	−0·63	−1·4
22. Titanium		24	47·8	46·78	+1·02	+2·1
23. Vanadium		25	51·0	49·15	+1·85	+3·6
24. Chromium		26	51·7	51·55	+0·15	+0·3
25. Manganese		27	54·6	53·94	+0·66	+1·2
26. Iron		28	55·5	56·37	−0·87	−1·6
27. Nickel		29	58·25	58·82	−0·57	−1·0
28. Cobalt		30	58·55	61·28	−2·73	−4·7
29. Copper	N = n + 2	31	63·1	63·76	−0·66	−1·0
30. Zinc		32	64·9	66·26	−1·36	−2·1
31. Gallium		33	69·5	68·78	+0·72	+1·0
32. Germanium		34	71·9	71·30	+0·60	+0·8
33. Arsenic		35	74·45	73·85	+0·60	+0·8
34. Selenium		36	78·6	76·41	+2·19	+2·8
35. Bromine		37	79·35	78·98	+0·37	+0·5
36. Krypton		38	81·15	81·57	−0·42	−0·5
37. Rubidium		39	84·75	84·17	+0·57	+0·7
38. Strontium		40	86·95	86·79	+0·16	+0·2
39. Yttrium		41	88·3	89·43	−1·13	−1·3
40. Zirconium		42	89·7	92·07	−2·37	−2·6
41. Columbium		43	93·0	94·74	−1·74	−1·9
42. Molybdenum		44	95·3	97·40	−2·10	−2·1
43. Ruthenium		45	100·9	100·1	+0·8	+0·8
44. Rhodium		46	102·2	102·8	−0·6	−0·6
45. Palladium		47	106·2	105·5	+0·7	+0·7
46. Silver		48	107·11	108·2	−1·1	−1·0
47. Cadmium		49	111·55	110·9	+0·7	+0·6
48. Indium		50	113·1	113·7	−0·6	−0·5
49. Tin		51	118·1	116·5	+1·6	+1·4

TABLE (*continued*).

n.	N.		w.	W.	$w-$W.	$\frac{(w-\text{W}}{w}\times 100$.
50. Antimony	$N=n+2$.	52	119·5	119·2	+0·3	+0·3
51. Iodine		53	125·89	122·0	+3·9	+3·1
52. Tellurium		54	126·1	124·8	+1·3	+1·0
53. Xenon		55	127	127·6	−0·6	−0·5
54. Cæsium		56	131·9	130·4	+1·5	+1·1
55. Barium		57	136·4	133·2	+3·2	+2·3
56. Lanthanum		58	137·6	136·1	+1·5	+1·1
57. Cerium		59	138·0	138·9	−0·9	−0·7
58. Praseodymium		60	139·4	141·8	−2·4	−1·7
59. Neodymium		61	142·5	144·6	−2·1	−1·5
60. Samarium		62	149·2?	147·5	+1·7	+1·1
......		63	......	150·4	...	...
......		64	......	153·3	...	...
61. Gadolinium		65	155·2	156·2	−1·0	−0·6
62. Terbium		66	158·8	159·1	−0·3	−0·2
......		67	......	162·0	...	...
63. Erbium		68	164·7	164·9	−0·2	−0·1
......		69	......	167·9	...	...
64. Thulium		70	169·4	170·8	−1·4	−0·8
65. Ytterbium		71	171·9	173·8	−1·9	−1·1
......		72	......	176·8	...	...
66. Tantalum		73	181·5	179·7	+1·8	+1·0
67. Tungsten		74	182·6	182·7	−0·1	0·1
......		75	......	185·7	...	...
68. Osmium		76	189·6	188·8	+0·8	+0·4
69. Iridium		77	191·7	191·7	0·0	0·0
70. Platinum		78	193·4	194·7	−1·3	−0·7
71. Gold		79	195·7	197·8	−2·1	−1·1
72. Mercury		80	198·50	200·8	−2·3	−1·2
73. Thallium		81	202·61	203·8	−1·2	−0·6
74. Lead		82	205·36	206·9	−1·5	−0·7
75. Bismuth		83	206·5	209·9	−3·4	−1·6
......		84	....	213·0	...	...
......		85	....	216·1	...	...
......		86	....	219·2	...	...
......		87	....	222·2	...	...
......		88	....	225·3	...	...
......		89	....	228·4	...	...
76. Thorium		90	230·8 ?	231·5	−0·7	−0·3
......		91	....	234·7	...	...
77. Uranium		92	237·8	237·8	0·0	0·0

We may add this statement to the rule: that if the atomic weights are from Clarke's 1902 list with hydrogen as unit, then the greatest difference between the computed and the determined value will not exceed 4 units, nor will the percentage difference be greater than 6; while in 36 cases the result will not be a unit wrong, and in 19 cases will not be 1 per cent. wrong.

