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PERIODIC CLASSIFICATION AND THE PROBLEM OF CHEMICAL EVOLUTION

GEORGE RUDORF

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THE PERIODIC CLASSIFICATION

AND

THE PROBLEM OF CHEMICAL EVOLUTION

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AND

THE PROBLEM OF CHEMICAL EVOLUTION

BY

GEORGE RUDORF, B.Sc.
UNIVERSITY COLLEGE, LONDON

WHITTAKER & CO.
2 WHITE HART STREET, PATERNOSTER SQUARE, LONDON
AND 66 FIFTH AVENUE, NEW YORK
1900

B

To

HIS TEACHER AND ADVISER

WILLIAM RAMSAY, F.R.S.
PROFESSOR OF CHEMISTRY AT UNIVERSITY COLLEGE, LONDON

THIS UNPRETENDING LITTLE TREATISE

IS DEDICATED

WITH THE GREATEST RESPECT

BY

THE AUTHOR

THE NEW ATMOSPHERIC GASES

Professor Ramsay has very kindly furnished me with the more important physical properties of his new gaseous elements as determined by himself in conjunction with Dr M. W. Travers. The data are as follows :—

Name of Gas	Helium	Neon	Argon	Krypton	Xenon
Density	1·98	9·96	19·96	40·88	64·0
Atomic Weight	3·96	19·92	39·92	81·76	128·0
Density of Liquid	...	...	1·212	2·155	3·52
Refractivity	0·1238	0·2345	0·968	1·449	2·364
Melting Point	...	...	85·1	104·0	133·0
Boiling Point	...	...	89·6	121·3	163·9
Critical Temperature	...	...	155·6	210·5	281·7
Critical Pressure	...	...	40·2	41·2	43·5

Temperatures are on the absolute scale, pressures in metres of mercury, refractivities compared with air = 1·0.

These gases all fit in the atomic volume curve and also the molecular refraction curve, and are all at the lower apices of the curves.

From these considerations, as also the ratio of the specific heats, they have had the above atomic weights assigned to them. They are non-valent, and hence form no compounds.

PREFACE

The present volume is intended to treat of the history of the periodic classification, and also of the various properties of the elements and of their chief compounds, with special reference to that method of classification. The subject has been taken up as fully as space permits, for the author has found that most text-books on General Chemistry allude in a more or less cursory manner to some of these periodic relations, without going into any further details. The second part of the work is devoted to the Problem of Chemical Evolution, which is at present in its infancy.

The following works have been freely consulted :—

E. von Meyer	*History of Chemistry ;*
Nernst	*Theoretical Chemistry ;*
Ostwald	*Lehrbuch der Allgemeinen Chemie ;*
Ramsay	*System of Inorganic Chemistry ;*
Van't Hoff	*Atoms in Space ;*
Sir Norman Lockyer	*Inorganic Evolution,*

and also the various scientific periodicals.

My best thanks are due (1) to the authors and translators of the above works, (2) to the editors of the journals, (3) to Professor H. L. Callendar, who has been good enough to read through those portions of the work appertaining to physics, and has served me with many valuable criticisms, and (4) to Sir Norman Lockyer for kindly reading through the *evolution* portion of the subject, and for his important notes, which I insert at the commencement of the book.

Numerous references have been given throughout, nearly all of which have been carefully verified. It is hoped that these may add to the general usefulness of this small treatise, which is intended to furnish a fairly complete summary of this important branch of general chemistry to those who may not have either time or opportunity to refer to the original literature.

GEORGE RUDORF.

UNIVERSITY COLLEGE,
LONDON, 1900.

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ABBREVIATIONS OF REFERENCES

Ann. . . .	*Annalen der Pharmacie, edited by Liebig and others,* 1832-39, *continued as Annalen der Chemie und Pharmacie,* 1840-73, *continued as Liebig's Annalen der Chemie.*
Ann. Chem. . .	*Liebig's Annalen der Chemie.*
Ann. Chim. Phys. .	*Annales de Chimie et de Physique.*
Am. J. Sc. . .	*The American Journal of Science and Arts.*
Astro. Jour. . .	*Astrophysical Journal.*
B. . . .	*Berichte der deutschen chemischen Gesellschaft.*
Ber. . . .	
Berichte . . .	
Bull. Acad. imp. St Péters. . .	*Bulletin de l'Académie impérial de St Pétersbourg.*
C. N. . . .	*Chemical News.*
C. R. . . .	*Comptes-rendus hebdomadaires des Séances de l'Académie des Sciences.*
Gazz. ch. it. . .	*Gazzetta chimica italiana.*
Gilb. Ann. . .	*Annalen der Physik, edited by Gilbert.*
J. Am. Ch. Soc. .	*Journal of the American Chemical Society.*
Journ. de phys. .	*Journal de physique.*
J. f. pr. Ch. . .	*Journal für praktische Chemie.*
J. C. S. . . .	*Journal of the Chemical Society.*

Phil. Mag.	*The Philosophical Magazine.*
P. M.	
Phil. Trans.	*The Philosophical Transactions of the Royal Society of London.*
Pogg. Ann.	*Annalen der Physik und Chemie, edited by Poggendorff.*
Proc. Chem. Soc.	*Proceedings of the Chemical Society.*
Proc. Col. Sci. Soc.	*Proceedings of the Colorado Scientific Society.*
Proc. Roy. Soc.	*Proceedings of the Royal Society of London.*
Proc. Roy. Soc. Edin.	*Proceedings of the Royal Society of Edinburgh.*
Roy. Soc. Proc.	*Proceedings of the Royal Society of London.*
Schweigg.	*Journal für Chemie und Physik, edited by Schweigger, continued after* 1833 *as J. f. pr. Ch.*
Wied. Ann.	*Annalen der Physik und Chemie, edited by Wiedermann; continuation of Pogg. Ann. after* 1877.
Zeit. anorg. Chem.	*Zeitschrift für anorganische Chemie.*
Zeit. Chem.	*Zeitschrift für Chemie und Pharmacie.*
Zeit. phys. Chem.	*Zeitschrift für physikalische Chemie.*

SIR NORMAN LOCKYER'S NOTES

As stated in the Preface, the portion of this work dealing with chemical evolution was submitted to Sir Norman Lockyer, together with a request for permission to insert any notes he might make, at least in part, in this volume. Some of these notes in his own words are given below, and are as follows :—

	Page		
A.	164	Section 2.	Why not insert the well-known German word "Urstoff," which preceded protyle?
B.	172	Lines 4-9.	This assertion is not justified. See J. J. Thomson's work. He has *determined* the *masses* of the smaller particles.
C.	176	Table.	Refer to *Inorganic Evolution* for some additional work on Silicium.
D.	182	Section 3.	This can be put much better. I assume that the ordinary molecule is *differently* dissociated in different elements.
E.	185	Lines 6-19.	See Note B. This is not justified unless it can be shown that J. J. Thomson's *masses* are wrong. "Resolving a motion" will not change a mass.
F.	186	Lines 3-6.	Same research applies.

Dear Sir,—In a great hurry I have made some notes. If you will consider J. J. Thomson's work in connection with the dissociation hypothesis, you will find its importance to be that he negatives the old suggestions which you reproduce.—Yours sincerely,

NORMAN LOCKYER.

It cannot but be noticed that great emphasis is laid on the researches of Professor Thomson.[1] A brief account of them will be given here :—

It is first shown that the cathode stream consists probably of material particles, and is not an ether effect.

The whole of the investigation is to show that the value of $\frac{m}{e}$ (where m is the mass of, and e the electric charge on, a particle) is constant for all gases. Its value is derived in two different ways, and the results obtained are of an order of magnitude of 10^{-7}, but vary within limits of about 10 per cent. on either side of the mean. The value for the hydrogen ion in electrolysis is about 10^{-4}, and hence Professor Thomson is inclined to think that in the cathode stream we have particles of matter smaller than a hydrogen ion. He then advances the explanation of this effect, cited on page 167 of this volume, together with the statement that the primordial substance cannot be hydrogen. Further, we read, "Thus, on this view, we have in the cathode rays matter in a new state, a state in which the subdivision of matter is carried very much further than in the ordinary gaseous state : a state in which *all matter*—that is, matter derived from different sources, such as hydrogen, oxygen, etc.—*is of one and the same kind*,[2] this matter being the substance from which all the elements are built up."

I would not venture to criticise Professor Thomson's work, but I hardly think the dissociation explanation to be completely proved by the evidence that m and e are independent of the nature of the gas. For the spectra of the cathode discharges in tubes containing various gases are simply those of the gases. Of course we know that to completely ionise the gas in a vacuum tube would take years to accomplish; yet, surely, after some time there ought to appear spectral lines common to all gases, and characteristic of this primordial substance. Further than this I will not go. The whole subject, however, offers a wide field for speculation. [G.R.]

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[1] *Phil. Mag.* [5] 44, 1897, p. 293.

[2] The italics are mine. [G.R.]

THE
PERIODIC CLASSIFICATION

PART I

CHAPTER I

THE HISTORY OF THE PERIODIC LAW

THAT branch of general chemistry dealing with the relations which the elements bear to one another has been almost entirely developed during the present century (1801-1901).

Richter (1762-1807).—We cannot do better than take the work of Jeremias Benjamin Richter as our starting-point for this particular portion of the subject. Richter was the first chemist who attempted to connect together, by means of a general law, the results obtained by him in his researches on the amounts of acid and of base in salts.

He was practically in a position to discover the important "Law of Neutralisation." However, his work was unnoticed, owing, no doubt, partly to his writings being obscured by the introduction of weird phlogistic terms, notwithstanding that he himself had ceased to be a phlogistonist.

But the importance of his experiments was at length recognised when they were made intelligible by G. E. Fischer, who also collected together the various scattered facts found in Richter's writings. The latter saw that his constants were subject to a general law, which he called the "Law of Progression." He thought that the combining weights of the bases formed an arithmetical series, whilst those of the acids formed a geometric series, and to this idea he adhered with such tenacity that he almost entirely lost sight of the far more important "Law of Neutralisation." This may have been partly due to his still having the opinion, which he certainly held in his youth, that chemistry was a branch of applied mathematics.

The "Law of Neutralisation" was ascribed through some misunderstanding by Berzelius to an earlier worker—Wenzel (1740-1793)—which error was rectified by H. Hess in 1840.

Prout and Meinecke.—We now come to the work of Prout and Meinecke. The former—a physician—advanced in 1815 a hypothesis which led to a great deal of dispute among the chemists of his time, and even at the present day is neither generally accepted nor discarded. This was formulated in two papers,[1] which stated that the atomic weights of the elements, taking hydrogen as equal to unity, were whole numbers and multiples of that of the lightest element. To suit his statements, he altered the atomic weights in an

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[1] *Annals of Philosophy*, Vol. VI. (1815), p. 321, and Vol. VII. (1816), p. 111.

exceedingly arbitrary fashion, and in such a manner that they showed regular differences among one another, *e.g.* :—

Calcium	20	Iron	28	Chlorine	36
Sodium	24	Zinc	32	Potassium	40

The hypothesis proper which followed from this was that *hydrogen may be looked upon as the primary matter from which all the other elements are formed by peculiar condensations.* The same idea was brought forward in 1817 by Meinecke.[1]

Th. Thomson (1773-1852).—Thomas Thomson thought that he saw in this statement a fundamental law of chemistry. By his own work, which was uncommonly bad for that time, he had concluded that the atomic weights of several elements were multiples of that of oxygen, neglecting the fact that the researches of Berzelius entirely disproved the theory.

L. Gmelin.—Amongst other chemists who inclined to the hypothesis was Leopold Gmelin, as the following extracts from his *Handbuch der Chemie* for 1843 will show (p. 44) :—

"The atomic weights of many bodies seem to be simple multiples of that of hydrogen, and therefore if H=1, we get the following simple values :—Carbon=6, oxygen=8, nitrogen=14, sulphur=32, etc."

However, that this was not always the case is clearly seen by referring to Table I., Column C, given in the Appendix.

Then again, on p. 52, we read :—

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[1] *Schweigg.* 22 (1818), p. 138.

"The atomic weights of the simple bodies are often multiples of a whole number, the atomic weight of hydrogen, *e.g.*, C, O, N, S, Se, Sr, Mo, etc. Will it then be a natural law, as Prout and Thomson think, that the atomic weights of all other elements are divisible by that of hydrogen? If one wanted to give place to this idea that there is only one primary ponderable matter, this would have to be hydrogen, because it has the smallest atom, and it would have to be accepted that, if these atoms combine together in such a way, in different numbers, that they cannot be again split up by any method as yet discovered, then the larger and heavier atoms of the remaining bodies would result, whose atomic weights would then necessarily be divisible by that of hydrogen. However, the atomic weights of most bodies show such a great deviation from this theory that Berzelius considered it only accidental that they are more or less exactly divisible by that of hydrogen, and absolutely exactly divisible they are never. The new researches of Dumas and Stas,[1] which put the atomic weight of carbon exactly $=6$, and those of Liebig and Redtenbacher, who found $C=6{\cdot}068$, show that the question is not yet decided."

Berzelius and Turner.—Berzelius and, later, Turner were the chief opposers of Prout's hypothesis from a consideration of their own researches on the atomic weights. The former held, without flinching, until his death to the fundamental law—No correction of the equivalent weights is permissible, if it

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[1] *Ann. Chim. Phys* 76 p. 1.

should challenge the results of experiment. The complete list of Berzelius' values is given in Table I., Column F, of the Appendix, but a few examples may be quoted here:—

For 1818:—

Carbon	12·12	Copper	129·0
Oxygen	16·00	Potassium	157·6
Sulphur	32·3	Mercury	406·0
Sodium	93·5	Lead	416·0
Iron	109·1	Silver	433·7

Some for 1826 are:—

Carbon	12·25	Iron	54·36
Nitrogen	14·18	Copper	63·42
Oxygen	16·02	Arsenic	75·34
Phosphorus	31·44	Potassium	78·52
Sodium	46·62	Mercury	202·86

These numbers have been calculated on the basis H = 1, but Berzelius took O = 100. We see from these figures that he seemed to be perfectly justified in opposing Prout's theory. The object of his taking oxygen as the most important element and as the basis of his atomic weights is expressed by him thus:—

"To refer the atomic weights to that of hydrogen offers not only no advantages but has, in fact, many inconveniences, seeing that hydrogen is very light and is seldom a constituent of inorganic compounds. Oxygen, on the other hand, unites all the advantages in itself. It is, so to speak, the centre-point round which the whole of chemistry revolves."

It will be noticed that Berzelius' values are in several cases twice as great as those in use at the present time. This is accounted for by his supposing that compounds had as simple formulæ as possible. Thus ratios like 2 : 3, 3 : 4, 2 : 7, etc., appeared to him too complicated. For example, he took the two oxides of iron as having the formulæ FeO_2 and FeO_3 instead of FeO and Fe_2O_3, thus getting a value for the atomic weight of iron twice as great as it should be, and so on for the other elements.

Döbereiner.—In the year 1817 Döbereiner[1] drew attention to the fact that the atomic weight of strontium lay midway between those of calcium and barium. In 1829[2] he showed this to be repeated in several other cases. Such groups as these he called "Triads." The coincidence is remarkable, although not quite accurate, as the following examples will show :—

Ca = 40	Ba = 137	$\frac{137\cdot0+40\cdot0}{2}=87\cdot5$	Sr = 87·5
Li = 7	K = 39	$\frac{39+7}{2}=23$	Na = 23
Cl = 35·5	I = 127	$\frac{127+35\cdot5}{2}=81\cdot1$	Br = 79·96
S = 32	Te = 125	$\frac{32+125}{2}=78\cdot5$	Se = 78·87

Dumas' Views.—In 1842 Liebig and Redtenbacher found that Berzelius had made an error in the determination of the atomic weight of carbon, and this was also confirmed by Erdmann and Marchand, and

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[1] *Gilb. Ann.* 26 (1817), p. 331.

[2] *Pogg. Ann.* 15 (1829), p. 301.

Dumas and Stas. These observers found that the correct value was 12·00. This caused a great commotion among chemists owing to the almost sacred reliance placed on Berzelius' work, and resulted in a redetermination of atomic weights. However, it was found that carbon was practically the only faulty one. Later, Dumas found the atomic weight of nitrogen to be 14·00 and that of oxygen to be 16·00. The determinations gave a new impetus to Prout's hypothesis, but as Pélouze, Marignac and others had confirmed Berzelius' value for chlorine—35·5—it did not appear in its original form, but it was thought that the atomic weights were multiples of 0·5, *i.e.*, of half the atomic weight of hydrogen. This alteration was made by Dumas. Later, however, he had to halve this unit also, so that the atomic weights might then be represented as multiples of 0·25. This hypothesis could not be really tested, as in many cases the limit of accuracy of the determinations did not reach this unit. Nevertheless, the exact determinations of Stas for iodine, chlorine, bromine, sulphur, silver, nitrogen, sodium, potassium, lithium and lead gave values which could not be made to fit in with the above views, and a further subdivision of the unit seems to be getting absurd.

Gmelin.—In Gmelin's *Handbuch der Chemie* for 1843 we find an attempt at a classification of the elements into a number of groups, not from the point of view of atomic weight relations, but rather with regard to physical and chemical properties. The table thus drawn up is here reproduced.

O	N	H
F, Cl, Br, I		Li, Na, K
S, Se, Te		Mg, Ca, Sr, Ba
P, As, Sb		G, Ce, La
C, B, Si		Zr, Th, Al
Ti, Ta, W		Sn, Cd, Zn
Mo, V, Cr		Ur, Mn, Ni, Fe
	Bi, Pb, Ag, Hg, Cu	
	Os, Ir, Rh, Pt, Pd, Au	

In another table a few more elements are included. Erbium, yttrium, terbium and didymium are added to the cerium group; niobium and pelopium to the tantalum group; cobalt and ruthenium to the iron and platinum groups respectively.

It will be seen that oxygen, nitrogen and hydrogen are placed alone at the head of the table. This is due to their being supposed to be without analogues, which we know now not to be the case for oxygen and nitrogen. Again elements, which we do not group together, are found in the same set in the table, *e.g.*, boron with carbon and silicon, beryllium (G) with the rare earths cerium, etc. Gmelin claims as a feature of his classification that the more electro-positive elements are on the right and the more electro-negative elements on the left of this table.

Pettenkofer.—In 1850 Pettenkofer[1] read a paper before the mathematical physics class of the Bavarian Academy of Sciences on "The Regular Differences between the Equivalent Numbers of the so-called Simple Radicals." The contents of this paper did not become generally known until 1858, when a reprint appeared in Liebig's *Annalen*

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[1] *Ann.* 105 (1858), p. 188.

for the purpose of showing his priority over Dumas concerning this relation of the atomic weights.

