

ART. XXXI.—*On Numerical Relations existing between the Equivalent Numbers of Elementary Bodies*; by M. CAREY LEA, Philadelphia. Part II.

(Concluded from p. 111.)

On Geometrical Ratios existing between Equivalent Numbers.

THE First Part of this paper was devoted to the examination of relations between the equivalent numbers of certain elementary bodies depending upon the number 44·45, and it was attempted to show:—

1st. That such relations extend to nearly all the elements:—

2d. That the particular groups collected together by this relation consist of bodies whose properties are analogous, and that the classification is in harmony with the distinguishing characteristics of the substances classified.

The first portion of this Second Part will present a species of relation wholly distinct, it is believed, from any that has hitherto been pointed out, and which may be not inappropriately termed Geometrical Ratios, to distinguish them from the more familiar arithmetical relations which have been heretofore exclusively studied by chemists.

The arithmetical relations are susceptible of at least an hypothetical explanation, on the supposition that the common difference in a series of elements may represent the equivalent number of a substance as yet undetermined, which, by its combinations in varying proportions, gives rise to the bodies constituting the successive terms of the series. The analogies which are now to be considered are more difficult of explanation, even by hypothesis. Their accuracy, sometimes absolute, renders improbable the supposition that they are mere casual coincidences. In science it is not permitted to neglect facts merely because we cannot satisfactorily account for them.

The nature of these relations consists in this, that if we take two substances and examine the ratio which subsists between the numbers representing their atomic weights, we may find in certain cases, that it is identical with the ratio subsisting between the atomic weights of two other substances, and so on through a considerable number of elements. The ratio between the atomic weights, for instance, of oxygen and nitrogen, is that of four to seven, so likewise is that between those of zirconium and potassium, potassium and barium, with absolute exactitude. What renders this the more remarkable is, that all three of these last substances are striking exceptions to Prout's law that the equivalents of the elements are exact multiples of that of hydrogen; they all have decimals, zirconium 22·4, potassium 39·2, barium 68·6. Now the ratio just mentioned gives these num-

bers with their decimals with perfect exactness. The same species of relation exists between many other elements, as will be seen by the table below :—

(1.)

Oxygen-Nitrogen Ratio, or that of Four to Seven.

			Atomic wts. calculated.		Atomic wts. received.
Nitrogen	= 14,	$\frac{4}{7}$ of 14	= 8	Oxygen	= 8
Barium	= 68·6,	$\frac{4}{7}$ "	68·6 = 39·2	Potassium	= 39·2
Potassium	= 39·2,	$\frac{4}{7}$ "	39·2 = 22·4	Zirconium	= 22·4
Calcium	= 20,	$\frac{4}{7}$ "	20 = 11·43	Magnesium	= 12
Magnesium	= 12,	$\frac{4}{7}$ "	12 = 6·86	Glucinum	= 7*
Strontium	= 43·75,	$\frac{4}{7}$ "	43·75 = 25	Titanium	= 25
Lead	= 103·5,	$\frac{4}{7}$ "	103·5 = 59·16	Tin	= 59
Antimony	= 120·3,	$\frac{4}{7}$ "	120·3 = 68·76	Vanadium	= 68·60
Bismuth	= 208,	$\frac{4}{7}$ "	208 = 118·84	Antimony	= 120·3
Mercury	= 100,	$\frac{4}{7}$ "	100 = 57·16	Cadmium	= 56
		$\frac{4}{7}$ "	57·16 = 32·66	Zinc	= 32·60
Molybdenum	= 48,	$\frac{4}{7}$ "	48 = 27·42	Chromium	= 26·70
Chlorine	= 35·5,	$\frac{4}{7}$ "	35·5 = 20·28	Silicon	= 21
Fluorine	= 19,	$\frac{4}{7}$ "	19 = 10·86	Boron	= 10·9†
Boron	= 10·9,	$\frac{4}{7}$ "	10·9 = 6·23	Carbon	= 6

It will be remarked that mercury, cadmium and zinc are here again brought together. Although four-sevenths of the atomic weight of mercury is not that of cadmium exactly, nevertheless four-sevenths the resulting number so obtained, viz. 57·16, gives for the atomic weight of zinc 32·66, an exceedingly close approximation.