Deviations from the Formula.

The elements deviating most from the formula, judging from the differences between the computed and experimental values, are:—

	$w-W$.
Iodine	+3·9
Barium	+3·2
Cobalt	−2·73
Praseodidymium	−2·4
Zirconium	−2·37
Calcium	−2·30
Selenium	+2·19
Molybdenum	−2·1
Neodidymium	−2·1

Iodine is thus a very marked exception to a rule which holds fairly correctly for 57 other elements. This may be explained by assuming either (1) that the real atomic weight of iodine is less than that accepted, or (2) that the order in the table is too low; and thus the suspicion of error in the atomic weight falls upon its next highest neighbour tellurium. The atomic weight of tellurium is a matter of some uncertainty owing to two causes. One of these is that successive attempts to determine its atomic weight do not yield concordant results, and the other is that unless the atomic weight of tellurium is below that of iodine these two elements constitute a serious exception to the periodic law. If we assume that its atomic weight is less than that of iodine, then iodine would have

$$n=52.$$

Its computed value would be 124·8, which differs from the determined value by 1·09, a quantity little greater than the mean deviation. The most probable atomic weight for tellurium on this view is 122.

The fact that the greatest variation of the rule leads to the same conclusion as the periodic law may be taken as tending to confirm the legitimacy of the former. No general relation has been found to connect the deviations, but a term could be inserted in the formula whose magnitude depended on whether n were odd or even, which would make the errors less.

It may be noted that iodine, molybdenum, and selenium are exceptions to Dulong and Petit's law.

Judged from the percentage standpoint, the elements deviating most from the formula are:—

	$\frac{w-W}{w}100.$
Calcium	−5·8
Cobalt	−4·7
Carbon	−4·0
Sulphur	−3·8
Fluorine	+3·7
Vanadium	+3·6
Potassium	+3·3
Boron	+3·3
Iodine	+3·1

Of these, calcium, carbon, fluorine, sulphur, boron, and iodine are exceptions to Dulong and Petit's law.

Argon is an exception to the periodic law, which would lead one to expect its atomic weight to be between those of chlorine and potassium. If, however, its atomic weight should be proved to be greater than that of calcium, the atomic weight of the latter would be given correctly by the rule. The value to be then expected for argon would be 42·1.

Extension of the Formula to all the Elements.

The evidence which has been adduced in favour of the formula

$$W = (n+2)_{1\cdot 21}$$

warrants an attempt being made to apply it to the remaining elements.

The plan adopted has been to replace the $(n+2)$ of the above formula by N, where N is the order in what will be called for short the augmented list. This augmented list is one in which, though the real order of arrangement is never reversed, a value for N is taken so that the particular element shall have its atomic weight given as nearly as possible by the formula. Thus the augmented list is a list of the elements in ascending order of magnitude, with gaps left in it so as to make the experimental results fit the formula.

The justice of this process may be tested by seeing whether the necessary gaps are too numerous, or are in any other way improbable; or whether the gaps can be reconciled with acknowledged chemical principles.

Over the range from lithium to samarium the change is simply to replace $n+2$ by N. That is, instead of regarding lithium as the third heaviest atom, it is taken as the fifth in the augmented list, germanium as the sixth instead of the fourth, and so on up to samarium. For hydrogen $N=1$, and for helium $N=3$. The formula is of such a type as to give the atomic weight of hydrogen correctly; the calculated weight of helium is only ·15 of a unit wrong, which, however, is a percentage error of 3·8. The most probable value for helium is 3·78.

These two gaps near the beginning of the augmented list have no chemical evidence in their favour. There is no room in the periodic table for an element between helium and lithium, and any theory based on the periodic law which would predict any elements between hydrogen and helium would predict several and not merely one.

It is necessary to assume thirteen other gaps in order to complete the augmented list. The table gives the positions and also the atomic weights which they would have on this theory.