Pettenkofer thought that similar elements formed an arithmetic series, and thus that they might be regarded as compounds similar to the organic radicals. In each series he puts the atomic weight of one element as a whole number, and then adds or subtracts another integer to obtain the series.

The results so obtained he tabulates thus:—

	Hypothetical.	Found.	Difference.
Li	7	6·51	0·49
Na	23	22·97	0·03
K	39	39·11	0·11
Mg	12	12·07	0·07
Ca	20	20·00	0·00
Sr	44	43·92	0·08
Ba	68	68·54	0·54
Cr	26	26·00-26·30	...
Mo	46	46	...
V	66	?	...
O	8	8	...
S	16	16	...
Se	40	39·62	0·38
Te	64	64·14	0·14
C	6	6	...
N	14	14	...
Hg	100	100	...
Ag	108	108	...

The differences between the successive elements is either 8 or a multiple of 8, except in the case of Cr, Mo and V, where it is 20. He further gives two more sets of elements:—

C	6	6	0
B	11	11	0
Si	21	21	0

Here the differences are 5 and 10 = 2 × 5.

N	14
P	32
As	75
Sb	129

The difference between the first two is 18, and between the last two 54 = 3 × 18.

The found atomic weight for vanadium—68·6—is not given, because Pettenkofer thinks it possible that this is not the true value.

This is practically all that is of importance in the paper.

Dumas.—In 1851 Dumas addressed the British Association on a subject concerning the further relations of triads like those of Döbereiner. A complete account of the address is to be found in the *Chemical Record* for 1851, July 12th.

His attentions were chiefly confined to the three elements—chlorine, bromine and iodine. He showed that bromine was always intermediate in properties between chlorine and iodine. The following table will make this clear:—

	Physical Condition.		*Colour.*
Cl	Gaseous	at ordinary temperatures	Yellowish green
Br	Liquid		Deep reddish-brown
I	Solid		Almost black

Specific Gravities.		Gaseous.	Liquid or Solid.	
Chlorine	2·47	Cl = 2·47	1·33	Cl = 1·33
Bromine	5·54	I = 8·716	3·187	I = 4·947
Iodine	8·716	2)11·186	4·947	2)6.277
		Br = 5·593		Br = 3·138

	Atomic Weights.	
Chlorine	35·5	$Cl = 35{\cdot}5$
Bromine	80	$I = 127{\cdot}0$
Iodine	127	$2\overline{)162{\cdot}5}$
		$Br = \overline{81{\cdot}25}$

He summed up his results in a general law thus:—

"When three bodies, having properties precisely similar, though not identical, are arranged in succession of their chemical powers, ~~their~~ there will also be a successive arrangement of mathematical powers, indicated by the respective atomic numbers of the substances and amenable to every mathematical law."

To this view, Faraday, who was in the chair, gave his complete assent.

Kremers.—In 1852 Kremers drew attention to the equivalents of several elements, showing differences among themselves approximately equal to 8, and to the fact that the equivalents of some metals (Mg, Ca, Fe) are nearly products of 4 with an odd integer, whilst those of others (O, S, P, Se, etc.) are products of 4 with an even integer.[1]

Gladstone.—In 1853 Dr J. H. Gladstone[2] published a paper "On the Relations between the Atomic Weights of Analogous Elements." He compares the atomic weights of the elements with the molecular weights of organic radicals, and divides the elements into three broad groups:—

(1.) Those having nearly the same atomic weight;

(2.) Those whose atomic weights form a geometrical series;

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[1] *Pogg. Ann.* 85 (1852), p. 56.

[2] *Phil. Mag.* (4), 5 (1853), p. 313.

(3.) Those whose atomic weights form an arithmetic series.

To the first belong Cr, Mn, Fe, Co and Ni with the atomic weights 26·7, 27·6, 28·0, 29·5 and 29·6 respectively; Pd, Rh, Ru with the atomic weights 53·3, 52·2 and 52·3, and Pt, Ir, Os, and perhaps Hg, with the atomic weights 98·7, 99·0, 99·6 and 100 respectively.

He then puts the question, "Would more accurate researches show these atomic weights to be not nearly but exactly the same?" This he himself doubts.

Into the second group are placed the following:—

Ti = 23·6	2 × 11·5 = 23
Mo = 46	4 × 11·5 = 46
Sn = 58	5 × 11·5 = 57·5
V = 68·6	6 × 11·5 = 69
W = 92	8 × 11·5 = 92
Ta = 184	16 × 11·5 = 184

It is further pointed out that the atomic weights of the platinum metals are equal to twice those of the palladium metals, and that the atomic weight of gold is twice that of platinum. Those of boron and silicon—10·9 and 21·3—are in the ratio 1 : 2, as are also oxygen and sulphur—8 and 16.

Again he states that aluminium should belong to the iron group from isomorphism. However, its equivalent—13·7—is half that of iron; and glucina, which is certainly an analogous earth, viewing it also as a sesquioxide, gives 7 as atomic weight of glucinum, which is half that of aluminium.

The third group contains lithium, sodium and potassium; calcium, strontium and barium; chlorine, bromine and iodine, and sulphur, selenium and tellurium. The increments in each group are respectively, 16·3, 24·2, 45·8 and 24·1.

The elements phosphorus, arsenic and antimony could not be fitted into any of these three groups. However, the atomic weight of antimony—129—is twice that of tellurium—64·2—to which it is supposed to bear some analogy.

Cooke.—In 1854 a further extension of Pettenkofer's idea was made by Cooke.[1] He considers that all the elements can be arranged in six series, each of which has a general formula expressing the atomic weights of the elements in that series. The series have the following general formulæ:—$8+n \, . \, 9$, $4+n \, . \, 8$ or $8+n \, . \, 8$, $8+n \, . \, 6$, $6+n \, . \, 5$, $4+n \, . \, 4$ or $2+n \, . \, 4$, and lastly $1+n \, . \, 3$.

To the first group belong O, F, Cl, Br, I, and (CN) is also included; to the second O, S, Se, Mo, Te, V, W, Ta; to the third O, N, P, As, Sb and Bi; to the fourth C, B, Si; and to the fifth Mg, Al, Ca, Ti, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Ba, Cd, Pt, Hg, Pb, Ag, Au and others; and to the sixth H, Li, Na and K, the atomic weights of the last three being doubled.

Lenssen.—In 1857 Lenssen[2] arranged all the elements then known in triads, and arrived at twenty of such groups. His table, which is of historical interest, being the complete carrying out of Döbereiner's original ideas, is here given.

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[1] *Am. J. Sc.* (2), 17 (1854), p. 387.

[2] *Ann.* 103 (1857), p. 121.

	Triad Groups.			Equivalents.		
(1.)	$\frac{\mathrm{K} + \mathrm{Li}}{2} = \mathrm{Na} =$ 23·03	instead of	23·00	39·91	23·00	6·95
(2.)	$\frac{\mathrm{Ba} + \mathrm{Ca}}{2} = \mathrm{Sr} =$ 44·29	,,	43·67	68·59	43·67	20·00
(3.)	$\frac{\mathrm{Mg} + \mathrm{Cd}}{2} = \mathrm{Zn} =$ 23·8	,,	32·5	12	32·5	55·7
(4.)	$\frac{\mathrm{Mn} + \mathrm{Co}}{2} = \mathrm{Fe} =$ 28·5	,,	28·0	27·5	28	29·5
(5.)	$\frac{\mathrm{La} + \mathrm{Di}}{2} = \mathrm{Ce} =$ 48·3	,,	47·3	47·0	47·3	49·6
(6.)	Y. Er. Tb			32·2	?	?
(7.)	Th. No. Al			59·5	?	13·7
(8.)	$\frac{\mathrm{Be} + \mathrm{Ur}}{2} = \mathrm{Zr} =$ 33·5	instead of	33·6	7	33·6	60
(9.)	$\frac{\mathrm{Cr} + \mathrm{Cu}}{2} = \mathrm{Ni} =$ 29·3	,,	29·6	26·8	29·6	31·7
(10.)	$\frac{\mathrm{Ag} + \mathrm{Hg}}{2} = \mathrm{Pb} =$ 104	,,	103·6	108	103·6	100
(11.)	$\frac{\mathrm{O} + \mathrm{C}}{2} = \mathrm{N} =$ 7	,,	7	8	7	6
(12.)	$\frac{\mathrm{Si} + \mathrm{F}}{2} = \mathrm{Bo} =$ 12·2	,,	11	15	11	9·5
(13.)	$\frac{\mathrm{Cl} + \mathrm{I}}{2} = \mathrm{Br} =$ 40·6	,,	40	17·7	40	63·5
(14.)	$\frac{\mathrm{S} + \mathrm{Te}}{2} = \mathrm{Se} =$ 40·1	,,	39·7	16	39·7	64·2
(15.)	$\frac{\mathrm{P} + \mathrm{Sb}}{2} = \mathrm{As} =$ 38	,,	37·5	16	37·5	60
(16.)	$\frac{\mathrm{Ta} + \mathrm{Ti}}{2} = \mathrm{Sn} =$ 58·7	,,	59·0	92·3	59	25
(17.)	$\frac{\mathrm{W} + \mathrm{Mo}}{2} = \mathrm{V} =$ 69	,,	68·5	92	68·5	46
(18.)	$\frac{\mathrm{Pd} + \mathrm{Rh}}{2} = \mathrm{Ru} =$ 52·2	,,	52·1	53·2	52·1	51·2
(19.)	$\frac{\mathrm{Os} + \mathrm{Ir}}{2} = \mathrm{Pt} =$ 98·9	,,	99·0	99·4	99	98·5
(20.)	$\frac{\mathrm{Bi} + \mathrm{Au}}{2} = \mathrm{Hg} =$ 101·2	,,	100·0	104	100	98·4

Niobium is the only element not included. Mercury occurs twice—in (10) and in (20)—and is thought to form a sort of connecting link between the series (1) to (10) and (11) to (20). He further shows that the middle members of these triads can be again arranged in groups of three, which he calls "Enneads." Six of these are obtainable directly, and a seventh by calculation. The natural groups are formed by the middle members of the following triads:—1, 2, 3; 7, 8, 9; 10, 11, 12; 18, 17, 16; 15, 14, 13; 12, 11, H. The calculated group, 4, 5, 6, is obtained thus:—$6\text{th} = \frac{4\text{th} + 5\text{th}}{2} = \frac{28+47}{2} = 37 = \text{Eb}$. From this Tb can be calculated, being given by $\text{Er} = \frac{\text{Y} + \text{Tb}}{2}$ whence $\text{Tb} = 42$. We have now seven enneads, of which the middle terms are $a=33$, $b=34$, $c=37$, $d=61$, $e=40$, $f=7$, $g=101$. The following relations exist between these figures:—$d+e=g$, $a+f=e$ and $\frac{b+e}{2}=c$, but they have no real significance.

Dumas.—In 1857 another attempt was made by Dumas to connect the atomic weights together. The elements are arranged in groups, and the atomic weights of the elements in each group are given by $pa+md+nd'$, where p, m and n are integers or zero. Thus the group F, Cl, Br, I, is expressed by the formula $19+m\,.\,16{\cdot}5+n\,.\,28$; that of N, P, As, Sb, Bi by the formula $14+17+n\,.\,44$. Of groups expressible by a two-term formula, the following may be cited:—C, B, Si, Zr by $p\,.\,6+n\,.\,5$; O, S, Se, Te by $8+n\,.\,8$;

Mg, Ca, Sr, Ba, Pb by $n \cdot 12 + p \cdot 8$; and finally Li, Na, K by $7 + n \cdot 16$.[1]

Strecker.—In 1859 A. Strecker drew attention to the following remarkable series of equivalents:—Cr = 26·2, Mn = 27·6, Fe = 28, Ni = 29, Co = 30, Cu = 31·7, Zn = 32·5, and wrote:—"It is scarcely probable that the above-mentioned relations between the atomic weights (or equivalents) of elements of similar chemical behaviour should be purely accidental. However, the discovery of the law of the relations existing between these figures we must leave to the future."

Lothar Meyer.—In 1860 Lothar Meyer, late Professor at Tübingen, published the accompanying tables (I., II., III.), from which he drew the following conclusions:—(1) that if the elements be arranged in order of their atomic weights, there was a regular and continuous change of valency as we pass from family to family; and (2) that the successive differences of elements in the same column were at first approximately 16, except beryllium, then increased to about 46, and finally approached a number ranging between 87 and 90. These relations are readily seen on referring to Tables I. and II. Table III. was arranged because the atomic weights of those elements were uncertain and the differences irregular. Table IV., which was probably prepared for a new edition of the *Moderne Theorien*, contains the elements chromium and aluminium in addition to those in the other tables. However, the former is placed in an isolated position, and that of the latter seemed doubtful.

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[1] v. *C. R.* 45 (1857), p. 709, and *Ann.* 105 (1858), p. 74.

THE TABLES OF LOTHAR MEYER, 1860.

TABLE I.

	Tetravalent.	Trivalent.	Divalent.	Monovalent.	Monovalent.	ivalent.
					Li 7·03	(Be 9·3 ?)
Difference	…	…	…	…	16·02	(14·7)
	C 12·0	N 14·04	O 16·0	F 19·0	Na 23·05	Mg 24·0
Difference	16·5	16·96	16·07	16·46	16·08	16·0
	Si 28·5	P 31·00	S 32·07	Cl 35·46	K 39·13	Ca 40·0
Difference	$\frac{89\cdot1}{2}=44\cdot55$	44·00	46·70	44·51	46·3	47·6
		As 75·00	Se 78·77	Br 79·97	Rb 85·43	Sr 87·6
Difference	$\frac{89\cdot1}{2}=44\cdot55$	45·6	49·5	46·8	47·6	49·5
	Sn 117·6	Sb 120·6	Te 128·3	I 126·8	Cs 133·0	Ba 137·1
Difference	$89\cdot4=2\times44\cdot7$	$84\cdot4=2\times42\cdot2$	…	…	$71=2\times35\cdot5$	…
	Pb 207·0	Bi 208·0	…	…	(Tl 204 ?)	…

TABLE II.

	Tetravalent.		Tetravalent.		Tetravalent.		Divalent.			
	Mn	55·1	Ni	58·7	Co	58·7	Zn	65·0	Cu	63·5
	Fe	56·0								
Difference		49·2 48·3		45·6		47·3		46·9		44·4
	Ru	104·3	Rh	104·3	Pd	106·0	Cd	111·9	Ag	107·9
Difference	92·8=2×46·4		92·8=2×46·4		93·0=2×46·5		88·3=2×44·15		88·8=2×44·4	
	Pt	197·1	Ir	197·1	Os	199·0	Hg	200·2	Au	196·7

TABLE III.

	Tetravalent.		Hexavalent.	
	Ti	48·0	Mo	92
Difference		42·0		45
	Zr	90·0	V	137
Difference		47·6		47
	Ta	137·6	W	184

TABLE IV.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.	XV.	XVI.
...	...	...	...	...	...	...	...	...	...	...	Li 7·03	Be 9·3	...	...	...
...	...	...	...	...	...	...	..	...	...	...	16·02	14·7	...	...	...
..	...	Al 27·3	Al 27·3	...	...	...	C 12·0	N 14·04	O 16·0	F 19·0	Na 23·05	Mg 24·0	...	...	...
...	...	$\frac{28\cdot7}{2}=14\cdot3$	...	...	...	...	16·5	16·96	16·07	16·46	16·08	16·0	...	...	...
...	...	...	...	...	...	...	Si 28·5	P 31·00	S 32·07	Cl 35·46	K 39·13	Ca 40·0	Ti 48·0	Mo 92	...
...	...	...	...	...	...	...	$\frac{89\cdot1}{2}=44\cdot55$	44·0	46·7	44 51	46·3	47·6	42·0	45	...
Cr 52·6	**Mn** 55·1	Fe 56·0	Co 58·7	Ni 58·7	Cu 63·5	Zn 65·0	...	As 75·0	Se 78·8	Br 79·97	Rb 85·4	Sr 87·6	Zr 90·0	V 137	...
...	49·2	48·3	47·3	...	44·4	46·9	$\frac{89\cdot1}{2}=44\cdot55$	45·6	49·5	46·8	47·6	49·5	47·6	47	...
...	Ru 104·3	Rh 104·3	Pd 106·0	...	Ag 107·94	Cd 111·9	Sn 117·6	Sb 120·6	Te 128·3	I 126·8	Cs 133·0	Ba 137·1	Ta 137·6	W 184	...
...	92·8 = 2 × 46·4	92·8 = 2 × 46·4	93 = 2 × 46·5	...	88·8 = 2 × 44·4	88·3 = 2 × 44·1	89·4 = 2 × 44·7	87·4 = 2 × 43·7	...	...	71 = 2 × 35·5	...	...	...	...
...	Pt 197·1	Ir 197·1	Os 199·0	...	Au 196·7	**Hg** 200·2	Pb 207	Bi 208	...	...	?7? 204	...	...	...	...

S. L. Gmelin, Hbd. 5 Aufl. i. 47 ff. ; *Münch. geb. Anz.* (1850), Bd. 30, S. 261, 272 abgedr. ; *Ann. Chem. Pharm.* (1858), 105, 187 ; J. Dumas, *C. R.* (1857) t. 45, p. 700 ; auch *Ann. Chem. Pharm.* 105, 374 ua.

Further, we notice that iron has taken the place of nickel, which element is now put between cobalt and copper. These tables have been taken from the *Journal of the Chemical Society*, 69 (1896), p. 1403, and form part of the Lothar Meyer Memorial Lecture delivered before the above-named society by Dr Bedson.

We see clearly that the germ of a general classification of the elements was fast developing, and that a decisive step taken in the right direction would be of great service in the final reaching of the goal.

De Chancourtois.—In 1862 M. A. E. Béguyer de Chancourtois announced his "Telluric Helix." The diagram represents a helix drawn on a right circular cylinder, having a constant slope of 45° to the axis. Lengths corresponding to the "characteristic numbers" or atomic weights of the elements were measured off, taking the one-sixteenth part of a complete turn of the helix as the unit. The extremities of these lengths gave the "characteristic points" on the helix. The annexed diagram is a portion of such a curve on a plane surface. It will be seen that analogous elements fall on the same vertical lines.[1] From the curve we see that the atomic weights could be expressed by the formula $A = n + 16m$, where m is an integer. Thus:—

$O = 16.$ $S = 16 + 16 = 32.$ $Se = 16 + 4.16 = 80.$ $Te = 16 + 7.16 = 128.$

The relations of the other elements were expressed by secondary helices.