The last three equations in the table show us that the atomic weight of silicon stands nearly in the same numerical ratio to that of boron, as that of chlorine does to that of fluorine, and that both these ratios, especially the latter, approach nearly to that existing between the atomic weight of boron and carbon.

Now as the atomic weight of boron is by no means positively determined, it may be allowable to examine how far an hypothetical number will fulfill these several ratios. Let us assume:—

Fluorine : Chlorine :: Carbon : Boron

we find:—

$$\frac{\text{Chlorine } 35\cdot5 \times \text{Carbon } 6}{\text{Fluorine } 19} = 11\cdot2104,$$

and obtain for the hypothetical equivalent of boron the number 11·21 (neglecting the last decimal figures).

Let us now examine how far the number 11·21 will fulfill the second proposed ratio, viz.

Carbon : Boron :: Boron : Silicon

* Taking Glucina as G_2O_3 .

† See Jahresbericht, 1858.

we have
$$\frac{(\text{Boron } 11.21)^2}{\text{Carbon } 6} = 20.944 : -$$

a close approximation to 21, the received number.

If, therefore, we assume the atomic weight of boron to be a mean proportional between those of carbon and silicon, which we may do by an alteration certainly within the bounds of possible error in determinations so far made, we find that the proportion between the weights of carbon and boron, of boron and silicon, is the same as that between those of fluorine and chlorine.

(2.)

Carbon-Nitrogen Ratio, or that of Three-Sevenths.

The atomic weight of Carbon stands to that of Nitrogen in the ratio of 3 to 7, a proportion which is found exactly or approximately to extend to certain other elements.

Nitrogen	= 14,	$\frac{3}{7}$ of 14	= 6	Carbon	= 6
Fluorine	= 19,	$\frac{3}{7}$ " 19	= 8.14	Oxygen	= 8
Iron	= 28,	$\frac{3}{7}$ " 28	= 12	Magnesium	= 12
Cerium	= 47,	$\frac{3}{7}$ " 47	= 20.14	Calcium	= 20
Phosphorus	= 31,	$\frac{3}{7}$ " 31	= 13.29	Nitrogen	= 14
Bromine	= 80,	$\frac{3}{7}$ " 80	= 34.29	Chlorine	= 35.5
Arsenic	= 75,	$\frac{3}{7}$ " 75	= 32.14	Zinc	= 32.6
Lead	= 103.5	$\frac{3}{7}$ " 103.5	= 44.4	Strontium	= 43.75
Cadmium	= 56,	$\frac{3}{7}$ " 56	= 24	2 Magnesium	= 24
Uranium	= 60,	$\frac{3}{7}$ " 60	= 25.71	Chromium	= 26.7

(3.)

The proportions expressed by the preceding tables may be differently presented, and perhaps rendered more striking. As the numbers which express the equivalent weights of the elements are altogether relative, it is of course a mere question of convenience which is selected as unity. If in place of adopting the equivalent of one substance, as that of hydrogen or oxygen, as a permanent unit, we successively make those of the substances contained in the right hand column of the table in section 1. our unit, and consider the effect of such a change upon the equivalents of the substances contained in the left-hand column, we shall obtain the following results:

Making the				
equivalent of Oxygen	100,	the eq. of Nitrogen	becomes	175
" Potassium	100,	" " " Barium	"	175
" Zirconium	100,	" " " Potassium	"	175
" Titanium	100,	" " " Strontium	"	175
" Tin	100,	" " " Lead	"	175.4
" Vanadium	100,	" " " Antimony	"	174.9
" Boron	100,	" " " Fluorine	"	174.3
&c.		&c.		

The same view may be extended to Section 2. Assuming the atomic weight of the substances in the left-hand column successively as unity, or one hundred, we obtain the following results :

Making the					
equivalent of Nitrogen	100	that of Carbon	becomes	42·8	
Fluorine	100	" "	Oxygen	"	42·1
Iron	100	" "	Magnesium	"	42·8
Cerium	100	" "	Calcium	"	42·6
&c.			&c.		

It is therefore clear that the atomic weight of each substance in the left hand column of these several tables bears to that of the corresponding substance in the right-hand column a definite numerical ratio, which is identical, or nearly so with that borne by the atomic weight of any other substance in the same column of the same table to that of the corresponding substance in the other column.

(4.)