The periodic table leaves five gaps between samarium and gadolinium. This table also shows that if there are not five missing elements then there are two. In the latter case elements analogous to rhodium, ruthenium, and palladium would not be represented. The augmented list agrees with this second view. The periodic law would lead us to expect a maximum of seven elements between gadolinium and terbium. The augmented list indicates that five only are to be expected. Their exact positions in the periodic table cannot be predicted until the positions occupied by terbium, erbium, and thulium are known. An element is predicted by the periodic law between ytterbium and tantalum, and between tungsten and osmium. These are also predicted by the augmented list, which agrees also in predicting only one element in each of these positions. An unbroken line of elements occurs from osmium to bismuth in both the periodic table and in the augmented list. Between bismuth and thorium both leave six elements to be discovered, while the last gap between thorium and uranium occurs in both the periodic table and the augmented list.

The results given in the table are shown graphically in Plates I. and II., in which + indicates the atomic weight given by the formula and ● shows the actual atomic weight. The sign ✱ marks the most probable atomic weight of a predicted element.

Pl. I. is drawn on ordinary squared paper, and is thus suited to show the differences between the computed and the experimentally found numbers.

Pl. II. is drawn on paper ruled logarithmically. The graph of an equation of the form $y=x^m$ is a straight line on this paper, so that all the computed points lie on a straight line. The actual distances of the points (●) showing the experimentally determined values above or below the straight line, are proportional to the percentage differences between the computed and the experimental numbers.

It will be seen that the actual values of the atomic weights lie very close to the straight line in Pl. II.

An equally good straight line would of course be obtained by plotting the cube roots of w instead of w.

Thus the formula is of a different type to Stoney's, from which it would follow that the actual values (not the logarithms) of the cube roots of the atomic weights plotted against the logarithm of the order would give a straight line.

On the Determination of the Power Constant and the Use of the Rule.

The whole of the preceding leads to the conclusion that a relationship of the form

$$W=N^q$$

expresses to a close degree of accuracy some fundamental connexion which exists between the masses of different kinds of atoms.

The equation has been thrown into the form

$$W=N^{1\cdot 21}$$

in the previous pages so as to render the whole as definite as possible. But no claim is made as to 1·21 being the best value to give to q. The value of q should be obtained from the list of elements from lithium to samarium, augmented or not as may appear most just to anyone who wishes to redetermine the value of q. If there is any truth in the views explained in this paper, the constant q is of primary importance, and its exact determination becomes a matter of interest. The value which will be obtained depends on whether or not an element analogous to manganese is to be assumed between molybdenum and ruthenium; q will be slightly less or greater according as a gap is or is not left.

The method might, however, be used to test this point. By considering only elements as far as molybdenum the best value of q could be found, and then the sum of the deviations with this value of q could be found 1st when no gap was left, 2nd with the gap.

If the second arrangement gave a smaller mean difference than the first, then this would justify the prediction of an element in the place under discussion.

It may well be, however, that the result of such an investigation would be different according as one regarded percentage differences or the differences themselves as of more importance. If the latter, then the mean error is less when no gap is left between molybdenum and ruthenium.

Thus if we regard any atomic weight w_N as giving us a value of q, we have a series of equations like

$$w_N = N^q,$$

or

$$\log w_N = q \log N.$$

Using the atomic weights of all the elements up to and including molybdenum, we have

$$\begin{aligned} \log 3{\cdot}93 &= q \log 3, \\ \log 6{\cdot}97 &= q \log 5, \\ \log 9{\cdot}0 &= q \log 6, \\ &\cdots\cdots \\ &\cdots\cdots \\ \log 95{\cdot}3 &= q \log 44. \end{aligned}$$

The value of q given by

$$q = \frac{\Sigma \log w}{\Sigma \log N}$$

will be such that the percentage errors will be least. This equation may be written

$$q = \frac{\Sigma \log w}{\log \underline{|44} - \log 8},$$

from which q may be found readily by using a table of the logarithms of factorials. The value obtained is

$$q = 1{\cdot}209.$$

Similarly q may be computed, when no gap is left between molybdenum and ruthenium, from the atomic weights of the elements from ruthenium to samarium. In this case

$$q=\frac{\Sigma \log w}{\log \underline{|62}-\log \underline{|44}}$$
$$=1\cdot211.$$

If, however, we leave the gap, we have

$$q=\frac{\Sigma \log w}{\log \underline{|63}-\log \underline{|45}}$$
$$=1\cdot205.$$

Thus the q when we leave no gap is nearer to the first value ($q=1\cdot209$) than is the value of q obtained when we leave the gap. This leads to the conclusion that no element of atomic weight about 101 with properties analogous to manganese is to be predicted.