However, being a mathematician and a geologist,

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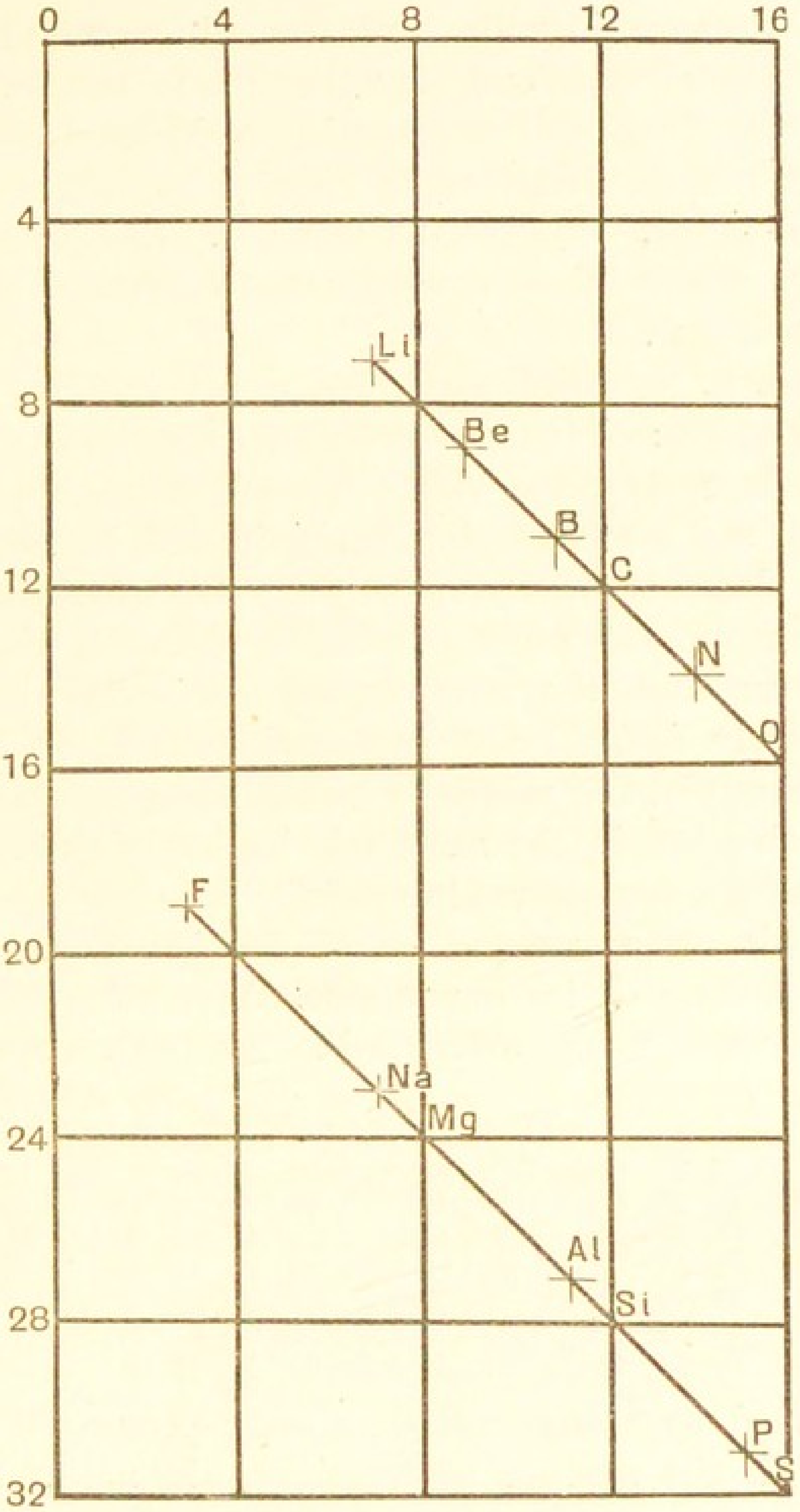
[1] This is not absolutely accurate.


0
4
8
12
16
4
8
12
16
20
24
28
32
Li
Be
B
C
N
O
F
Na
Mg
Al
Si
P
S

he did not consider his spiral from the point of view of chemical facts, and thus the "vis tellurique," as it was called, received no attention, and fell entirely into oblivion until unearthed in 1889.[1]

Newlands.—In 1863-64 was published Newlands' work, which was the actual forerunner of the periodic law.

J. A. R. Newlands stated his results in the following manner:—"If the elements be arranged in order of their equivalents, with a few slight transpositions as in the accompanying table, it will be observed that elements belonging to the same group usually appear on the same horizontal line. It will also be seen that the numbers of analogous elements generally differ by 7 or some multiple of 7. In other words, the members of the same group stand to each other in the same relation as the extremities of one or more octaves in music." [2]

Little notice was taken of Newlands' discovery at the time of its announcement, and, in fact, not for several years afterwards. He was, moreover, ridiculed by many, including some persons of note, who, in the absence of foresight, did not conceive

NEWLANDS' TABLE.[3]

H	1	F	8	Cl	15	Co&Ni	22	Br	29	Pd	36	I	43	Pt&Ir	50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Tl	51
Be	3	Mg	10	Ca	17	Zn	24	Sr	31	Cd	38	Ba&V	45	Pb	52
B	4	Al	11	Cr	18	Y	25	Ce&La	32	U	39	Ta	46	Th	53
C	5	Si	12	Ti	19	In	26	Zr	33	Sn	40	W	47	Hg	54
N	6	P	13	Mn	20	As	27	Di&Mo	34	Sb	41	Nb	48	Bi	55
O	7	S	14	Fe	21	Se	28	Rh&Ru	35	Te	42	Au	49	Os	56

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[1] See *Nature* (1889), and *C. N.* 63 (1891), p. 51.

[2] v. *C. N.* 12 (1865), p. 83.

[3] *C. N.* 12, p. 83.

the importance and fruitfulness of the law. Some went so far as to suggest to Newlands that he might try to arrange the elements in alphabetical order with a similar result.

However, eventually Newlands got the credit he deserved, and, in recognition of his services to the furtherance of chemistry, was awarded the Davy Medal of the Royal Society in 1887. Of course, it must be borne in mind that Newlands' arrangement was by no means perfect, and that it had to be considerably modified to make it appear satisfactory. It is known as the "Law of Octaves."

Meyer and Mendeléeff.—In 1869-70, Lothar Meyer[1] and D. Mendeléeff,[2],[3] independently published papers, in which they stated that the properties of the elements were periodic functions of their atomic weights.

This was practically the outcome of Newlands' Law. However, their work was considered original, and both chemists were awarded Davy Medals in 1882, five years prior to the date at which Newlands was thus deservedly honoured.

This discovery was called the "Periodic Law," and remains in practically its original form at the present day.

Lothar Meyer's table, as published in the *Ann. Chem.*, is given here, but his second modified table, as also those of Mendeléeff, will be deferred till Chap. III. (pp. 44, 46, 48).

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[1] *Ann. Chem. Suppl.* VII. (1870), p. 354.

[2] *Zeit. Chem.* (2), 5 (1869), p. 405.

[3] *Ann. Chem. Suppl.* VIII. (1872), p. 405.

LOTHAR MEYER'S TABLE FOR 1870.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
...	B 11·0	Al 27·3	...	..	..	? In 113·4	...	Tl 202·7
...	...	...	..	..	...	...	...	...
...	C 11·97	Si 28·4	...	...	...	Sn 117·8	...	Pb 206·4
..	...	...	Ti 48·0	...	Zr 89·7	...	..	..
...	N 14·01	P 30·9	..	As 74·9	...	Sb 122·1	...	..
...	...	...	V 51·2	...	Nb 93·7	...	Ta 182·2	...
...	O 15·96	S 31·98	...	Se 78·0	...	Te 128·?	...	...
...	...	...	Cr 52·4	...	Mo 95·6	...	W 183·5	...
...	F 19·1	Cl 35·38	...	Br 79·75	...	I 126·5	...	...
...	...	...	Mn 54·8	...	Ru 103·5	...	Os 188·6	...
...	...	...	Fe 55·9	...	Rh 104·1	...	Ir 196·7	...
...	...	...	Co=Ni 58·6	...	Pd 106·2	...	Pt 196·7	...
Li 7·01	Na 22·99	K 39·04	...	Rb 85·2	...	Cs 132·7	...	...
...	...	...	Cu 62·3	...	Ag 107·66	...	Au 196·2	...
? Be 9·3	Mg 23·9	Ca 39·9	...	Sr 87·0	...	Ba 136·8	...	...
...	...	...	Zn 64·9	...	Cd 111·6	...	Hg 199·8	...

Since 1870 several attempts have been made at an improved form of the table; but they are all substantially the same as the original, differing only in being rearranged and twisted about. A few of these will be considered in a subsequent chapter.

For a brief account of the history of the Periodic Law, Mendeléeff's Faraday Lecture[1] and Bedson's Lothar Meyer Lecture[2] may be advantageously consulted. Mention must also be made of the excellent article by Douglas Carnegie on the "Periodic Law" in Watt's *Dictionary of Chemistry*, Vol. III.

It is most remarkable that Meyer and Mendeléeff, by boldly leaving gaps for elements which, in their opinion, yet remained to be discovered, should have been successful in drawing up a classification of the elements which so well illustrates the variations of properties with atomic weight.

Also when we remember how unsettled the atomic weights were at this time, the discovery is yet the more worthy of the highest praise. But this praise must not be reserved entirely for Meyer and Mendeléeff, who really only extended the original ideas of Newlands, to whom the other share of the credit is in no small degree due.

The numbers given in this chapter for the various atomic weights are those given by the authors of the papers in which they appear. In some cases they

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[1] *J. C. S.* 55 (1889), p. 634.

[2] *J. C. S.* 69 (1896), p. 1403.

represent equivalents, and in some cases actual atomic weights; however, it is not thought that there will be any confusion, especially as the older writers used these two terms indiscriminately.

CHAPTER II

THE LAWS OF AVOGADRO, DULONG AND PETIT, AND MITSCHERLICH

THESE three most important physical laws have been the means of determining and fixing such a large number of atomic weights that a short account of them in this book cannot be out of place. We will consider each one separately in order of time sequence.

The Law of Avogadro.

Gay-Lussac.—In 1808, Gay-Lussac published some important researches in the *Mémoires de la Société d'Arçeuil,* in which he stated that—

(1.) There is a simple relation existing between the volumes of gases which combine.

(2.) There is a similar simple relation between the volumes of the combining gases and the volume of the resulting gaseous compound.

From these it follows that "The weights of equal volumes of both simple and compound gases, and therefore their densities, are proportional to their empirically found combining weights or to rational multiples of the latter."

This statement is known as Gay-Lussac's "Law of Volumes."

Avogadro.—A law closely allied to this was formulated by Avogadro in 1811, and is known as "Avogadro's Law."

It stated that "equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules." From this it follows that the molecular weights of gases are proportional to their densities; that is to say, the Law of Gay-Lussac follows at once from the Law of Avogadro. This latter must not be confounded with a very similar one put forward by Berzelius, which states that "Simple bodies in the gaseous state at the same volume consist of an equal number of atoms." We know now that this is not true.

The Law of Avogadro cannot be any more proved by actual observation than the Atomic Theory. However, it appears to be very probable, and is so useful that it is convenient to retain it. And further, if we accept the Kinetic Theory of Gases, then Avogadro's Rule can be mathematically deduced from it in the following manner :—

The product of pressure and volume of a gas is equal to two-thirds of the kinetic energy of its molecules, or in symbols—

$$pv = \frac{2}{3} mn \frac{C^2}{2}.$$

This is the fundamental point of the kinetic theory.

Now consider two gases under the same conditions of pressure and volume, that is we have $p_1 v_1 = p_2 v_2$

$$\text{therefore } \frac{2}{3} m_1 n_1 \frac{C_1^2}{2} = \frac{2}{3} m_2 n_2 \frac{C_2^2}{2}.$$

Now, according to the kinetic theory the kinetic energy of the separate molecules of two gases is the same, if the temperatures of these gases are the same, *i.e.*,

$$m_1\frac{C_1^2}{2}=m_2\frac{C_2^2}{2},$$

therefore it follows that $n_1=n_2$.

Hence if the pressures, temperatures and volumes of two gases are the same, then these gases contain the same number of molecules.

The Law of Dulong and Petit.

In 1819 Physical Chemistry was greatly enriched by a relation between the specific heats of the elements and their atomic weights discovered by P. L. Dulong and T. A. Petit. They expressed their results in the form of a law, which is known by their names, and is that "The atoms of simple substances have equal capacities for heat."

Their researches were published in the *Ann. Chim. Phys.* for 1819, Vol. X. p. 395, from which the annexed table has been taken. It is to be noticed that in many cases both the atomic weights and the specific heats are quite different from those in use at the present day, and further, that the methods of working which they employed were none too accurate. Yet, notwithstanding this, they were able to discover the law which has made them famous.

Of course it is known that in several cases the results given for the specific heats were more imaginary than experimental.

The Table of Dulong and Petit.

Element.	Specific Heat.	Relative Weight, O=1.	Product of 2nd and 3rd Columns.
Bismuth	0·0288	13·30	0·3830
Lead	0·0293	12·95	0·3794
Gold	0·0298	12·43	0·3704
Platinum	0·0314	11·16	0·3740
Tin	0·0514	7·35	0·3779
Silver	0·0557	6.75	0·3759
Zinc	0·0927	4·03	0·3736
Tellurium	0·0912	4·03	0·3675
Copper	0·0949	3·957	0·3755
Nickel	0·1035	3·69	0·3819
Iron	0·1100	3·392	0·3713
Cobalt	0·1498	2.46	0·3685
Sulphur	0·1880	2·011	0.3780

The product of the specific heat and atomic weight is called the "Atomic Heat," and the law can be stated thus :—The atomic heats of the elements are constant. The value of this constant ranges between 6·0 and 6·4 for solids, but it is approximately equal to 3·4 for gases. Assuming their law, Dulong and Petit soon saw that some of the atomic weights of Berzelius must be halved. To this the latter would not give his consent, as he considered that such a proceeding would occasion improbable proportions between the elements present in the molecules of some compounds. But later, as more experimental evidence was forthcoming in favour of alteration of the atomic weights, he gave way.

There are, however, several exceptions to this law, and these are chiefly those elements of low atomic weight, although some elements, *e.g.*, sodium and lithium, whose atomic weights are not high, have nearly normal values for their atomic heat.

Weber.—The most marked exceptions are beryllium, boron, carbon and silicon. Weber, who has worked a great deal with these elements, showed that their specific heats vary largely with temperature, and also depend on the crystalline form or condition of the substance experimented on.

The following tables, as also the curve, will make these relations clear :—

TABLE I.

VARIATION OF SPECIFIC HEAT WITH CONDITION.

Element—Carbon.

Form.	Specific Heat.	Atomic Heat.
Diamond . . .	0·147	1·76
Graphite	0·200	2·40
Charcoal	0·241	2·90

Here the difference between the values of the specific heats for different forms is very considerable.

VARIATIONS OF SPECIFIC HEAT WITH TEMPERATURE.

TABLE II.

Diamond and Graphite.[1]

Temperature (Approx.)	Specific Heat.		Atomic Heat.	
	Diamond.	Graphite.	Diamond.	Graphite.
− 50° C.	0·0635	0·1138	0·76	1·36
− 10°	0·0955	0·1437	1·15	1·72
+ 10°	0·1128	0·1604	1·35	1·92
33°	0·1318	...	1·58	...
58°	0·1532	0·1990	1·84	2·39
86°	0·1765	...	2·12	...
140°	0·2218	0·2542	2·66	3·05
206°	0·2733	0·2966	3·28	3·56
247°	0·3026	...	3·63	...
600°	0·4408	0·4431	5·29	5·32
800°	0·4489	0·4529	5·39	5·43
1000°	0·4589	0·4670	5·50	5·60

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[1] Weber, *Pogg. Ann.* 154 (1875), p. 367.

TABLE III.

Beryllium.[1]

Temperature.	Specific Heat.	Atomic Heat.
100° C.	0·4702	4·28
200°	0·5402	4·93
300°	0·5910	5·38
400°	0·6172	5·61
500°	0·6206	5·65

TABLE IV.

Boron.[2]

Temperature.	Specific Heat.	Atomic Heat.
− 40° C.	0·1915	2·10
+ 27°	0·2382	2·62
77°	0·2737	3·01
126°	0·3068	3·37
177°	0·3378	3·71
233°	0·3663	4·03

TABLE V.

Silicon.[3]

Temperature.	Specific Heat.	Atomic Heat.
− 40° C.	0·1360	3·31
+ 27°	0·1697	4·73
57°	0·1833	5·13
86°	0·1901	5·32
129°	0·1964	5·50
184°	0·2011	5·63
232°	0·2029	5·68

The results embodied in these tables indicate that as the temperature is increased the atomic heat

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[1] Humpidge, *Proc. Roy. Soc.* 39 (1885), p. 1.
[2] Weber, *Phil. Mag.* (4), 49 (1875), pp. 161-276.
[3] Weber, *Pogg. Ann.* 154 (1875), p. 367.

approaches more and more nearly to the normal value. It will also be noticed that the atomic heats of diamond and graphite, though very different at low temperatures, are nearly the same at high temperatures.

In the case of several other elements, *e.g.*, cadmium, iron, lead, etc., the atomic heat is nearly normal at about 50° C., and increases in some cases, *e.g.*, iron, very rapidly with the temperature. A few examples may prove interesting.[1]

Element.	Specific Heat.		Atomic Heat.	
	At 50° C.	At 300° C.	At 50°.	At 300°.
Cadmium	0·0551	0·0617	6·18	6·92
Zinc	0·0929	0·1040	6·08	6·81
Iron	0·1113	0·1376	6·23	7·71
Silver	0·05556	0·06091	6·00	6·57
Copper	0·09316	0·09846	5·90	6·24
Nickel	0·1090	0·1327	6·43	7·83
Antimony	0·04947	0·05366	5·95	6·46
Lead	0·03040	0·03380	6·29	7·00
Aluminium	0·2164	0·2401	5·87	6·51

When we actually consider what goes on when a body is heated these results lose a part of their remarkability. We have—

(1.) Increase of temperature.

(2.) Internal work done on the molecules in increasing their rate of motion and the distance between them.

(3.) External work done due to the expansion of the body.