We have seen that many elements stand to other elements in the same relation as nitrogen to oxygen—many in the same relation as nitrogen to carbon. Apart from these more general ratios, many elements may be classed together in double or treble pairs, such that the two elements in one pair stand to each other in the same numerical ratio as the two elements of a second or third pair, the two elements constituting each pair being more or less closely allied to each other in properties, though the pairs are not necessarily analogous with those with which they are compared.

For example, arsenic stands to antimony in the same numerical ratio as selenium to tellurium, within an extremely small fraction, so that by multiplying and dividing we have:—

$$\text{Arsenic } 75 \times \frac{\text{Tellurium } 64}{\text{Selenium } 40} = 120, \text{ Antimony} = 120\cdot3,$$

So in like manner magnesium stands to zirconium in the same ratio as fluorine to chlorine:—

$$\text{Magnesium } 12 \times \frac{\text{Chlorine } 35\cdot5}{\text{Fluorine } 19} = 22\cdot42, \text{ Zirconium} = 22\cdot40,$$

So carbon stands to boron in the same ratio as silver to gold:—

$$\text{Carbon } 6 \times \frac{\text{Gold } 197}{\text{Silver } 108} = 10\cdot94, \text{ Boron} = 10\cdot90.$$

These ratios, as well as those that follow, are very close approximations, certainly within the limits of error which may easily exist in the determinations on which we depend. For antimony we find 120, the recent determinations vary from 119 to 122, that which appears most reliable is 120·3, as adopted by the Jahres-

bericht. In the second case, the number found for zirconium varies but $\frac{1}{11\frac{1}{2}}$ from that generally received. In the third, the number found for boron is intermediate between the number adopted in the Jahresbericht 10·90 and that found by Deville, 11. Discrepancies such as these are trifling in the extreme, and have not the slightest real significance.

Phosphorus stands to nitrogen in nearly the same ratio as strontium to calcium :—

$$\text{Phosphorus } 31 \times \frac{\text{Calcium } 20}{\text{Strontium } 43\cdot77} = 14\cdot16, \text{ Nitrogen} = 14.$$

Tin stands to titanium in nearly the same ratio as iron to magnesium :—

$$\text{Tin } 59 \times \frac{\text{Magnesium } 12}{\text{Iron } 28} = 25\cdot28, \text{ Titanium} = 25.$$

Tin stands to zinc in almost exactly the same ratio as gold to silver, or as boron to carbon :—

$$\text{Tin } 59 \times \frac{\text{Silver } 108}{\text{Gold } 197} = 32\cdot35, \text{ Zinc} = 32\cdot60.$$

$$\text{Tin } 59 \times \frac{\text{Carbon } 6}{\text{Boron } 10\cdot9} = 32\cdot48, \text{ Zinc} = 32\cdot60.$$

These and many other analogies of the same character are brought together in the following table, by which the ratios of comparison between each pair are shown, up to the second place of decimals, beyond which it is pseudo-accuracy to go, in view of the data.

Ratio of tellurium to selenium, or	$\frac{\text{Te } 64}{\text{Se } 40} = 1\cdot60$	}
Ratio of antimony to arsenic, or	$\frac{\text{Sb } 120}{\text{As } 75} = 1\cdot60$	
Ratio of zirconium to magnesium,	$\frac{\text{Zr } 22\cdot4}{\text{Mg } 12} = 1\cdot87$	}
Ratio of chlorine to fluorine,	$\frac{\text{Cl } 35\cdot5}{\text{F } 19} = 1\cdot87$	
Ratio of boron to carbon,	$\frac{\text{B } 10\cdot9}{\text{C } 6} = 1\cdot82$	}
Ratio of gold to silver.	$\frac{\text{Au } 197}{\text{Ag } 108} = 1\cdot82$	
Ratio of strontium to calcium,	$\frac{\text{Sr } 43\cdot77}{\text{Ca } 20} = 2\cdot19$	}
Ratio of phosphorus to nitrogen,	$\frac{\text{P } 31}{\text{N } 14} = 2\cdot21$	