The mean value of q can now be calculated from

$$q=\frac{\Sigma \log w}{\log \underline{|62}-\log \underline{|8}},$$

which gives

$$q=1\cdot210.$$

When the value of q has been determined as accurately as possible, then the formula may be employed to determine what empty places in the periodic table are to be filled by predicted elements, in the same way as has been already done above on the assumption that $q=1\cdot21$.

CONCLUSION.

The consequence which follows from the assumption that

$$W=N^q,$$

where N is a + integer and q a positive number whose actual value approximates to 1·21, is that the list of atomic weights starts abruptly at hydrogen but has no end.

The fact that for many years all the elements that have been discovered have atomic weights greater than that of hydrogen and less than that of uranium would point to the conclusion that any law for the connexion between the masses of different kinds of atoms should lead to the list of elements being limited at both the beginning and end.

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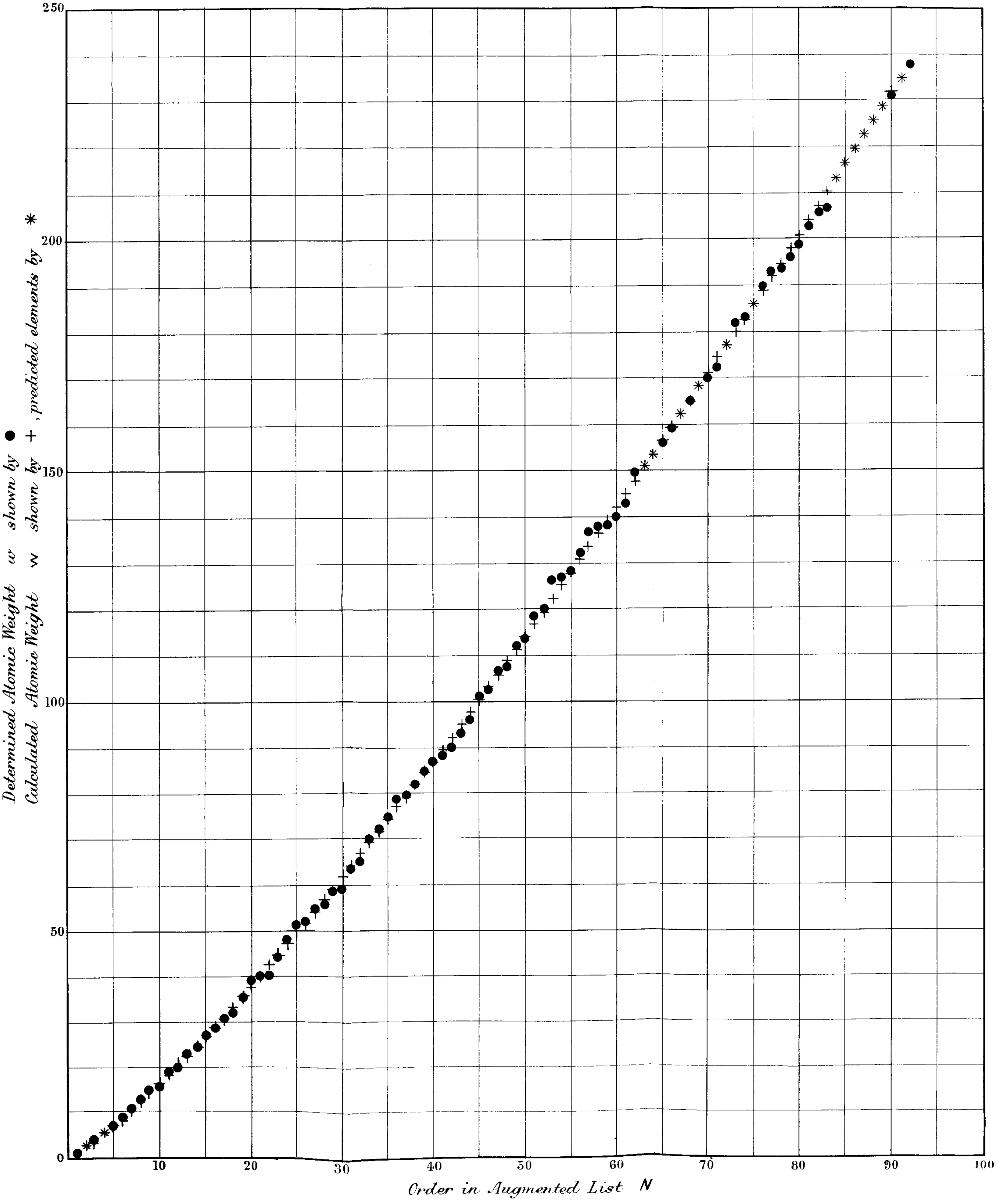
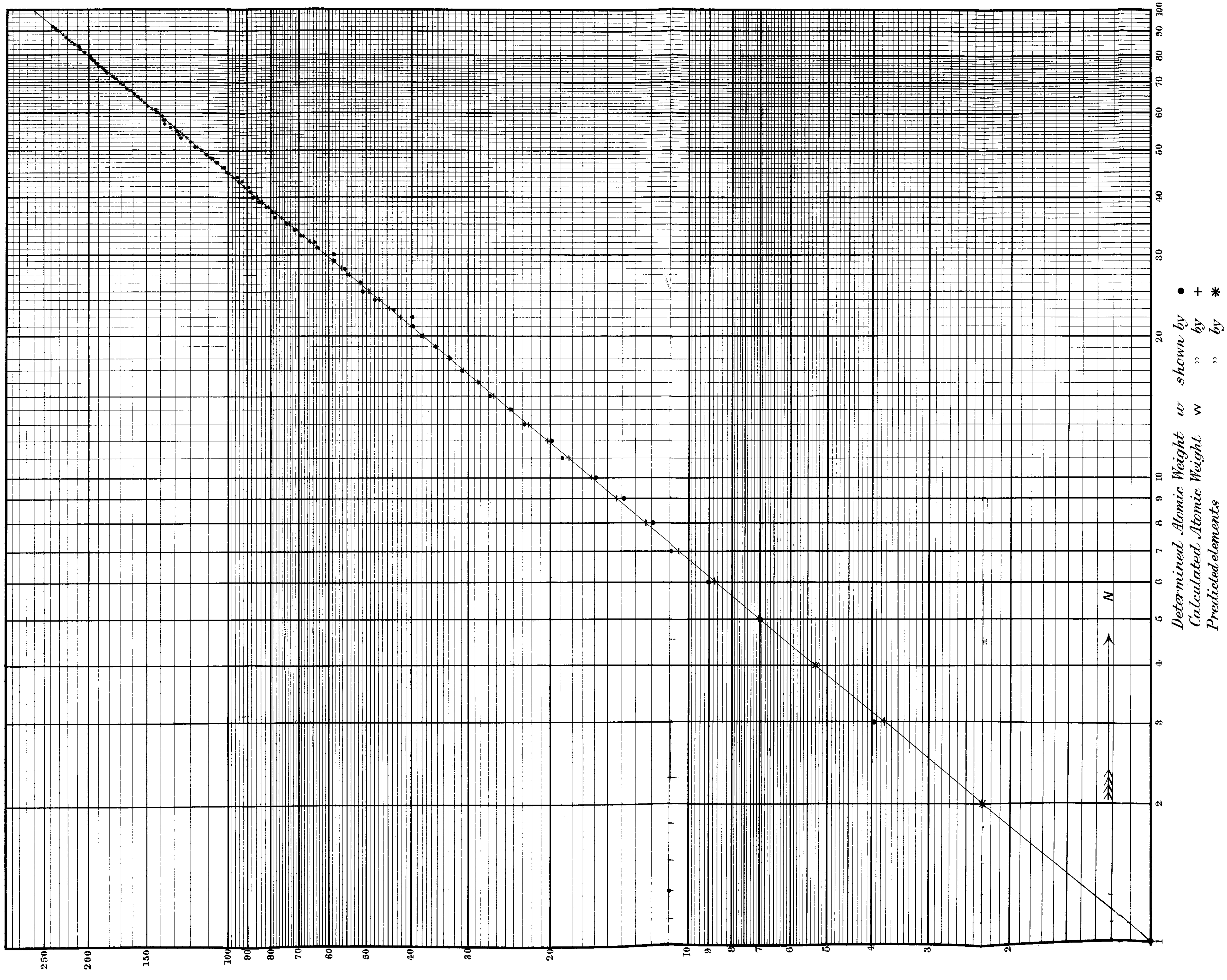


Mintern Bros. lith.



Mintern Bros. lith.