Until we know a little more about these factors, it seems useless to attempt to explain the true nature of the specific heat. However, Dulong

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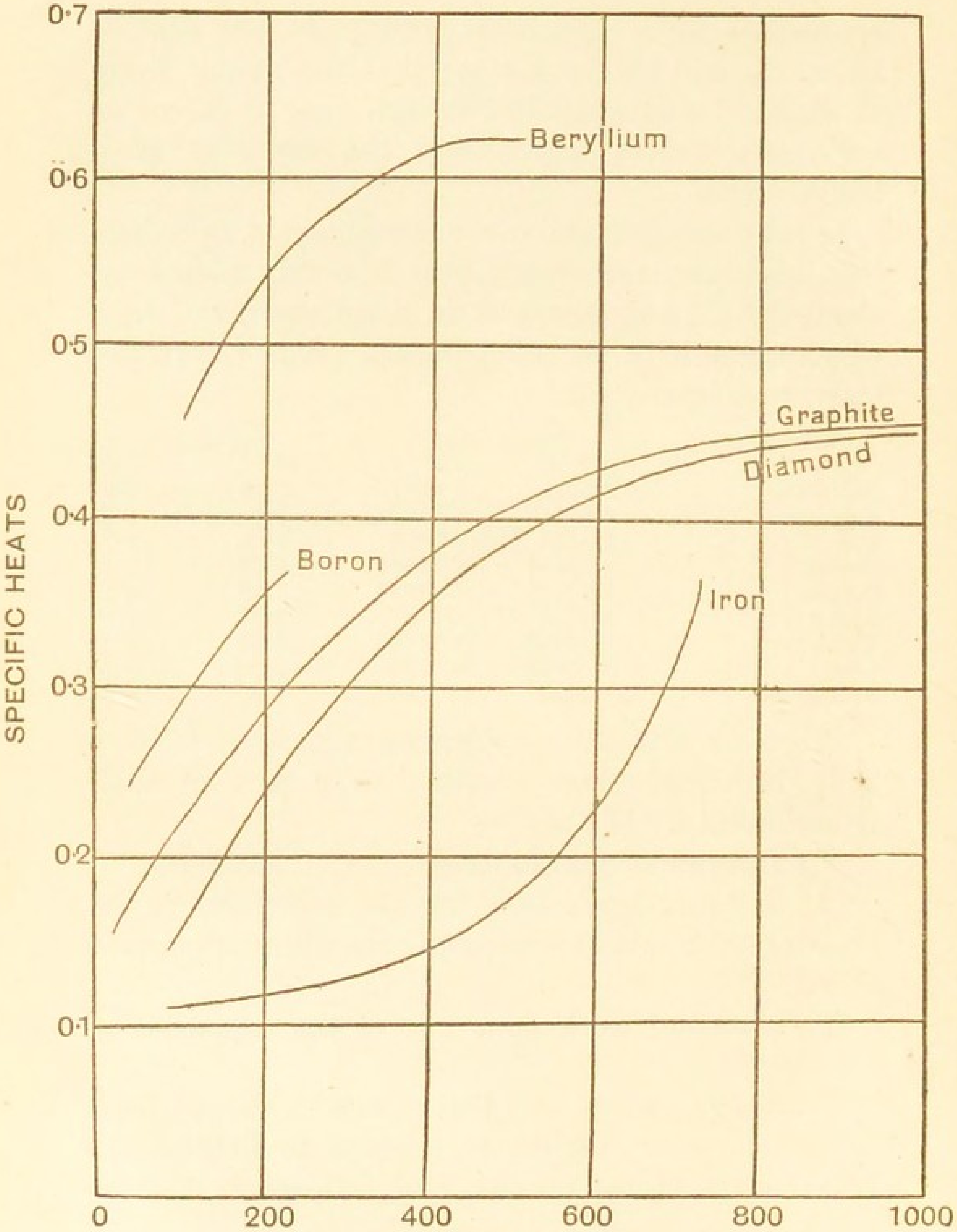
[1] *Gazz. ch. it.* 18 (1888), p. 31, and *J. C. S.* 54 (1888), p. 1237.


0·7
0·6
0·5
0·4
0·3
0·2
0·1
SPECIFIC HEATS
0
200
400
600
800
1000
TEMPERATURES
Beryllium
Graphite
Diamond
Boron
Iron

and Petit's law, which must at present be regarded as purely empirical, has been of great service to chemists in the confirmation of atomic weights, a point which will be discussed later.

Neumann and Woestyn.—The law has been extended by Neumann (1831), Woestyn and others, to show a relation between the specific heats and molecular weights of compounds. The extension states that the molecular heat of a compound is the sum of the atomic heats of the constituent atoms. The law is not by any means completely verified by experiment, and is at present of little importance, as in many cases the results obtained do not even agree among themselves.

We have seen that temperature has a deep influence on the value of the specific heat, and it appears that if one always observed the specific heats at temperatures equidistant from the melting points more uniform and comparable results might be obtained. But, as in a great many cases the melting points are not known with any degree of accuracy, the truth of such a suggestion cannot be demonstrated. The fact that the elements boron, silicon, carbon and beryllium, whose melting points are very high, have such low atomic heats, seems to indicate that some such restriction as the above must be put upon the value of a specific heat before making any comparisons.

We know that many physical properties of gases and liquids are only comparable at temperatures equidistant from their critical temperatures, *e.g.*, molecular surface energy, and as the melting point of a solid is very little affected by change of pressure, it seems that this is the best temperature to take for solids to correspond to the critical temperature of a liquid.

The complete carrying out of the relations existing between the specific heats and atomic weights of the elements must remain a problem for future chemists and physicists to solve.

Professor Tilden has been recently working at this subject, and his researches seem to indicate that at low temperatures the atomic heats all approach that of hydrogen. Yet this requires more confirmatory experimental data to completely establish it.

The Law of Isomorphism.

It is not intended to enter fully into a discussion of the subject of isomorphism, as such a proceeding would require an undue amount of space, and is beyond the scope of this present treatise.

In 1821 Eilhard Mitscherlich announced his "Law of Isomorphism." It ran thus:—"The same number of atoms combined in the same way give rise to the same crystalline form, which is independent of the chemical nature of the atoms present, being influenced only by their number and mode of arrangement."

Subsequent experiments have, however, shown that the law, as thus stated, is rather too general, and that the converse, namely, that similar crystalline form is the criterion of similar chemical composition, is by no means true.

Except in the case of the regular system, the exact agreement of the angles of isomorphous bodies with one another is scarcely ever perfect. But the differences are not, as a rule, very great, although they have been known to amount to several degrees.[1] Strictly speaking, then, it would be better to reserve the term isomorphism only for the regular system, and use the expression homœomorphism for the other systems.

The criterions of the existence of isomorphism are these:—

(1.) If a crystal of one compound, on being immersed in a solution of another compound, continues to grow, then the two bodies are said to be isomorphous.

(2.) If two bodies form mixed crystals, that is, if on mixing their solutions and allowing to crystallise the crystals separating contain indefinite amounts of both constituents and have a similar form to that of each pure salt, then the two substances are isomorphous.

It may be here noted that some time after the development of crystallography by Haüy and Romé de l'Isle, several experimenters observed that substances of different chemical composition crystallised in the same form.

Beudant.—As examples of this, mention may be made of Beudant, who found that copper sulphate crystallised in the same form as iron sulphate, if a small quantity of the latter be added to a solution

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[1] See later, p. 39 and 40.

of the former,[1] and also Gay-Lussac, who showed that crystals of potash alum grew in a solution of ammonia alum. But it was left to Mitscherlich to discover any relation between crystalline form and chemical constitution. Berzelius regarded the Law of Isomorphism as "the most important discovery since the establishment of chemical proportions," and used it largely to determine atomic weights, and to correct some of his former values.

Boisbaudran. — In later years Lecoq de Boisbaudran drew conclusions as to the atomic weight of his new element—Gallium—by means of the isomorphism of its potash alum with the similar alum of aluminium, and thus decided that the formula for the sulphate was $Ga_2(SO_4)_3$. Using this formula, the atomic weight works out to 69·9, which value fits into the periodic table.

Mitscherlich himself discovered isomorphism from the four following salts: — H_2KPO_4, H_2KAsO_4, $H_2(NH_4)PO_4$ and $H_2(NH_4)AsO_4$, all of which crystallise in the tetragonal system, and also from corundum —Al_2O_3—and hæmatite—Fe_2O_3—which crystallise in the hexagonal system.

For more detailed information on this very broad and interesting subject, reference must be made to the larger works on crystallography. The long and very thorough researches of A. E. Tutton on this subject are specially recommended as an example of the method with which the problem should be attacked.[2]

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[1] *Ann. Chem. Phys.* (2). 4 (1817), p. 72 ; 7, p. 399, and 8, p. 5 (1818).

[2] *Journ. Chem. Soc.* 63 (1893), p. 337 and ff., and 69 (1896), p. 344 and ff.

The appended table is a list of isomorphous elements. Partial isomorphism alone is displayed by elements separated with a semicolon.

Isomorphous Series.

1. Cl, Br, I, F ; Mn (in Permanganates).
2. S, Se; Te (in the Tellurides); Cr, Mn, Te (in the acids of the forms H_2RO_4) ; As, Sb in the glances MR_2.
3. As, Sb, Bi; Te (as an element) ; P, Vd (in salts); N, P (in organic bases, *e.g.*, Phosphonium and Ammonium compounds).
4. K, Na, Cs, Rb, Li; Tl, Ag.
5. Cu, Ba, Sr, Pb ; Fe, Zn, Mn, Mg ; Ni, Co, Cu ; Ce, La, Di, Er, Y with Ca ; Cu, Hg with Pb; Cd, Be, In with Zn ; Tl with Pb.
6. Al, Fe, Cr, Mn ; Ce, U (in sesquioxides).
7. Cu, Ag, in "ous" compounds ; Au.
8. Pt, Ir, Pd, Ru, Rh, Os ; Au, Te, Ni ; Sn, Te.
9. C, Si, Ti, Zr, Th, Sn ; Fe, Ti.
10. Ta, Nb.
11. W, Cr, Mo.

It was previously noted that the agreement of the angles of isomorphous crystals is never perfect, except in the case where these crystals belong to the regular system. As examples of this the following may be cited :—

Aragonite	$CaCO_3$	116° 10′	These crystallise in the rhombic system.
Strontianite	$SrCO_3$	117° 19′	
Witherite	$BaCO_3$	118° 30′	
Cerussite	$PbCO_3$	117° 14′	

Calcite	$CaCO_3$	105° 8′	These crystallise in the rhomohedral system.
Magnesite	$MgCO_3$	107° 10′	
Calamine	$ZnCO_3$	107° 40′	
Spathic Iron Ore	$FeCO_3$	107° 0′	
Dolomite	$Ca(Mg)CO_3$	106° 15′	

It will be noticed that the angle of dolomite lies between those of calcite and magnesite.

It will not be necessary to go further into this subject of isomorphism for our present purpose.

Vapour-Density Determinations.

We must not conclude this chapter without mentioning the value of vapour-density determinations in the fixing of atomic weights.

The method cannot be used for the actual determination of atomic weights owing to the errors of experiment involved by the use of the high temperatures required in some cases for the volatilisation of the compounds. However, it affords an excellent means of ascertaining the maximum atomic weight of an element, when its equivalent has been found by analysis.

The compounds most frequently employed are the halides or hydrides, these being usually the most easily volatile.

Of the three methods of determination available, namely, those of Dumas, of Hofmann, and of Victor Meyer, the first and last are the most frequently used. In cases where the substance does not volatilise below a high temperature, Victor Meyer's method is always used. A description of these various methods and a discussion of their respective advantages and disadvantages would be superfluous, as these are generally well known to most students of general chemistry; and further, they are all well described in the different text-books on the subject. As an example of the many cases in which the knowledge of the vapour density of a compound has been the means of settling the atomic weight of an element, beryllium chloride may be cited.

The formula assigned to this body was $BeCl_3$, and the equivalent of beryllium being 4·6, its atomic weight would thus be $3 \times 4{\cdot}6 = 13{\cdot}8$. This was disputed because such an element would not fit in with the periodic classification. A determination of the vapour density of the compound gave 40·42. Hence the molecular weight must be 80·84. Obviously, therefore, there cannot be more than two atoms of chlorine in the molecule. Assuming the formula to be $BeCl_2$, beryllium would have an atomic weight of 9·2, and the vapour density of the chloride would be $\frac{1}{2}(9{\cdot}2 + 70{\cdot}92) = 40{\cdot}06$, which is sufficiently near to the observed vapour density to justify the assumption of the formula chosen. This is only one of many such cases, but it serves to show the method of applying the result of a vapour-density determination to the settling of atomic weights. The following papers on the subject may be consulted :—

Dumas, *Ann. Chim. Phys.* (2), 33 (1826), p. 341.
Habermann, *Ann.* (*Liebig*) 187 (1877), p. 341.
Hofmann, *Berichte*, 1 (1861), p. 198.
Do., do., 9 (1868), p. 1304.
Victor Meyer, *Berichte*, 10 (1868), p. 2068.

Victor Meyer, *Berichte*, 11 (1869), pp. 1867 and 2253.

Demuth and V. Meyer, *Berichte*, 23 (1875), p. 311.

The various cases to which these physical laws have been applied will be found in the next chapter in that portion dealing with the selection of the atomic weights. Their great value will be quite obvious, and this is probably a sufficient excuse for their introduction here, although, of course, strictly speaking, they do not come under the category of the Periodic Law.

CHAPTER III

A DISCUSSION ON THE PERIODIC LAW

(A) *The Relations existing between the Properties of the Elements.*

THE ideas of Mendeléeff and Lothar Meyer were at first difficult to carry through, owing to the fact that there was no systematic way of selecting the true atomic weight from the possible values, and further, that several determinations of this important constant had proved to be false. Mendeléeff was most energetic in the task of setting these points right, for he thoroughly believed in his discovery, and we shall see later how justified he was in so doing.

Some of the values had to be doubled to make them fit into the table and others had to be halved, whereas again several were either a few units too high or too low. However, it was found that the determinations, and not the law, were at fault. The only exception was tellurium, which will be found discussed below.

Lothar Meyer's table and Mendeléeff's first table are practically identical. They are, however, both given here for the sake of completeness.

The table here reproduced is not the original one, but a slight modification of it. The latter was given

L. Meyer's Table.

HYDROGEN = 1

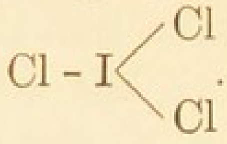
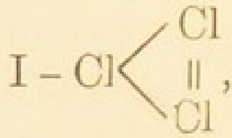
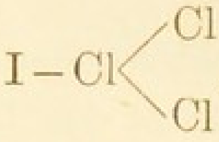
A I	B	A II	B	A III	B	A IV	B	A V	B	A VI	B	A VII	B	VIII
Li		Be		B		C			N		O		F	
Na		Mg		Al		Si			P		S		Cl	
K		Ca		Sc		Ti		V		Cr		Mn		Fe. Co. Ni
	Cu		Zn		Ca		Ge		As		Se		Br	
Rb		Sr		Y		Zr		Nb		Mo				Ru. Rh. Pd
	Ag		Cd		In		Sn		Sb		Te		I	
Cs		Ba		La		Ce		Di						
		Er		Yb				Ta		W				Os. Ir. Pt.
	Au		Hg		Tl		Pb		Bi					
						Th.				U				

1 [2, 3] 2 [1] 3 [1] 4 [2] 5 [3] 6 [2] 7 [1] 8 [2, 3, 4]

in Chap. I. (*q.v.*). It will be seen from this modified table that the sequence of the elements is a continuous one, the last member of one row immediately preceding the first of the next. This becomes at once apparent if such a table be cut out and pasted on a cylinder so that Group VIII. of the Li-F line is touching Group I. of the Na-Cl line and so on.

The numbers at the bottom of the table refer to the valencies of the elements in the same vertical column. The numbers not in brackets indicate the normal valency, whilst those in brackets show the other valencies, which the elements exhibit under certain conditions. For example, take the case of sulphur. Its normal valency is 6, which it possesses in sulphur trioxide SO_3 and in the sulphates R_2SO_4. But in sulphuretted hydrogen H_2S and in carbon disulphide CS_2 it is divalent. It must be understood that the numbers at the bottom of the table do not include all the valencies which an element exhibits. Thus, in sulphur dioxide SO_2 sulphur is tetravalent, and this is also the case in many organic compounds, *e.g.*, the sulphines, of which the following may be taken as typical:—$(C_2H_5)_3SI$—triethyl sulphine iodide. Here the expression (C_2H_5) represents the monovalent radical ethyl, three of which, together with an atom of iodine, are joined to the sulphur atom.

However, the question as to what valency an element actually possesses in a compound is in many cases a very difficult one to settle. For example, a compound of the formula ICl_3 is known.

Here iodine is probably trivalent, and the graphic formula of this compound would be  $\mathrm{Cl-I}{<}\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\end{array}$. But another possible formula might be  $\mathrm{I-Cl}{<}\begin{array}{l}\mathrm{Cl}\\ \|\\ \mathrm{Cl}\end{array}$, or  $\mathrm{I-Cl}{<}\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\end{array}$, in which iodine is monovalent, and at least one chlorine is trivalent. Now it is not impossible that iodine may be trivalent in the above-mentioned organic compound, in which case sulphur would then be hexavalent.

This question of valency will be more fully entered into in a subsequent portion of this treatise (*v.* Chap. IV.).

Returning again to the subject proper, we have the first table of Mendeléeff.

MENDELÉEFF'S FIRST TABLE.

Series. 1	H	...	...	RH_4	RH_3	RH_2	RH	Hydrogen cpds.
2	Li	Be	B	C	N	O	F	
3	Na	Mg	Al	Si	P	S	Cl	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe, Co, Ni, Cu
5	(Cu)	Zn	Ga	Ge	As	Se	Br	
6	Rb	Sr	Y	Zr	Nb	Mo	...	Ru, Rh, Pd, Ag
7	(Ag)	Cd	In	Sn	Sb	Te	I	
8	Cs	Ba	La	Ce	(Di?)	...	...	
9	...	...	...	...	...	...	...	
10	...	...	Yb	...	Ta	W	...	Os, Ir, Pt, Au
11	(Au)	Hg	Tl	Pb	Bi	...	..	
12	...	...	...	Th	...	U	...	
	1	2	3	4	5	6	7	8

Groups.

It will be seen that this table is almost the same as that of Lothar Meyer, but the following little differences between the two may be noted :—

(1.) What Mendeléeff calls a group Lothar Meyer calls a natural family, and divides each family into two groups, A and B.

(2.) Mendeléeff introduces the elements Cu, Ag, and Au in two places:—in Group 8, and again in the next series in Group 1.