Ratio of iron to magnesium,	$\frac{\text{Fe } 28}{\text{Mg } 12} = 2.33$	}
Ratio of tin to titanium,	$\frac{\text{Sn } 59}{\text{Ti } 25} = 2.36$	
Ratio of tin to zinc,	$\frac{\text{Sn } 59}{\text{Zn } 32.6} = 1.81$	}
Ratio of gold to silver,	$\frac{\text{Au } 197}{\text{Ag } 108} = 1.82$	
Ratio of zirconium to aluminum,	$\frac{\text{Zr } 22.4}{\text{Al } 13.7} = 1.64$	}
Ratio of calcium to magnesium,	$\frac{\text{Ca } 20}{\text{Mg } 12} = 1.67$	
Ratio of potassium to sodium,	$\frac{\text{K } 39.2}{\text{Na } 23} = 1.70$	}
Ratio of arsenic to phosphorus,	$\frac{\text{As } 75}{\text{P } 31} = 2.42$	
Ratio of cobalt to magnesium,	$\frac{\text{Co } 29.5}{\text{Mg } 12} = 2.46$	}
Ratio of nickel to magnesium,	$\frac{\text{Ni } 29.6}{\text{Mg } 12} = 2.47$	
Ratio of lead to tin,	$\frac{\text{Pb } 103.5}{\text{Sn } 59} = 1.75$	}
Ratio of cadmium to zinc,	$\frac{\text{Cd } 56}{\text{Zn } 32.6} = 1.72$	

(5.)

It has been the object of this paper to develop as far as possible those numerical relations existing between the atomic weights of the elements which have not been previously observed. It is, perhaps, impracticable in the present state of chemical science to explain why such relations should exist, nevertheless, nothing which tends to an exacter knowledge of the laws which govern the proportions in which the elements combine should be neglected. In this way, little by little, the materials are collected for future generalizations, with the reasonable hope of eventually arriving at an intimate knowledge of the true constitution of the materials which compose our globe.

The substances which compose the chlorine group form a well marked family to which fluorine seems also to belong. The analogies which unite chlorine, bromine and iodine, appear to multiply with each new investigation of their properties. By none have they been more strikingly illustrated than by the recent experiments of Plücker on the spectra obtained from the light of electric discharges through gases in a state of extreme

rarefaction, demonstrating that those given by Cl, Br and I, resembled each other in exhibiting great numbers of black lines of extreme fineness, so fine indeed as to be almost mathematical lines, and that in this respect these elements differed wholly from all others. With so remarkable an experiment as this before us, supported by the very numerous other relations which exist between these substances, we might naturally look to find striking numerical correspondences between their atomic weights, but the analyses upon which we at present depend give us numbers which afford no relations positively exact. Of the four numbers 19, 35·5, 80 and 127, two are prime, one fractional, and one has many divisors. Such numbers are very unpromising for the development of numerical relation.

Thus far, however, at least relations do exist: that it is possible to express the value of the equivalent of any one of these substances in terms of any two of the remaining—each equivalent is a function of any other two, thus:—

$$\begin{array}{ll}
 \text{I} = 10 \text{ Cl} - 12 \text{ F} & \text{Cl} = \frac{12 \text{ Br} - 7 \text{ I}}{2} \\
 \text{I} = \frac{5 \text{ Br} - \text{F}}{3} & \text{Cl} = \frac{\text{I} + 12 \text{ F}}{10} \\
 \text{I} = \frac{12 \text{ Br} - 2 \text{ Cl}}{7} & \text{Cl} = \frac{\text{Br} - 7 \text{ F}}{6} \\
 \text{Br} = \frac{6 \text{ Cl} - 7 \text{ F}}{2} & \text{F} = \frac{10 \text{ Cl} - \text{I}}{12} \\
 \text{Br} = \frac{2 \text{ Cl} + 7 \text{ I}}{12} & \text{F} = \frac{6 \text{ Cl} - \text{Br}}{7} \\
 \text{Br} = \frac{3 \text{ I} + \text{F}}{5} & \text{F} = 5 \text{ Br} - 3 \text{ I}
 \end{array}$$

If these equations represented approximations, no matter how close, they would not be worthy of consideration. They are perfectly exact. The quasi-connection of oxygen with this series will be pointed out further on.

(6.)

It has been remarked that the atomic weights of the members of the oxygen series proper differ from each other by whole multiples of the atomic weight of oxygen, but the extent to which differences of this kind exist amongst the atomic weights of the elementary bodies has perhaps not been pointed out.