(3.) The Groups 4, 5, 6, and 7 of the first series are occupied by undiscovered compounds of hydrogen.

(4.) Mendeléeff places hydrogen with the metals of the alkalis Li, Na, etc., whereas Lothar Meyer puts it at the head of his table.

(5.) Mendeléeff puts Li, Be, B, C, N, O, and F in the same vertical columns as K, Ca, Sc, Ti, V, Cr and Mn respectively, whilst Na, Mg, Al, Si, P, S and Cl are placed with Cu, Zn, Ga, Ge, As, Se and Br respectively. In Meyer's arrangement we find Li, Na, K in the same column, as also Be, Mg, Ca; B, Al, Sc; C, Si, Ti; but N is placed with P, O with S, and F with Cl. These facts are at once obvious on comparing the tables.

The above are the only differences existing between the two tables, otherwise they are identical.

It will be seen that every element bears a resemblance to its succeeding member of the same vertical column, and also to the element intermediate between these in the other vertical column of the same group:—Beryllium resembles both calcium and magnesium, sulphur resembles chromium and selenium, carbon resembles silicon and titanium, and so on.

It was this fact that induced Mendeléeff to formulate his second table. In this the number of rows is doubled so as to separate these groups, and in this way the most closely allied elements are in the same row. The table is here reproduced—

MENDELÉEFF'S SECOND TABLE.

R_2O	I	Li	K	Rb	Cs	...	...
RO	II	Be	Ca	Sr	Ba	...	...
R_2O_3	III	B	Sc	Y	La	Yb	..
RO_2	IV	C	Ti	Zr	Ce	...	Th
R_2O_5	V (III)	N	V	Nb	Di	Ta	...
RO_3	VI (II)	O	Cr	Mo	..	W	U
R_2O_7	VII (I)	F	Mn	..	...	...	...
RO_4	VIII	...	Fe Co Ni	Ru Rh Pd	...	Os Ir Pt	...
R_2O	I	Na	Cu	Ag	...	Au	..
RO	II	Mg	Zn	Cd	...	Hg	...
R_2O_3	III	Al	Ga	In	...	Tl	...
RO_2	IV	Si	Ge	Sn	...	Pb	...
R_2O_5	V (III)	P	As	Sb	...	Bi	...
RO_3	VI (II)	S	Se	Te	...	...	...
R_2O_7	VII (I)	Cl	Br	I	...	...	...

This table is practically the previous one rotated through a right angle and arranged in fifteen rows, and six columns instead of eight rows and twelve columns. The contents of both tables are the same. Before commencing the systematic study of the properties of the elements in relation to their atomic weights, it will be convenient to briefly consider the periodic arrangement as a whole. We have first the chemical properties. Referring to Mendeléeff's second table, we see that each vertical column begins with an alkali metal, followed by one of the alkaline earths, then by one of the earths proper, and so on. The elements of the first row are the strongest bases, whilst those of the seventh and fifteenth rows have strong acidic properties, and there is a gradual transition as we pass from the first to the seventh, and from the ninth to the fifteenth.

We also notice a gradual gradation of properties as we pass along a horizontal row.

Thus P_2O_5 combines with water forming the powerful phosphoric acids, the acid of As_2O_5 is decidedly weaker, whilst the oxide of bismuth Bi_2O_5 is devoid of acid properties. Similarly, the chemical activity of chlorine, bromine and iodine shows a gradual falling off as we pass from chlorine to iodine.

The valency of the elements also varies in a marked way. This is indicated by the Roman numerals in the table. Thus we have the valency increasing from 1 to 8 in the oxygen compounds as we pass down a vertical column, whilst the valency towards hydrogen reaches a maximum at the fourth row and then decreases again. This is repeated in the lower half of the table. A more detailed consideration is given later.

The elements in the eighth row form a sort of transition between those of the seventh and ninth rows, thus we see that Fe, Co and Ni resemble both manganese and copper in some of their properties.

The expressions R_2O, RO, etc., in the table indicate the general formula of the highest oxide. But it must be remembered that several elements form many different oxides, *e.g.*, manganese; the highest oxide is Mn_2O_7, but it also forms MnO, Mn_2O_3, MnO_2, Mn_3O_4, and MnO_3.

The formulæ of the hydroxides and halides also show a regular change as we pass along the series, *e.g.*, $Na(OH)$, $Mg(OH)_2$, $Al(OH)_3$, $Si(OH)_4$, $PO(OH)_3$, which is $P(OH)_5$ less one molecule of water, $SO_2(OH)_2$, which is $S(OH)_6$ less two molecules of water, and $ClO_3(OH)$, which is $Cl(OH)_7$ less three molecules of water. Similarly for the halides, and indeed for almost all the definite compounds.

Secondly, as regards physical and mechanical properties, we also notice a marked periodicity. Among the many such properties investigated the following may be cited:—Melting Points, Atomic Volumes, Heats of Formation of Salts, Colour of the Ions, Conductivity for Heat and Electricity, Young's Modulus, etc. In short, we may say, that every well-defined property of an element is a function of its atomic weight.

We will now discuss each of these properties in turn, and as it is thought desirable to make this branch of the subject as complete as possible, considerable space will be devoted to it.

Also tables comprising all the known data will be given either in the text or in the Appendix, whichever seems to be the more convenient. The most recent will be employed wherever this is possible, but in cases where the older values are of interest historically they will be also inserted.

The properties of the elements will be considered under the following headings:—

(1.) Numerical Relations of the Atomic Weights themselves.

(2.) The Physical Properties of the Elements in Relation to their Atomic Weights.

(3.) The same with reference to the Chief Compounds.

(4.) Uses of the Periodic Arrangement in Fixing Atomic Weights, and also in the Prediction of Properties of Undiscovered Elements.

Before considering the relations existing between the numbers expressing the atomic weights, it will be desirable to give in a clear and concise form the reasons for accepting the values assigned to the elements. This has been very well done by Professor Ostwald in his *Outlines of General Chemistry*, 1895, pp. 180-182, from which the following summary is mainly taken. For a more complete digest of atomic weight determinations the reader is referred to Clarke's *Constants of Nature and Recalculations of the Atomic Weights*. Also to the same author's *Annual Reports of the Committee on Atomic Weights*. And further, to Ostwald's *Lehrbuch der Allgemeinen Chemie*.

No account is given of the methods used to determine the equivalent of the element. This is assumed to be known, and then the atomic weight is fixed from the consideration of the methods given in the summary. The values here given are only approximate.

Hydrogen	H=1·0.	Being the lightest substance known, it served as a standard. If H=1·000, then O=15·88. However, later it was found more convenient to take O=16·00, whence H=1·008.
Helium	He=4·0.	From the density, specific heat, and ratio of the two specific heats.
Lithium	Li=7·03.	From the specific heat, which is normal in spite of the low atomic weight (*v.* Chap. II.).
Beryllium	Be=9·08.	From the composition and vapour density of its volatile chloride.
Boron	B=11·0.	From the vapour density of its volatile compounds.
Carbon	C=12·0.	From the vapour densities of a great many inorganic and organic compounds.
Nitrogen	N=14·0.	From the volume composition of ammonia and the various oxides, and from the equality of its atomic heat with those of hydrogen and oxygen.
Oxygen	O=16·0.	From the volume composition of water, and from the equality of its atomic heat with that of hydrogen.
Fluorine	F=19·0.	From the complete analogy to chlorine.
Neon	Ne=20·0.	Same as helium (*q.v.*).
Sodium	Na=23·05.	From the specific heat.
Magnesium	Mg=24·3.	Do.
Aluminium	Al=27·0.	From the vapour density of its chloride and the specific heat of the metal.
Silicon	Si=28·4.	From the vapour density of the halide and the isomorphism with zirconium and titanium.
Phosphorus	P=31·0.	From the vapour density of hydrogen phosphide, and with some uncertainty from the specific heat.
Chlorine	Cl=35·45.	From the volume composition of hydrogen chloride and the vapour densities of several chlorine compounds.
Argon	Ar=39·9.	Same as helium (*q.v.*).
Potassium	K=39·1.	From the specific heat.
Calcium	Ca=40·1.	Do.
Scandium	Sc=44·1.	From the isomorphism with aluminium.
Titanium	Ti=48·1.	From the vapour density of the tetrachloride and the isomorphism with silicon and tin.
Vanadium	V=51·4.	From the vapour densities of chloride and oxychloride, and from the isomorphism with phosphorus and arsenic.

Chromium	Cr = 52·1.	From the specific heat, and from the vapour density of its volatile compounds.
Manganese	Mn = 55·0.	From the specific heat.
Iron	Fe = 56·0.	From the specific heat, the vapour density of its trichloride and partial isomorphism with calcium.
Nickel	Ni = 58·7.	From the specific heat.
Cobalt	Co = 59·0.	Do.
Copper	Cu = 63·6.	From the specific heat and isomorphism with iron.
Zinc	Zn = 65·4.	From the vapour density of the metal and its chloride, from the specific heat, and the isomorphism with magnesium.
Gallium	Ga = 69·9.	From the isomorphism with aluminium, from the specific heat, and from the vapour density of its volatile compounds.
Germanium	Ge = 72·5.	From the specific heat (uncertain).
Arsenic	As = 75·0.	From the vapour density of the chloride, the specific heat, and the isomorphism with phosphorus.
Selenium	Se = 79·2.	From its isomorphism with, and analogy to, sulphur.
Bromine	Br = 79·9.	From its analogy to chlorine.
Krypton	Kr = 82·0.	Same as helium (*q.v.*).
Rubidium	Rb = 85·4.	From its isomorphism with potassium.
Strontium	Sr = 87·6.	From its isomorphism with lead and calcium.
Yttrium	Y = 89·0.	From its isomorphism with cerium, etc.
Molybdenum	Mo = 95·9.	From the isomorphism with chromium, the specific heat, and from the vapour density of the volatile compounds.
Ruthenium	Ru = 101·7.	From the specific heat.
Rhodium	Rh = 103·0.	Do.
Palladium	Pd = 106·4.	Do.
Silver	Ag = 107·9.	Do.
Cadmium	Cd = 112·4.	From the vapour density and the specific heat.
Indium	In = 113·8.	From the specific heat (uncertain).
Tin	Sn = 119·0.	From the vapour density of the chloride, the specific heat, and the isomorphism with silicon, titanium and zirconium.
Antimony	Sb = 120·4.	From the vapour density of the volatile compounds, the specific heat, and the analogy to arsenic.
Tellurium	Te = 127·5.	From the isomorphism with, and analogy to, sulphur and selenium.
Iodine	I = 126·8.	From its perfect analogy to chlorine and bromine.

Xenon	X=128·0.	Same as helium (*q.v.*).
Cæsium	Cs=132·9.	From its isomorphism with potassium and rubidium.
Barium	Ba=137·4.	From its isomorphism with calcium, strontium and lead.
Lanthanum	La=138·6.	From the specific heat.
Cerium	Ce=139·3.	Do.
Didymium (Praseodymium)	Prd=140·5.	Do.
,, (Neodymium)	Ndi=143·6.	Do.
Ytterbium	Yb=173·2.	Is analogous to, and isomorphous with, the preceding.
Tantalum	Ta=182·8.	From the vapour densities of its volatile compounds.
Tungsten	W=184·8.	From the vapour density of its chloride, the specific heat, and the analogy to chromium and molybdenum.
Osmium	Os=191·0.	From the specific heat.
Iridium	Ir=193·1.	Do.
Platinum	Pt=194·9.	Do.
Gold	Au=197·2.	Do.
Mercury	Hg=200·00.	From the vapour densities of metal and chloride, and from the specific heat.
Thallium	Tl=204·1.	From the vapour density of the monochloride, the specific heat, and the isomorphism with potassium.
Lead	Pb=206·9.	From the specific heat, the vapour density of the chloride, and the analogy to calcium.
Bismuth	Bi=208·1.	From the specific heat, the vapour density of the chloride, and the analogy to arsenic and antimony.
Thorium	Th=232·6.	From the specific heat and the isomorphism with zirconium.
Uranium	U=239·6.	From the specific heat, the vapour densities of the halides, and the analogy to chromium.

This table does not include all the data for the selection of the atomic weights, but only the most important. However, the facts mentioned are in nearly all cases quite sufficient to justify the acceptance of the atomic weights now in use.

It cannot but be noticed that in the above table nearly all the confirmations given are the outcome of at least one of the three physical laws discussed in the preceding chapter, and hence their introduction into this book has seemed perfectly justifiable.

The position of the new inactive gaseous elements —helium, neon, argon, krypton and xenon—in the periodic table will be considered at a later stage. Suffice it to state here that they do not, as was at first supposed, upset the arrangement at all, but, on the contrary, supply a missing link between two groups of elements of very different properties.

The elements (?) of the rare earths, such as terbium and gadolinium, will not be discussed here, as they are at present in a state of chaos, and little is to be gained by trying to insert them in the table. The extensive and laborious researches of Crookes, Krüss, Nilson and others have led to nothing definite, for the observers obtain different results according to the method of attacking the problem employed. A few words about these very tantalising bodies will be said later.

Again, tellurium has been rather difficult to reconcile to our present views. For with an atomic weight 127·49, it should follow iodine, whose atomic weight is 126·85. However, from its complete analogy to selenium, and, in a less degree, to sulphur, it theoretically should precede iodine. Therefore we should expect its atomic weight to be about 125. Brauner, who has carried out some extensive researches on this subject, concluded, in 1889, that tellurium was not a simple substance, and he succeeded in obtaining from tellurium a body with an atomic weight 125-126. However, in his later papers, he has again assigned to tellurium the atomic weight 127·4. It is most probable that tellurium is really a mixture, and that the actual atomic weight of the element following selenium is about 125. The impurities might probably be the next elements in the same column. But time and experiment can alone settle this question. It is not very likely that the periodic classification is here at fault.

We now come to a consideration of the relations between the numbers expressing the atomic weights. The references as to rows and groups are to Mendeléeff's first table.

(*a*) VERTICAL GROUPS.

It will be seen that in many cases the atomic weight of one element in the right-hand column of a group is approximately the mean of the atomic weights of the two nearest elements to it in the left-hand column of the same group, *e.g.*, Mean of At. Wts. of B and $\text{Sc}=\frac{1}{2}(10{\cdot}95+44{\cdot}12)=27{\cdot}53$, and the atomic weight of aluminium is 27·1. Proceeding in this way, we get the following results:—

	Na.	Mg.	Al.	Si.	P.	S.	Cl.
Calculated .	23·07	24·57	27·53	30·07	32·71	34·07	37·02
Found .	23·05	24·28	27·11	28·40	31·02	32·07	35·45
Difference .	+0·02	+0·29	+0·42	+1·67	+1·69	+2·00	+1·57

	Cu.	Zn.	Ga.	Ge.	As.	Se.	Br.
Calculated .	62·27	63·84	66·57	69·27	72·55	74·06	?
Found .	63·60	65·41	69·91	72·48	75·01	79·17	79·76
Difference .	−1·33	−1·57	−3·34	−3·21	−2·46	−5·11	?

	Ag.	Cd.	In.	Sn.	Sb.	Te.	I.
Calculated .	109·16	112·52	113·83	114·87	117·34	?	?
Found .	107·92	112·38	113·85	119·05	120·43	127·49	126·85
Difference .	+1·24	+0·14	−0·02	−4·18	−3·09	?	?

These are all the data at our disposal. Let us now similarly calculate the atomic weights of elements in the left-hand columns from those in the right-hand column of the same group as before, *e.g.*, $\frac{1}{2}(\mathrm{Na}+\mathrm{Cu})=\frac{1}{2}(23{\cdot}05+63{\cdot}60)=43{\cdot}32$, whilst $\mathrm{K}=39{\cdot}11$.

Note.—In this and all other calculations involving the atomic weight of didymium, the mean of those of praseodymium, 139·41, and neodymium, 142·52, will be taken. This gives 142·03. Proceeding as above, we get the following results :—

	K.	Ca.	Sc.	Ti.	V.	Cr.	Mn.
Calculated .	43·32	44·84	48·51	50·44	52·63	55·62	57·60
Found .	39·11	40·07	44·12	48·15	51·38	52·14	54·99
Difference .	+4·21	+4·77	+4·39	+2·29	+1·25	+3·48	+2·61

	Rb.	Sr.	Y.	Zr.	Nb.	Mo.	?
Calculated .	85·76	88·89	91·88	95·76	97·72	103·33	103·31
Found .	85·43	87·61	89·02	90·40	93·73	95·99	?
Difference .	+0·33	+1·28	+2·86	+5·36	+3·99	+7·34	?

This is all that is possible owing to lack of further data.

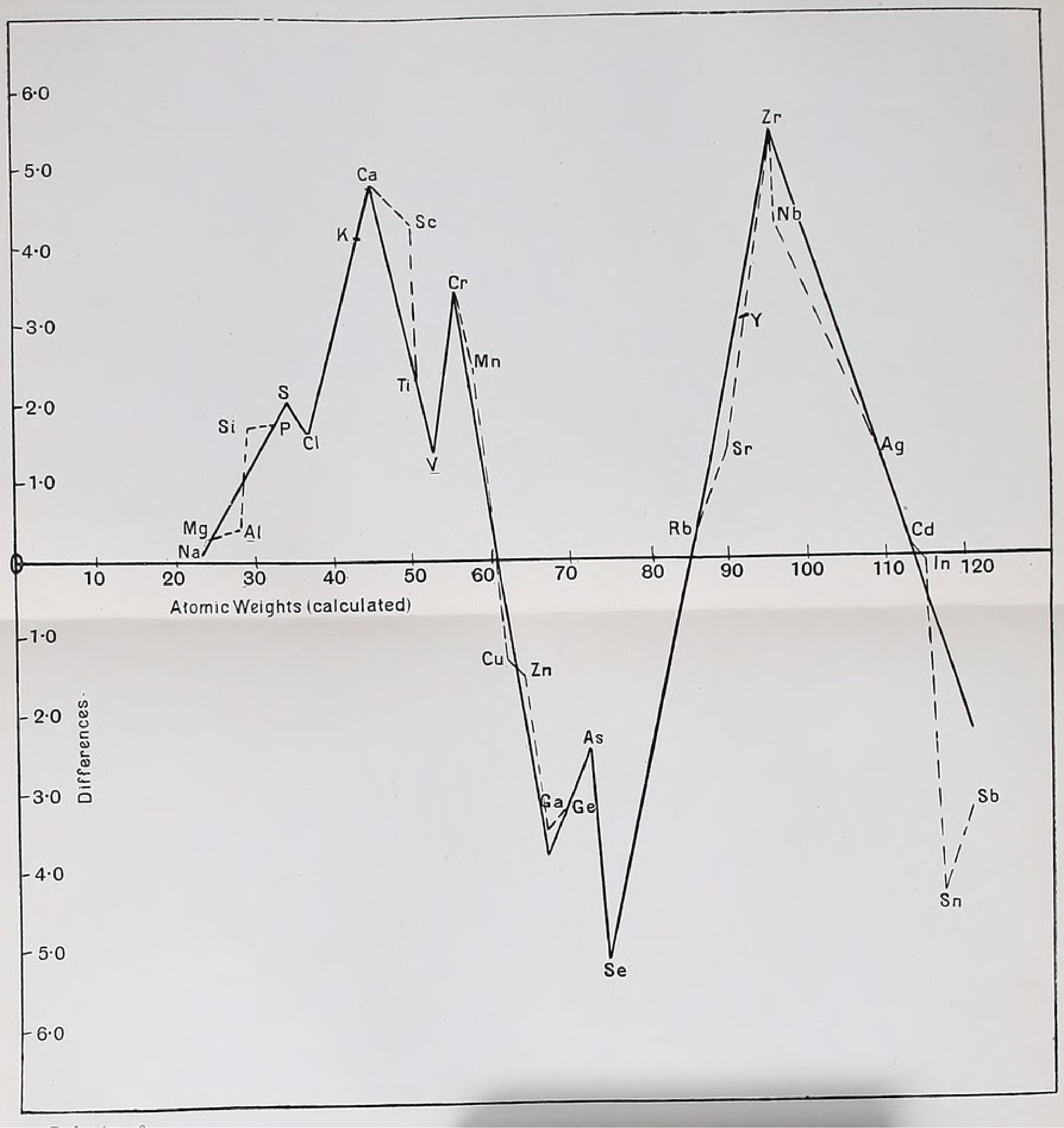
Let us now arrange all the elements, with their calculated and found atomic weights and differences, in order of observed atomic weight sequence, and we arrive at the following interesting table :—

Element.	Obs. At. Wt.	Calc. At. Wt.	Difference.	Element	Obs. At. Wt.	Calc. At. Wt.	Difference.
Na	23·05	23·07	+0·02	Ga . .	69·91	66·57	−3·34
Mg . .	24·28	24·57	+0·29	Ge . .	72·48	69·27	−3·21
Al	27·11	27·53	+0·42	As . .	75·01	72·55	−2·46
Si	28·40	30·07	+1·67	Se . .	79·17	74·06	−5·11
P	31·02	32·71	+1·69	Rb . .	85·43	85·76	+0·33
S	32·07	34·07	+2·00	Sr . .	87·61	88·89	+1·28
Cl	35·45	37·02	+1·57	Y . .	89·02	91·88	+2·86
K	39·11	43·32	+4·21	Zr . .	90·40	95·76	+5·36
Ca	40·07	44·84	+4·77	Nb . .	93·73	97·72	+3·99
Sc	44·12	48·51	+4·39	Mo . .	95·99	103·33	+7·34
Ti	48·15	50·44	+2·29	Ag . .	107·92	109·16	+1·24
V	51·38	52·63	+1·25	Cd . .	112·38	112·52	+0·14
Cr . .	52·14	55·62	+3·48	In . .	113·85	113·83	−0·02
Mn . .	54·99	57·60	+2·61	Sn . .	119·05	114·87	−4·18
Cu	63·60	62·27	−1·33	Sb . .	120·43	117·34	−3·09
Zn	65·41	63·84	−1·57				

From these figures it appears that as the atomic weight increases the "difference" steadily increases until we reach sulphur.

Here there is a small drop, and then a further increase to a maximum at calcium. After this the "difference" decreases to vanadium, rises slightly to chromium, and decreases again to gallium, whence there is a further increase to arsenic, a drop to selenium, and a steady rise to zirconium. Then (omitting molybdenum) a gradual decrease to tin takes place, and after this the difference is again on the increase. Molybdenum has been omitted because it involves the atomic weight of tellurium, a number which cannot at present be relied on in its calculation.

These results are better studied by plotting them in the form of a curve, taking atomic weights as


6·0
5·0
4·0
3·0
2·0
1·0
0
1·0
2·0
3·0
4·0
5·0
6·0
Differences
10
20
30
40
50
60
70
80
90
100
110
120
Atomic Weights (calculated)
Na
Mg
Al
Si
P
S
Cl
K
Ca
Sc
Ti
V
Cr
Mn
Cu
Zn
Ga
Ge
As
Se
Rb
Sr
Y
Zr
Nb
Ag
Cd
In
Sn
Sb

abscissæ and differences as ordinates. In this way we obtain the curve here produced.

It will be seen that there is here a tendency towards periodicity, the curve approaching to one, which might be represented by a formula of the type $y = A\sin(\omega t + \eta)$. However, owing to the irregularities, it does not seem possible to find a suitable expression which will connect the "differences" with the atomic weights.

Perhaps, in later years, when more and better data are available, the results arrived at in this way will be more uniform and lie more nearly on a continuous curve, but in the present state of our knowledge we must be content with approximations.

If we calculate the geometric and the harmonic means in the same way, we arrive at no better results.

There is another method available to elements in the same group, which is as follows:—The atomic weight of an element is compared with the mean of those of the preceding and succeeding elements in the *same* vertical column, *e.g.*, mean of K and Cs $= \frac{1}{2}$ (39·11 + 132·89) = 86·00, and Rb = 85·43. Proceeding in this manner we get the following table :—

	K.	Ca.	Sc.	Ti.	V.	Cr.	Mn.
Calculated .	46·23	48·34	49·98	51·20	53·88	55·99	?
Found .	39·11	40·08	44·12	48·15	51·38	52·14	54·99
Difference .	+7·12	+8·26	+5·86	+3·05	+2·50	+3·85	?

	Cu.	Zn.	Ga.	Ge.	As.	Se.	Br.
Calculated .	65·49	68·33	70·48	73·74	75·73	79·78	81·15
Found .	63·60	65·41	69·91	72·48	75·01	79·17	79·95
Difference .	+1·89	+2·92	+0·57	+1·26	+0·72	+0·61	+1·20

	Rb.	Sr.	Y.	Zr.	Nb.	La.	Di.
Calculated.	86·00	88·75	91·38	93·75	96·70	131·10	138·28
Found .	85·43	87·61	89·02	90·40	93·73	138·64	142·03
Difference.	+0·57	+1·14	+2·36	+3·35	+2·97	−7·54	−3·75

There are no further data. The differences are in most cases small, except in the first row, K to Cr and La and Di, but they are irregular, and no information of any service is to be obtained by plotting the results as before.

(*b*) Horizontal Rows or Series.

We now come to the consideration of the relations existing between the atomic weights of an element with those immediately before and after it in the same horizontal row, *e.g.*, phosphorus with silicon and sulphur. The following results are thus obtained, calculating in a precisely similar manner to the previous ones:—

	Be.	B.	C.	N.	O.	F.
Calculated .	8·99	10·54	12·49	14·00	16·50	?
Found .	9·08	10·95	12·00	14·04	16·00	19·06
Difference .	−0·09	−0·41	+0·49	−0·04	+0·50	?

	Mg.	Al.	Si.	P.	S.	Cl.
Calculated .	25·08	26·34	29·06	30·24	33·23	?
Found .	24·28	27·11	28·40	31·02	32·07	35·45
Difference .	+0·80	−0·77	+0·66	−0·78	+1·16	?

	Ca.	Sc.	Ti.	V.	Cr.	Mn.
Calculated .	41·61	44·16	47·75	50·14	53·18	54·08
Found .	40·07	44·12	48·15	51·38	52·14	54·99
Difference .	+1·54	+0·04	−0·40	−1·24	+1·04	−0·91

	Zn.	Ga.	Ge.	As.	Se.	Br.
Calculated .	67·25	68·94	72·46	75·82	77·48	?
Found .	65·41	69·91	72·48	75·01	79·17	79·75
Difference .	+1·84	−0·97	−0·02	+0·81	−1·69	?

	Sr.	Y.	Zr.	M.	Mo.	?
Calculated .	87·22	89·00	91·37	93·18	?	98·83
Found .	87·61	89·02	90·40	93·73	95·99	?
Difference .	−0·39	−0·02	+0·97	−0·55	?	

	Cd.	In.	Sn.	Sb.	Te.	I.
Calculated .	110·88	115·71	117·14	123·27	123·64	?
Found .	112·38	113·85	119·05	120·43	127·49	126·85
Difference .	−1·50	+1·86	−1·91	+2·84	−3·85	?

	Ba.	La.	Ce.	Hg.	Tl.	Pb.
Calculated .	135·76	138·39	140·33	200·69	203·46	206·13
Found .	137·43	138·64	139·35	200·00	204·15	206·92
Difference .	−1·67	−0·25	+0·98	−0·69	−0·69	−0·79

Here again the results are too irregular to lead to any definite law. The differences are in most cases small, except for antimony and tellurium.

Various attempts have from time to time been made to reduce the numbers expressing the atomic weights to order.

De Chancourtois.—Perhaps the first attempt of the kind may be ascribed to De Chancourtois in 1862, who represented the elements on a helix described round a right circular cylinder, and having a constant slope of 45° to the axis. This has been described and figured in Chap. I. (*q.v.*). His results do not lead to much, and, being himself a geologist and a mathematician, he was not able to follow up his work from a chemical standpoint.

Mills.—In 1884 Dr E. J. Mills published a paper on the "Numerics of the Elements"[1] and another[2] in 1886. He arranges all the elements in order of their atomic weights, and divides them into sixteen groups. He then finds that the atomic weights can be embodied in an expression of the form $y = \mathrm{K} - \mathrm{B}\beta^{x}$, where y represents the atomic weight and x is an integer different for different elements, K is nearly

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[1] *Phil. Mag.* [5], 18, p. 393.

[2] *Phil. Mag.* [5], 21, 151.

equal to $n \cdot 15$, and B is nearly 15. The value of β is ·93727, but for all practical purposes the value $\beta = {\cdot}9375 = \frac{15}{16}$ is sufficiently accurate.

The following is a brief summary of the paper. The numbers after the elements denotes the values of x.

Group 1. Formula $y = 15 - 15\beta^x$.
Li 10. Be 14. B 20. C 25. N 42.
Group 2. $y = 30 - 15\beta^x$.
O 1. F 5. Na 12. Mg 15. Al 25. S 32.
Group 3. $y = 45 - 15\beta^x$.
P 1. S 2. Cl 7. K 14. Ca 17. Sc 42.
Group 4. $y = 60 - 15\beta^x$.
Ti 6. V 8. Cr 10. Mn 17. Fe 20. Ni 31. Co 41.
Group 5. $y = 75 - 15\beta^x$.
Cu 4. Zn 6. Ga 17. As ∞.
Group 6. $y = 90 - 15\beta^x$.
Se 5. Br 6. Rb 18. Sr 27. Y 41. Zr 49.
Group 7. $y = 105 - 15\beta^x$.
Nb 5. Mo 7. Rh 42. Ru 46.
Group 8. $y = 120 - 15\beta^x$.
Pd 1. Ag 3. Cd 9. In 13. Tb 14. Sn 29. Sb ∞.
Group 9. $y = 135 - 15\beta^x$.
I 9. Te 12. Cs. 28.
Group 10. $y = 150 - 15\beta^x$.
Ba 2. La 5. Ce 9. Di 18.
Group 11. $y = 165 - 16\beta^x$.
Sm 1.
Group 12. $y = 180 - 15\beta^x$.
Er 1. Yb 12.
Group 13. $y = 195 - 15\beta^x$.
Ta 2. W 4. Ir 38. Pt 50.
Group 14. $y = 210 - 15\beta^x$.
Au 1. Os ? Hg 6. Tl 13. Pb 22. Bi 28.
Group 15. $y = 225 - 15\beta^x$.
Ng (Norwegium) 14 ?
Group 16. $y = 240 - 15\beta^x$.
Th 10. U ∞.

The differences between the observed and calculated values are in all cases small.

The formula is interesting inasmuch as it points to an upper limit to the existing system of atomic weights, for after a time the value of β^x ceases to be of importance compared with the value of K. If we assume such a limit, then the atomic weights can be expressed by a formula of the type $y=pn-n\left(\frac{n}{n+1}\right)$ where $(n+1)$ is the number of the groups. Further, hydrogen may then be viewed as a relic of some earlier system expressible by the formula

$$y=1\times1-1\left(\frac{1}{1+1}\right)^x.$$

It is worthy of note that the sum of all terms of the form $15(0{\cdot}9375)^x$ between the limits $x=0$ and $x=\infty$ is, according to Mills, exactly equal to 240. However, a recalculation shows it to be equal to 232·4 for

$$\int_0^\infty 15(0{\cdot}9375)^x dx = -\frac{15}{log_e(\cdot9375)} = -\frac{15.log_{10}e}{log_{10}(\cdot9375)} = 232{\cdot}4.$$

Now 240 is the atomic weight of uranium, which is at present the element of greatest atomic weight known. This was also considered to point to a superior limit to the elements.

Mills assumes the elements to be stable, more or less incomplete stages, in the condensation of a primary matter as it gradually cooled, and from this he deduces the above formula. The method of argument is as follows:—The law of free cooling was shown by Dulong and Petit[1] to be of the form $x=ba^t$, where x is the number of centigrade degrees lost per minute, t is the temperature, a is a constant

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[1] *Ann. Chim. Phys.* (vii.), 1817, p. 252.

and has the value 1·0075, whilst b is also a constant. The law of heating is the inverse of this, and is of the form $x=b\left(\frac{1}{1{\cdot}0075}\right)^{t}$ or $x=m\,(0{\cdot}99256)^{t}$.

Now, at the temperature at which polymerisation takes place, there is an evolution of heat, and therefore a slight dissociation again sets in. If, then, the elements depend on polymerisations, more or less inverted by heat at the formation point, then they must correspond to an equation of the form $y=(1, 2, 3\ldots)n-ba^{t}$. Now in the actual case n and b have practically the same value—15, whilst a is 0·9375.

This system may be typically represented as $y=(1, 2, 3\ldots)n-\left(\frac{n}{n+1}\right)^{t}$. The equation $y=-15({\cdot}9375)^{t}$ represents a rate of heating under constant conditions in a unit of time.

Tchitchérin.—In 1888 B. N. Tchitchérin, from a study of the alkali metals, found that their atomic volumes could be represented by the formula $y=\mathrm{A}\,(2-0{\cdot}00535\mathrm{A}n)$ where y is the atomic volume, A the atomic weight, and n an integer, which has the value 8 for lithium and sodium, 4 for potassium, 3 for rubidium, and 2 for cæsium.

If n were always equal to 8, then when $\mathrm{A}=46{\cdot}6$ the atomic value would be zero, and when $\mathrm{A}=23{\cdot}3$ it would have a maximum value. The fact that 23·3 is very nearly equal to the atomic weight of sodium and that 46·6 is approximately the difference between the atomic weights of succeeding elements in the same groups, *e.g.*, Cs – Rb, I – Br, etc., together with the fact that *n* is always an integer, make Tchitchérin believe that this formula affords a clue to the nature of the elements. No other classes of elements were so satisfactorily examined, and hence no similar formula were devised to express their atomic volumes.

Stoney.—In 1889 we have the "Logarithmic Law of the Atomic Weights" by Dr G. Johnstone Stoney embodied in a paper read before the Royal Society. He represents the atomic weights on a spiral curve, which closely approaches a logarithmic or an elliptic spiral.

The prominent feature of the diagram is that it represents atomic weights by the volumes of concentric spheres. These spheres are, of course, represented on a plane surface by means of a system of concentric circles. Now, since the volumes of spheres are to one another as the cubes of their radii, we can describe circles with radii equal to the cube roots of the atomic weights which will then represent the spheres. A circle of 1 cm. radius represents hydrogen. The circumference is divided into sixteen equal parts by radii drawn at equal angles—$22\frac{1}{2}°$ to one another. Taking any one of these radii, we mark off on it a distance equal to $\sqrt[3]{7{\cdot}03}$ cms. from the centre to represent lithium. On the next one to the right we map beryllium, *i.e.*, $\sqrt[3]{9{\cdot}08}$, on the next boron and so on, leaving a vacant space for every element missing in Mendeléef's table. By joining all the points thus obtained, we get a spiral curve closely corresponding to a mathematical curve derived from a logarithmic or from an elliptic formula. The deviations from this theoretical curve are in most cases small, and seem to vary periodically. By continuing the curve we can find the position of hydrogen. It is found that similar elements fall on the same radius, for example Na, K, Rb and Cs. In this way hydrogen comes in the same category as zinc, cadmium, magnesium and mercury, to none of which it shows the slightest analogy.

Among the good points of this curve the following may be mentioned:—

(1.) The deviations from a mathematical curve are in most cases very small, the chief exceptions being H, Li, Ca, Ti, Fe, Te and W.

(2.) Similar elements do in all cases except those of hydrogen and helium fall on the same radius.

(3.) The figure can be divided into four quadrants containing elements, which are alternately electro-positive and electro-negative.

(4.) The transition between the electrical states is gradual, but becomes abrupt between the radius containing Cl, Br and I (No. 15), and the radius Li, K, Rb, Cs (No. 1), between which lies the vacant radius which is called number 16 on the diagram.

(5.) The vacant radius 16 has now been partly filled by the new atmospheric gases discovered by Professor Ramsay, which are inert, and whose electrical states can thus be denoted by $\pm\infty$. In this way they form the transition between the elements on radii 15 and 1.

However, there are also a few objections to be raised to the law, and these are :—

(1.) If hydrogen should fall on Na, Cu radius, then it shows a deviation of nearly three (2·92) millimetres from the mathematical curve, whereas if there be no such deviation, then it falls on the Zn, Cd, etc., radius. Either of these shows that hydrogen does not fit in well.

(2.) There are six vacant spaces between lithium and hydrogen, that is between the atomic weights 1 and 7, and this seems very improbable when compared with the way in which the atomic weights of the known elements differ from one another.

(3.) Helium again falls badly off the curve, if it be considered as a member of radius 16 to which it undoubtedly belongs.

(4.) Neon comes with iron, cobalt, nickel and the platinum metals, to none of which it can be said to bear much resemblance except as a transition element.

(5.) The curve requires three elements lighter than hydrogen. It is shown that one of these has an atomic weight equal 1-64th part of that of hydrogen. The existence of these elements in our atmosphere seems rather questionable owing to their extreme lightness. They could not possibly be solids or liquids. Whether they exist in the stars remains yet to be proved.