The elements having the highest atomic weights are bismuth and gold, commencing with the first of these substances, and diminishing its atomic weight successively by whole multiples (in one case by a sub-multiple) we obtain the following results:—

metal itself, corresponds with those of the metals of the arsenic series, viz.:

Vanadic acid,	VO_3	Specif. Vol.	26.5
Arsenious acid,	AsO_3		26.6
Antimonic oxyd,	SbO_3		25.9
Bismuthic oxyd,	BiO_3		25.9* 28.4†

They also point out the fact that vanadinite (vanadinbleierz) is isomorphous with the analogous compounds of the arsenic series, mimetene (kampylit) and pyromorphite. Professor Mallet has shown that reasons can be given for classifying osmium also in the arsenic series.†

Again, commencing with gold we obtain the following succession of numbers.

Differences.			
8×11	196 Gold	=	197
	108 Silver	=	108
8	100 Mercury	=	100
8	92 Tungsten	=	92
$8 \times 3\frac{1}{2}$	64 Tellurium	=	64
8	56	Cadmium	=56
8	48 Molybdenum	=	48
8	40 Selenium	=	40
8	32	Zinc	=32.6
8×2	16 Sulphur	=	16
8	8 Oxygen	=	8§

In an interesting paper published in the Memoirs of the Am. Acad. of Boston, vol. v, Prof. J. P. Cooke, of Harvard University, attempted a classification of all the elementary bodies by making them all functions of a general series of the form $a+dx$. By giving fixed values to a and d particular expressions were obtained, giving rise to series by the changes in the value of the variable x . These particular series were characterized by the value of d , which in different series became successively 3, 4, 5,

* Boullay.

† Karsten.

‡ Am. Jour. Science, xxix, 49.

§ If to the at. wt. of Li which may be taken at 7, we add $16=2 \times 8$, we have 23 the exact at. wt. of Na, and a further addition of 16 gives very nearly the at. wt. of K.

6, 8 and 9. The values of a were likewise always small, never exceeding 8. The values of x were restricted to whole numbers.

This view, although new and ingenious, is evidently exposed to a serious objection: the series include too much. The form entitled by Prof. Cooke the "Three Series," and expressed by $1+3x$, includes one-third of all possible whole numbers, and so to a proportionally great extent with all the other forms. As the author did not make positive exactness essential, it is evident that a wide scope was given for the classification of elements under any particular series: therefore this theory could only find favor as far as it might be made to conform to a wholly unobjectionable classification of the elements. In this it only partially succeeded, as will appear from an examination of the substances included in the various groups.

In the first series, chromium, manganese, osmium and gold are classed as affiliated to the chlorine group, into which however the series only admits fluorine with an error of 2, or 12 per cent.

In the second, arsenic and manganese are made affiliated with the sulphur group, which includes also molybdenum, vanadium, &c.

In the third, oxygen is classed with the nitrogen-phosphorus group, into which antimony only enters with an error of 7.7.*

In the fifth we find tin and titanium, the platinum group, gold, mercury, and most of the magnesia group.

In the sixth we have part of the remainder of the magnesia group, the metals of the alkaline earths and lead, the alkaline metals, hydrogen and silver, with copper and manganese as affiliations. Rendering all justice to the author for the originality and ingenuity of his views, it must be admitted that the flexibility of his series has led to a classification not in all respects supported by analogies. Five out of his six series contain one or more members of the magnesia group either directly or as affiliated members.

Dumas has followed out these ideas of Prof. Cooke and extended them. In place of referring his series to the type of the formic acid series alone, he includes the types of substituted ammoniums and stannethyls, under the general form $na+xd+yd'$; thus adopting an expression even more general than that of Prof. Cooke, but restricting it more closely in its application.

Perhaps the most beautiful and important of the relations pointed out by Dumas, are the parallel series of numbers, which by the subtraction of each term of the one from the corresponding term of the other, exhibit a constant difference within a certain degree of approximation.

* This probably arises from the fact that the equivalent of antimony as generally received at the time when Prof. Cooke wrote was higher than it is now known to be, and by diminishing the value of the variable x corresponding to this term, by 1, a nearer approximation would be obtained.

The analogies pointed out in the several parts of this paper evidently lead directly to the construction of series of the same kind some of which, together with others depending upon yet different relations are given below.