These few points make the logarithmic law appear rather open to doubt, although the other elements seem to fit in remarkably well.

Carnelley.—In 1890 the late Professor Carnelley published an interesting paper[1] in which he showed that the atomic weights might be represented with a tolerable degree of accuracy by the formula $A=c(m+\sqrt{v})$ where A is the atomic weight, m is a term of an arithmetical series depending on the group to which the element belongs, v is the number of the group, and c is a constant. Excluding the elements of the first three series, the formula becomes $A=c(3{\cdot}5a\div 9+\sqrt{v})$ where a is the number of the series, c is a constant, and has approximately the value 6·64. This is nearly the same as the value of the atomic heat. If this were so, then the specific heats should be given by the formula $s=\frac{1}{m+\sqrt{v}}$. This is found to be actually the case, although it may simply result accidentally from the particular choice of the units employed.

Adkins.—In 1892 H. Adkins published a relation between the atomic weights.[2] He states that all the elements can be formed from the series 7 Li, 9 Be, 11 B and 12 C, in regular sequence by taking a basic number, which is either an alkali, an alkaline earth, or a mixture of the two, and adding this successively to each member of the series. He claims for his scheme that it exhibits a degree of sequence of the atomic weights. The only exceptions are a small anomalous group, and a reduplication of 12 in the case of magnesium.

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[1] *Phil. Mag.* [5], 29, 27.

[2] *C. N.* 65, p. 123.

Below is given a condensed summary of the arrangement. It will be seen that several numbers, which have no counterpart in the periodic classification, have to be omitted. The scheme has little to recommend itself, and is merely introduced here as an example of various attempts of a similar nature.

TABLE.

Basic number	7	7	7	7	Alkali	12
Sequence .	7	9	11	12		12
	14 N	16 O	(18)	19 F		24 Mg.
Basic number	9	9	9	9	Earth	
Sequence .	14	16	18	19		
	23 Na	(25)	27 Al	28 Si		

Anomalous group alternately alkali and earth base.

Basic number	24	23	24	24	24	23	24
Sequence .	7	9	11	12	14	16	19
	31 P	32 S	35 Cl	36 Cl	(38)	39 K	(43)
			$\underbrace{\qquad\qquad\qquad}$				

The base now changes to 16, *i.e.*, 7 Li alkali + 9 Be earth.

Basic number	16	16	16	16	16	16	16	16
Sequence .	23	24	27	28	31	32	35	36
	39 K	40 Ca	(43)	44 Sc	(47)	48 Ti	51V	52 Cr

The next basic number is 56, *i.e.*, 40 Ca earth + 7 Li alkali + 9 Be earth = 56.

Basic number	56	56	56	56	56	56	56	56	56
Sequence .	7	9	11	12	14	16	19	23	24
	63 Cu	65 Zn	(67)	(68)	70 Ga	72 Ge	75 As	79 Se	80 Br

Base now is 78 = 2 × 39 K alkali.

Basic number	78	78	78	78	78	78	78	78
Sequence .	7	9	11	12	14	16	18	19
	85 Rb	87 Sr	87 Y	90 Zr	(92)	94 Nb	96 Mo	97

The next group takes 94 for its base, *i e.*, 2×39 K $+ 7$ Li $+ 9$ Be $= 94$.

Basic number	94	94	94	94	94	94	94	74
Sequence	7	9	11	12	14	16	18	19
	(101)	103 Ru	105 Rh	107 Pd	108Ag	(110)	112Cd	113 In

Basic number	94	94	94	94	94	94
Sequence	23	24	27	28	31	32
	(117)	118 Sn	(121)	122 Sb	125 Te	(126)

The remaining groups are incomplete.

Summing up, we have the following list of basic numbers :—7, 9, $7+9=16$, $40+7+9=56$, $39+39=78$, $39+39+16=94$; and in the anomalous group, $12+12=24$, and $7+9+7=23$.

Dulk.—In 1898 a paper appeared by Dr Ludwig Dulk on "Atomic Weight or Atomic Gravitation,"[1] in which the atomic weights and specific gravities of a number of elements are calculated from formulæ derived from geometric figures. A brief description of the method used will be given here.

The atoms are not thought to be polymers of one primary material, but are conceived as systems of geometric points, or as a collection of rotating vibrations in the ether of equal weight arranged in a fixed position. These bring the cosmic ether into motion, and the quicker this motion the closer they are together. This motion is considered inversely proportional to the squares of the distances, and in this way the gravitation or atomic weights of the atoms are obtained.

The alkalis, for example, are calculated from simple points arranged symmetrically in circles of the same

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[1] *Ber.* 1898, p. 1865.

size. The diameter was divided successively by the numbers 2, 3, 4, 6 and 7·5, and the values calculated from the gravitation law are obtained by the following formulæ :—

$$2.\quad \frac{1}{\left(\frac{1}{2}\right)^2}\quad \frac{1}{1^2}=7{\cdot}0=\text{Li.}$$

$$2.\quad \frac{1}{\left(\frac{1}{3}\right)^2}+\frac{1}{\left(\frac{1}{3}\right)^4}\cdot\left(\frac{1}{\frac{2}{\left(\frac{1}{3}\right)}-2}\right)^2=23{\cdot}06=\text{Na.}$$

$$2.\quad \frac{1}{\left(\frac{1}{4}\right)^2}+\frac{1}{\left(\frac{1}{4}\right)^4}\cdot\left(\frac{1}{\frac{2}{\left(\frac{1}{4}\right)}-2}\right)^2=39{\cdot}111=\text{K.}$$

$$2.\quad \frac{1}{\left(\frac{1}{6}\right)^2}+\frac{1}{\left(\frac{1}{6}\right)^2}\cdot\left(\frac{1}{\frac{2}{\left(\frac{1}{6}\right)}-2}\right)^2=84{\cdot}96=\text{Rb.}$$

$$2.\quad \frac{1}{\left(\frac{1}{7\cdot5}\right)^2}+\frac{1}{\left(\frac{1}{7\cdot5}\right)^4}\cdot\left(\frac{1}{\frac{2}{\left(\frac{1}{7\cdot5}\right)}-2}\right)^2=131{\cdot}1=\text{Cs.}$$

It will be seen that they agree closely with the experimental numbers.

Similar artifices are employed to calculate the other atomic weights. The following includes the elements thus calculated :—Li, Na, K, Rb, Cs, Cl, Br, I, B, C, Si, Cu, Ag, Au, Hg, Zn, Cd and Tl.

For further details reference must be made to the original paper, as it is impossible to satisfactorily abstract such a one.

The idea is more mathematical than chemical, and depends simply on the properties of regular geometrical figures inscribed in circles. It is, however, very remarkable that in all cases there is a very close agreement between observed and calculated values, both for specific gravities and for atomic weights.

Delaunay.—One more example of the various attempts made to reduce the atomic weights to order will be cited, and it is that of Professor N. Delaunay.[1] He shows that if the elements be arranged in order of their atomic weights in series, the sum of the atomic weights of those elements equidistant from each end of the series is very nearly constant, and equal to that of the last element in that series.

The first series is Helium to Sodium. Here we get—

$$\begin{aligned}
\mathrm{He}+\mathrm{F} &= 4+19=23\,\mathrm{Na}\\
\mathrm{Li}+\mathrm{O} &= 7+16=23\,\mathrm{Na}\\
\mathrm{Be}+\mathrm{N} &= 9+14=23\,\mathrm{Na}\\
\mathrm{B}+\mathrm{C} &= 11+12=23\,\mathrm{Na}
\end{aligned}$$

The second series is Helium to Potassium.

$$\begin{aligned}
\mathrm{He}+\mathrm{Cl} &= 4{\cdot}00+35{\cdot}45=\mathrm{K}+0{\cdot}34\\
\mathrm{Li}+\mathrm{S} &= 7{\cdot}03+32{\cdot}07=\mathrm{K}-0{\cdot}01\\
\mathrm{Be}+\mathrm{P} &= 9{\cdot}08+31{\cdot}02=\mathrm{K}+0{\cdot}90\\
\mathrm{B}+\mathrm{Si} &= 10{\cdot}95+28{\cdot}40=\mathrm{K}+0{\cdot}24\\
\mathrm{C}+\mathrm{Al} &= 12{\cdot}01+27{\cdot}11=\mathrm{K}+0{\cdot}01\\
\mathrm{N}+\mathrm{Mg} &= 14{\cdot}04+24{\cdot}28=\mathrm{K}-0{\cdot}79\\
\mathrm{O}+\mathrm{Na} &= 16{\cdot}00+23{\cdot}05=\mathrm{K}-0{\cdot}06\\
\mathrm{F}+\mathrm{Ne} &= 19{\cdot}06+20{\cdot}05=\mathrm{K}-0{\cdot}00
\end{aligned}$$

The third series is Helium to Copper, and so on.

It is also to be noted that—

$$\begin{aligned}
\mathrm{Na}+\mathrm{K} &= 23{\cdot}05+39{\cdot}11=\mathrm{Cu}-1{\cdot}44\\
\mathrm{Na}+\mathrm{Cu} &= 23{\cdot}05+63{\cdot}6=\mathrm{Rb}+0{\cdot}22\\
\mathrm{Na}+\mathrm{Rb} &= 23{\cdot}05+85{\cdot}43=\mathrm{Ag}+1{\cdot}01\\
\mathrm{Na}+\mathrm{Ag} &= 23{\cdot}05+107{\cdot}92=\mathrm{Cs}-1{\cdot}92
\end{aligned}$$

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[1] *C. N.* 81 (1900), p. 70.

There have been several other schemes suggested to find out the relations between the atomic weights, besides those mentioned in this chapter. However, sufficient has been said to give an idea of the kind of work done on this subject, and may also suggest other methods of attacking this very fascinating yet difficult problem.

It must be borne in mind that most mathematical formulæ give curves of infinite length, and hence we should expect an infinite number of elements. This we know not to be the case, and hence one must be exceedingly cautious when trying to find out some general expression embodying all the known atomic weights. Of course, in the present state of our knowledge with regard to the actual values of the constants in question, we cannot hope to get more than approximations, although the deviations must not be beyond a certain superior limit.

CHAPTER IV

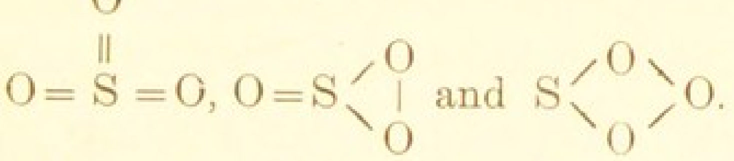
A DISCUSSION ON THE PERIODIC LAW—*continued*

(B) *The Relations existing between the Properties of the Elements and their Atomic Weights.*

WE now come to the examination of the various properties of the elements with regard to their atomic weights.

Valency.

By valency is meant the combining capacity of an element. Elements like carbon, which require four hydrogen atoms or their equivalent for complete saturation, are called tetravalent, and the terms mono-, di-, tri-, penta- and hexavalent sufficiently explain themselves from this example. Hydrogen is taken as the unity of valency. The elements fluorine, chlorine, bromine and iodine can combine with only one atom of hydrogen, and *vice versâ*. Hence these are said to be univalent or monovalent, and, consequently, in cases where the element does not form a hydrogen compound, we can find its valency by ascertaining the composition of its halogen compounds. In cases where the element forms both halogen and hydrogen compounds, it is often found that it does *not* exhibit the same combining capacity in the one case as in the other. For example, sulphur forms no higher hydride than H_2S, whilst the highest chloride is SCl_4.[1] Again, oxygen[2] is divalent, and hence we can also use the oxides to find the valency of an element. Here, again, the results are not always the same as those obtained from the hydrides and halides. For example, sulphur forms the oxide SO_3, that is, it is hexavalent. But it is quite possible that a ring formation has taken place, and that sulphur may still be either divalent or tetravalent in SO_3, which might have the following formulæ,



However, sulphur is usually considered hexavalent, as a great many formulæ can be graphically represented on this assumption.

The highest value of the valency for any element is usually taken as being *the* valency of that element, and thus we find chlorine, bromine and iodine to be heptavalent, and from analogy we also take fluorine as heptavalent.

It is remarkable that in the case of an element exhibiting several valencies, these almost always differ by two from one another—for example, uranium, 6, 4, 2; gold 3, 1, and so on. It seems, therefore, that

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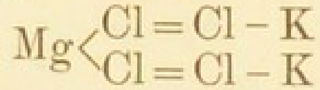
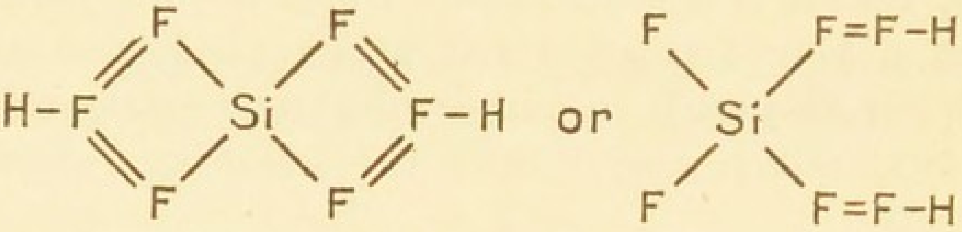
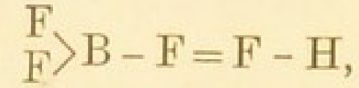
[1] Moissan has recently obtained a compound having the composition SF_6.

[2] See note at end of Section.

two of the combining capacities can become mutually satisfied within the atom.[1]

A great many double halides can be satisfactorily explained on this hypothesis; for example, $MgCl_2$, 2KCl might then be  $\mathrm{Mg}\left\langle\begin{array}{l}\mathrm{Cl=Cl-K}\\ \mathrm{Cl=Cl-K}\end{array}\right.$ where chlorine is trivalent. Similarly H_2SiF_6 hydrofluosilicic acid might be either



and fluoboric acid HBF_4 might be  $\left.\begin{array}{l}\mathrm{F}\\ \mathrm{F}\end{array}\right\rangle\mathrm{B-F=F-H}$, and the examples could be almost indefinitely multiplied.

It appears, therefore, that the active valency is by no means a constant property of an element. It is usual to speak of the valency towards hydrogen or chlorine and the valency towards oxygen or sulphur, and to separate these two groups as shown in Mendeléeff's second table.

The complete variation of valency with atomic weight is well shown in the appended table, which is due to Mendeléeff.

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[1] It is to be noticed that as a rule the valency decreases with rise in temperature, *e.g.*, nitrogen is pentavalent in NH_4Cl, and this on heating gives NH_3, where the nitrogen is trivalent, similarly with phosphorus pentachloride.

That the variations are periodic is sufficiently obvious from an examination of the table, and hence no discussion of this subject need be taken up here.

It will be noticed that sodium hydride is given the formula NaH. But it appears that the correct formula is Na_2H, that is to say, it contains less hydrogen than the compound given in the table. This point, however, requires further investigation. Potassium forms a similar alloy of the same composition. An alloy of silver and hydrogen having the composition AgH has recently been obtained. Lithium also absorbs about seventeen times its volume of hydrogen.

Iron forms a hydride, of which the conjectural formula is FeH_2. This has not been experimentally proved. Nickel in the porous state absorbs about 165 times its volume of hydrogen, which it gradually loses again when out of contact with hydrogen gas.

Vanadium absorbs about 1·3 per cent. of its weight of hydrogen, which corresponds to a formula Vd_3H_2 for the hydride.

The compositions of the hydrides of niobium and palladium are respectively NbH and PdH_2.

A hydride of copper having the formula CuH is known.

There are also a great number of other oxides besides those given in the table, but they are unimportant. For the preparation and properties of these compounds the larger text-books on inorganic chemistry must be referred to, also the various chemical dictionaries.

MENDELÉEFF'S VALENCY TABLE.

Hydrogen Compounds or Organo-Metallic Compounds RH_m and $R(CH_3)_m$	Element.		Formulæ of the Oxides R_2O_n
	Symbol.	At. Wt.	
$m=1$	H	1	$n=1$
	Li	7	1†
	Be	9	— 2
3 — —	B	11	— — 3
4 — — —	C	12	— — — 4
3 — —	N	14	1 — 3* — 5*
2 —	O	16	
1	F	19	
1	Na	23	1†
2 —	Mg	24	— 2†
3 — —	Al	27	— — 3
4 — — —	Si	28	— — _3_ 4
3 — —	P	31	— — _3_* _4_* 5*
2 —	S	32	— — — 4* 5* 6*
1	Cl	35·5	1 — _3_ — _5_* — _7_*
	K	39	1†
	Ca	40	— 2†
	Sc	44	— — 3†
	Ti	48	— — _3_ 4
	V	51	— _2_ 3 4 5
	Cr	52	— _2_ 3 — — 6*
	Mn	55	— 2† 3 4 — _6_* _7_*
	Fe	56	— 2† 3 — — _6_*
	Co	58·5	— 2† _3_ _4_
	Ni	59	— 2† _3_
	Cu	63	1† 2†
_2_ —	Zn	65	— 2†
_3_ — —	Ga	70	— — 3
_4_ — — —	Ge	72	— 2 — 4
3 — —	As	75	— — 3 — 5*
2 —	Se	79	— — — 4 — 6*
1	Br	80	_1_ — — — _5_* — _7_*
	Rb	85	1†
	Sr	87	— 2†
	Y	89	— — 3†
	Zr	90	— — — 4
	Nb	94	— — _3_ — 5*
	Mo	96	— _2_ _3_ 4 — 6*
	(1)		
	Ru	101	— _2_ 3 _4_ — _6_ — 8

Mendeléeff's Valency Table—*continued.*

Hydrogen Compounds or Organo-Metallic Compounds. RH_m and $R(CH_3)_m$	Element.		Formulæ of the Oxides R_2O_n
	Symbol.	At. Wt.	
	Rh	103	— *2* 3 4 — *6*
	Pd	106	1 2 — *4*
	Ag	108	1†
2 —	Cd	112	— 2†
3 — —	In	113	— *2* 3
4 — — —	Sn	118	— 2 — 4
3 — —	Sb	120	— — 3 4 5
2 —	Te	125	— — — 4 — 6*
1	I	127	1 — *3* — 5* — 7*
	Cs	133	1†
	Ba	137	— 2†
	La	138	— — 3†
	Ce	140	— — 3 4
	Di	142	— — 3 — 5
	(14)		
	Yb	173	— — 3
	(1)		
	Ta	182	— — — — 5
	W	184	— — — *4* — 6
	(1)		
	Os	190	— — 3 *4* — *6* — 8
	Ir	193	— — 3 *4* — *6*
	Pt	194	— 2 — 4
	Au	197	*1* — 3
2 —	Hg	200	1† 2†
3 — —	Tl	204	1† — 3
4 — — —	Pb	206	— 2† — 4
3 — —	Bi	208	— — 3 — 5
	(5)		
	Th	232	— — — 4
	(1)		
	U	240	— — — 4 — 6

resembling its analogue sulphur. The above mentioned do not include all the evidence, but only the most important points.