-Oxygen = -8	Chlorine = 35.5	Bromine = 80	Iodine = 127
-Zinc = -32.6	Magnesia = 12	Cadmium = 56	Lead = 103.5
<u>24.6</u>	<u>23.5</u>	<u>24</u>	<u>23.5</u>

In connection with these two parallel series we may remark that oxygen appears to constitute a negative term in the chlorine series, precisely as nitrogen does in the phosphorus and zinc in the cadmium series, with considerable approximation to exactness. If the atomic weight of chlorine were taken at 36 instead of 35.5 it would constitute an exact numerical mean between the atomic weights of bromine and oxygen supposing the latter to be taken with a negative sign. We have before seen that nitrogen, the negative member of the phosphorus series, is less closely allied with the rest than they are with each other. Still greater is the step between chlorine and oxygen, so great indeed that it is very doubtful whether they can properly be classed in the same series, although certain cases of isomorphism can be urged in favor of such a classification.

We here see a new instance of the existence of the relation of 44—45 developed in the first part of this paper.

Differences.	Calculated equivalents.	Received equivalents.
44	- 8	Oxygen = 8
44	36	Chlorine = 35.5
44	80	Bromine = 80
44	124	Iodine = 127

Gold = 197	M = 152.5	Silver = 108	Mercury = 100
Mercury = 100	Cadmium = 56	Magnesium = 12	Glucinum = 4.7
<u>97</u>	<u>96.5</u>	<u>96</u>	<u>95.3</u>

M here represents a possible metal as yet unknown. In the first part of this paper mention was made of the possibility of the existence of such a metal, having an atomic weight representing the arithmetical mean between those of gold and silver.

Bismuth = 208	M' = 164	Antimony = 120.3	Lead = 103.5
Antimony = 120.3	Arsenic = 75	Phosphorus = 31	Nitrogen = 14
<u>87.7</u>	<u>89</u>	<u>89.3</u>	<u>89.5</u>

In this double series we find nearly the same number (89 approximately) obtained by subtraction, as by addition in the last of the double series, part first, section 8. If in that just presented we replace lead by arsenic and give a negative sign to

the atomic weight of nitrogen, we shall still have a number conforming to the character of the series, viz., 89.

In this and the following series the symbol *M'* represents a possible metal constituting an intermediate term between antimony and bismuth. That such a metal might exist was pointed out in the consideration of the phosphorus series.

Bismuth =208	<i>M'</i> =164	Antimony =120·3	Arsenic =75
Gold =197	<i>M</i> =152·5	Silver =108	Copper =63·4
11	11·5	12·3	11·6

M as before represents an hypothetical metal having for its atomic weight a mean term between those of silver and gold.

Uranium 60	Vanadium 68·6	Tungsten 92	
Magnesium 12	Calcium 20	Strontium 43·75	
48	48·6	48·25	
Molybdenum 48	Vanadium 68·6	Tungsten 92	2 Tantalum 137·6
Magnesium 12	Zinc 32·6	Cadmium 56	Mercury 100
36	36	36	87·6

The parallelism between the three first terms of these last two series commencing respectively with molybdenum and magnesium is positively exact, perhaps the only known case in which absolute exactitude obtains. It is probable that other cases of parallel series exist, and will be discovered.

It is not easy to fix the exact amount of importance which attaches to the numerical relations up to this time ascertained to exist between the atomic weights of the elements. Some are no doubt mere casual coincidences, and relations remarkably exact and symmetrical may exist between the atomic weights of bodies which have no analogies in their properties: for example we may take calcium 20, selenium 40, uranium 60, bromine 80, mercury 100. Here the differences are not only exact, but all the subsequent numbers are multiples of the first, and this between bodies remarkably dissimilar in their properties—a striking proof of the necessity of caution in inferring relations of properties as following from relations of numbers. But on the other hand, to reject the relations of number when accompanied by analogy of properties, as unmeaning and unimportant, would be to err quite as much on the other side. When the received equivalent of an element forming a term in a well marked series differs from that obtained by calculation, it naturally leads, as Prof. Mallet has remarked, to suspect an error and desire a re-determination. The fact that a group of elements allied in their chemical characters may be arranged in a series having a common difference or a definite ratio between its terms, confirms the propriety of grouping those elements together, and such analogies may in doubtful cases assist us in arriving at a correct classification.

Philadelphia, Feb. 27, 1860.