Specific Heats.

It was shown in the second chapter that the product of the specific heat in the solid state of an element and its atomic weight was approximately constant. The same law holds for gases, although here the constant has about half the value of that for the solid state. For liquids the law fails to hold. From this law, known as Dulong and Petit's Law, it is obvious that if we plot specific heats against atomic weights we shall approximately get a rectangular hyperbola for the locus of these points, since the characteristic property of this curve is that $xy =$ constant where x is the abscissa and y the ordinate of any point. We cannot at the best hope to get more than approximations to a smooth curve, for the specific heats vary with temperature, as pointed out in the previous chapter, and to save repetition reference should be made to that chapter.

The fact that the greater the atomic weight of an element the less should be the amount of heat required to raise unit mass of that element through one degree is a most remarkable property, and seems to be quite contrary to our usual ideas regarding specific heats of molar masses. Hinrichs[1] tries to explain this in the following way[2]:—

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[1] *C. N.* 66 (1892), p. 116.

[2] This proof, as far as our present knowledge goes, can only hold for elements in the gaseous state.

Let m be the mass of an elementary atom and v its maximum undulatory velocity. Let M be the mass and V the velocity of the centre of gravity of a compound atom composed of n of the above elementary atoms. Suppose the total energy of the vibrations to be denoted by E.

Then we have $\quad \mathrm{M} = \Sigma(m)$

$$\text{and } 2\mathrm{E} = \Sigma(mv^2) + \mathrm{MV}^2.$$

But $\mathrm{MV}^2 = 2k\mathrm{T}$ where T is the absolute temperature of the body and k is a constant.

Similarly $mv^2 = 2\rho k\mathrm{T}$ where ρ is another constant, $\therefore$ substituting in the original equation we get

$$\mathrm{E} = k(1 + \rho n)\mathrm{T}.$$

The specific heat of an atom representing the vibrations only is given by $\mathrm{S} = \dfrac{d\mathrm{E}}{d\mathrm{T}}$

$$\therefore \quad \mathrm{S} = \frac{d(k + k\rho n)\mathrm{T}}{d\mathrm{T}} = k(1 + \rho n).$$

Hence, since both k and ρ are constants, the atomic heat of every element must have the same value.

Whether this is the correct proof of Dulong and Petit's Law remains yet to be confirmed.

In the following table are given the values of the specific and atomic heats of the elements, together with the temperatures of the observations, as far as these are known. Since, however, the variation of specific heat with temperature is in most cases unknown, and also the melting points having been in many cases only roughly determined, we cannot expect the value of the atomic heat to be more than approximately the same for all elements. Until these facts, and also the true nature of the specific heat are certain, little more can be done.

TABLE OF SPECIFIC HEATS.

Element.	Specific Heat.	Temperature of Observation.	Atomic Heat.
Aluminium	0·2253	0° to 100°	6·1
Antimony	0·0495	0° to 100°	5·9
Arsenic	0·083 C.	...	6·2
	0·076 A.	...	5·7
Beryllium	0·4702	100°	4·3
	0·6206	500°	5·6
Bismuth	0·0305	20° to 48°	6·5
Boron	0·1915	−40°	2·11
	0·3663	233°	4·03
Bromine	0·08432	−78° to −20°	6·7
Cadmium	0·0548	0° to 100°	6·1
Calcium	0·1686	0° to 100°	6·7
Carbon	0·1128 D.	10°	1·35
	0·1604 G.	10°	1·92
	0·4589 D.	1000°	5·50
	0·4670 G.	1000°	5·60
Cerium	0·0448	0° to 100°	6·3
Chlorine (gas)	0·12199 at C. P.	...	4·32
Chromium	0·0998	22° to 50°	5·2
Cobalt	0·1067	9° to 97°	6·3
Copper	0·0933	15° to 100°	5·99
Didymium	0·04563	...	6·5
Gallium	0·079	12° to 23°	5·4
Germanium	0·077	0° to 200°	5·6
Gold	0·0316	0° to 100°	6·2
Hydrogen (gas)	3·409	...	3·41
Indium	0·0569	0° to 100°	6·5
Iodine	0·0541	9° to 98°	6·8
Iridium	0·0323	0° to 100°	6·2
Iron	0·1124	50°	6·3
Lanthanum	0·04485	...	6·2
Lead	0·0315	19° to 48°	6·5
Lithium	0·9408	27° to 100°	6·6
Magnesium	0·245	20° to 51°	5·9
Manganese	0·1217	14° to 97°	6·7

TABLE OF SPECIFIC HEATS—*continued.*

Element.	Specific Heat.	Temperature of Observation.	Atomic Heat.
Mercury	0·0319	– 78° to – 10°	6·4
Molybdenum	0·0659	5° to 15°	6·3
Nickel	0·10916	14° to 97°	6·4
Nitrogen (gas)	0·2438 at C. P.	...	3·41
Osmium	0·03113	19° to 98°	5·9
Oxygen (gas)	0·2175 at C. P.	...	3·48
Palladium	0·0582	0°	6·2
Phosphorus	0·1699	– 78° to – 10°	5·26
Platinum	0·03243	0° to 100°	6·3
Potassium	0·166	– 78° to – 10°	6·5
Rhodium	0·058 (impure)	10° to 97°	6·0
Ruthenium	0·0611	0° to 100°	6·4
Selenium	0·0746 A.	– 27° to – 8°	5·9
	0·0732 C.	– 20° to – 7°	5·77
Silicon	0·136	– 40°	3·31
	0·2029	232°	5·68
Silver	0·0557	0° to 100°	6·1
Sodium	0·2934	– 28° to 6°	6·3
Sulphur	0·163	17° to 45°	5·2
Tellurium	0·0475	21° to 51°	5·9
Thallium	0·0335	17° to 100°	6·8
Thorium	0·02787	0° to 100°	6·4
Tin	0·0559	0° to 100°	6·6
Titanium	0·1135	0° to 100°	5·4
	0·162	0° to 440°	7·7
Tungsten	0·035	6° to 15°	6·4
Uranium	0·0276	100°	6·6
Zinc	0·0935	0° to 100°	6·1
Zirconium	0·066	0° to 100°	6·0

ABBREVIATIONS.—C. = crystalline. A. = amorphous. D. = diamond. G. = graphite. C. P. = constant pressure.

Specific Gravity and Atomic Volume.

The weight of one cubic centimetre of any substance is called its density, whilst the volume of one gram is known as the specific volume. It is therefore obvious that the one is the reciprocal of the other.

The terms density and specific gravity are often used indiscriminately for one another. However, they have not both precisely the same meaning. As before stated, the former is the actual mass of 1 c.c., whilst the latter is the ratio of the weight of that body to the weight of the same volume of water. The mass of 1 c.c. of water at 4° C. is 1 gm., hence at this temperature the two terms become identical. The densities of all bodies are, more or less, dependent on the temperature, and hence, when quoting a density, we should also state the temperature at which the observation was made, and further, the temperature of the water with which it is compared. This is conveniently done as indicated by the following example :—$1{\cdot}5\,\frac{12^{\circ}}{4^{\circ}}$ signifies that the density of a body at 12° was 1·5 when compared with the density of water at 4°. Fortunately for most practical purposes the variations of this most important property are of little consequence.

The product of the specific volume into the atomic weight is called the atomic volume, and it is with this that we are chiefly concerned. If we were certain that the spaces between the atoms were the same in all cases, then of course the atomic volumes would represent the relative volumes of the atoms ; since, however, this is in all probability not the case, the numbers simply represent the relative volume of an atom, together with the space which it inhabits.

We have now to examine the relations between these constants and the atomic weights.

This was done as early as 1870 by Lothar Meyer, and he showed that the atomic volumes of the elements were most emphatically periodic functions of their atomic weights. The following table will show this clearly. The numbers are those compiled from the most recent data, and represent atomic volumes in the solid state.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.		
Li	Be	B	C	N	O	F			
11·9	4·9	4·13	3·41	15·6	14·3				
Na	Mg	Al	Si	P	S	Cl			
23·3	13·9	10·4	11·8	14·7	15·4	26·6			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
44·9	21·6		13·4	9·3	7·7	7·45	7·1	6·9	6·5
Cu	Zn	Ga	Ge	As	Se	Br			
7·0	9·4	11·8	13·2	15·9	17·6	25·0			
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd
56·4	33·9		21·8	13·3	11·2		8·0	8·5	8·8
Ag	Cd	In	Sn	Sb	Te	I			
10·2	13·1	15·3	16·2	17·9	19·5	25·6			
Cs	Ba	La	Ce						
70·7	36·5	22·6	20·8						
				Ta	W		Os	Ir	Pt
				17·6	9·8		8·5	9·0	9·1
Au	Hg	Tl	Pb	Bi					
10·2	14·7	17·2	18·2	20·8					
			Th		U				
			21·1		12·8				

If these numbers be plotted with atomic weights as abscissæ, and atomic volumes as ordinates, and the points thus found joined, a curve is formed appearing as a series of undulations, which grow larger as the atomic weight increases. This represents the periodicity of the atomic volume in a most striking manner. The maxima are formed by the alkali elements, whilst the elements of Mendeléeff's eighth group (Fe, Co, Ni, Os, etc.) are found on the minima, and further similar elements are situated on corresponding branches of the curve.

On the ascending branches are to be found the more acidic elements, and on the descending branches the more basic ones. In fact, this curve represents the periodicity of the elements in a most marked degree.

Bayley published a paper on this subject in 1898,[1] in which he showed that the atomic volumes were most decidedly periodic, and that the atomic volumes of similar elements were in many cases approximately on a straight line in the diagram of Lothar Meyer.

Deeley, in 1893,[2] showed a relation between the atomic weights and the volume atoms. This latter term is used to denote the ratio of the density to the atomic weight. He shows that a portion of the curve thus obtained corresponds to a formula of the type $y = \mathrm{AB}^{-x} \dfrac{x}{x+c}$, which is a hyperbolic formula multiplied by an exponential factor. However, the results thus obtained seem to have little meaning, and do not by any means agree well with the mathematical curve derived from the above formula.

In the Appendix a table of specific gravities is given derived from the best data.

Obviously, since the atomic volumes are periodic functions of the atomic weights, the specific gravities must also be so. This is readily seen by plotting the

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[1] *J. Am. Ch. Soc.* 20.

[2] *J. C. S.* 63, p. 852.

values given in the Appendix against the atomic weights.

Professor Palmer, in 1890,[1] showed that the curves obtained by plotting these atomic volumes become very regular if one does so on the basis of the specific atomic volumes and the specific atomic weights of hydrogen as unity.

Owing to the general completeness of the data, for this portion of the subject, it has been most fully investigated, and a great many other properties of the elements are examined from the standpoint of the atomic volume curve. These will be pointed out in their proper places.

Melting Points and Boiling Points.

The melting point of a substance is that temperature at which both solid and liquid can exist together without any change, whilst the boiling point of a substance is that temperature at which its vapour exerts a pressure equal to that of the atmosphere.

The melting point changes so little with alteration of pressure that it may be taken as being constant. However, the boiling point depends a great deal on the pressure, and varies much with it, hence in stating boiling points it is necessary to give the pressure at the time of observation.

Unless otherwise stated, it is understood that the pressure is 760 mm. Now, under ordinary circumstances, the atmospheric pressure is generally different from 760 mm., and therefore we must correct our

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[1] *Proc. Col. Sci. Soc.* p. 287.

boiling point. This can be done, at least theoretically, by means of an equation devised by Clausius, and which is as follows:—$dT = T\frac{V - V'}{l}dp$, where dT is change in boiling point due to a change of pressure dp, l is the latent heat of vaporisation, whilst V and V′ are the specific volumes of the saturated vapour and of the liquid respectively.

The investigation of the relation between the melting points and the atomic weights of the elements was first undertaken by Lothar Meyer, and then in 1873 by Carnelley.

The results show that here again we have to deal with a periodic function, for if the melting points be plotted against the atomic weights an undulating curve is obtained similar to that of the atomic volumes, only that here the undulations are alternately large and small. The elements of the eighth group are at the maxima, whilst the alkalis and halogens are at the minima, and similar elements occur on similar portions of the curve.

Until recently the melting point of antimony was taken as 437°; however, Heycock and Neville have shown it to be much higher, viz., 630°, and this value is probably correct.

The following table will illustrate what has been said above regarding the melting points. The numbers are those on the absolute scale.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.		
H									
c.17									
Li	Be	B	C	N	O	F			
453	a.1270	v.h.	n.f.	59	v.l.	?			
Na	Mg	Al	Si	P	S	Cl			
368	905	928	c.1500	317	387	171			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
335	1033	?	n.f.	a.2100	a.2800	c.2100	2080	c.1780	1723
Cu	Zn	Ga	Ge	As	Se	Br			
1354	692	303	c.1173	723	490	266			
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd
311	h.t.Ba	?	a.1300	n.f.	a.2100		a.2300	c.2300	1823
Ag	Cd	In	Sn	Sb	Te	I			
1234	594	449	605	903	c.728	387			
Cs	Ba	La	Ce						
300	748	a.750	b.1200						
				Ta	W		Os	Ir	Pt
				n.f.	v.h.		v.h.	c.2200	2093
Au	Hg	Tl	Pb	Bi					
1334	234	555	601	542					
			Th		U				
			?		v.h.				

The abbreviations used have the following signification:—n.f., denotes not fused, v.h., very high, v.l., very low, h.t., higher than, a., above, b., below, c., about, ? unknown. If we compare the elements comprising a natural group, we see that generally the melting point increases with atomic weights; the opposite, however, is the case in the alkalis Li, Na, K, Rb, Cs, also Mg, Zn, Cd and Hg, and also Be, Ca, Sr and Ba.

A comparison of the melting-point curve with the curve of the atomic volumes shows that all gaseous and easily fusible elements are on ascending branches and at the maxima of the volume curve, whilst the difficulty fusible and practically infusible elements are on the descending branches, or at the minima of that curve.

With regard to the boiling points, the data are unfortunately very scanty, and by no means definite, being only known in a very few cases with anything like accuracy. The results, as far as they go, are collected together in the following table:—

Cl 239	Br 332	I 457		
Na 1015	K 940			
O 92	S 717	Se 950	Te c. 1560	
N 79	P 560	As ?	Sb a. 1090	Bi b. 1450
Zn 1189	Cd 1029	Hg 630		
Sn c. 1800	Pb c. 1800			
Tl at a bright red heat				
H 21				

These results seem to be following the same course as the melting points, *e.g.*, the boiling points in the alkali series and in the zinc series decrease with increase of atomic weight, just like the melting points, and for the remaining series the boiling points increase with increase of atomic weight, thus again resembling the melting points. However, little definite can be said until more data are obtained, and researches in this direction would be most desirable and valuable.

Coefficients of Expansion.

Since the coefficient of cubical expansion is very nearly equal to three times the coefficient of linear expansion, it is obvious that whatever applies to one will also apply to the other, and hence only the latter will be considered here.

The data are in this case better and more abundant than for the boiling points, but there is still plenty of room for improvement in this direction.

The following is a summary of the mean coefficients between 0° and 100° expressed in hundred-millionths of a cm. per cm.

Na 7590	K 8411		
Mg 2762	Zn 2905	Cd 3102	Hg 6006
Al 2336	In 4590	Tl 3021 (40°)	
C 132	Si 763 (40°)	Sn 2269	Pb 2848
P 686	As 602	Sb 895	Bi 1316
S 7453	Se 3792	Te 1675	
Fe (hard) 1362	Ni 1286	Co 1244	
Ru 991	Rh 858	Pd 1189	
Os 679	Ir 708	Pt 907	
Cu 1666	Ag 1936	Au 1451	

R. Pictet, in 1879,[1] from theoretical considerations found that the following relation existed between the melting point (T) on the absolute scale, the linear coefficient of expansion (α) and the atomic volume (V) of the elements:—$T\alpha \sqrt[3]{V} = \text{constant}$.

The cube root of V is a measure of the distance between the centres of the atoms.

Deerr,[2] in 1895, noted that for elements of the same periodic group the expression $T\alpha = \text{constant}$ was more nearly in accordance with the experimental data than the formula of Pictet.

The following table, given originally by Deerr,[3] but recalculated from the values here given for the melting points and the linear coefficients of expansion, is intended to show this.

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[1] *C. R.* 88, p. 855. [2] *C. N.* 71, p. 303. [3] *C. N.* 76, p. 234.

Element.	$\alpha \times 10{,}000$	T	$\sqrt[3]{V}$	$T\alpha$	$T\alpha \sqrt[3]{V}$
Na	0·76	368	2·86	0·028	0·095
K	0·84	335	3·55	0·030	0·099
Ag	0·19	1234	2·17	0·023	0·051
Cu	0·17	1354	1·91	0·023	0·044
Au	0·14	1334	2·17	0·018	0·050
Mg	0·28	905	2·40	0·025	0·061
Zn	0·29	692	2·11	0·020	0·042
Cd	0·31	594	2·36	0·018	0·043
Hg	0·61	234	2·45	0·014	0·035
Al	0·23	928	2·18	0 021	0·047
In	0·46	449	2·48	0 021	0·051
Tl	0·30	555	2·58	0·017	0·043
C	0·01	n. f.	1·50	...	...
Si	0·07	c. 1500	2·28	0·011	0·024
Sn	0·23	605	2·53	0·014	0·035
Pb	0·28	601	2·63	0·017	0·044
P	0·07	317	2·42	0·002	0·005
As	0·06	723	2·51	0·004	0·011
Sb	0·09	903	2·62	0·008	0·020
Bi	0·13	542	2·75	0·007	0·019
S	0·74	387	2·49	0·029	0·071
Se	0·38	490	2·60	0·016	0·041
Te	0·17	c. 728	2·69	0·012	0·021
Fe	0·11	2080	1·92	0·023	0·043
Co	0·12	c. 1780	1·90	0·021	0·041
Ni	0·13	1723	1·86	0·022	0·041
Ru	0·099	a. 2300	2·00	0·023	0·045
Rh	0·086	c. 2300	2·03	0·019	0·039
Pd	0·12	1823	2·06	0·022	0·044
Os	0·068	c. 2500	2·03	0·017	0·034
Ir	0·07	c. 2200	2·08	0·015	0·032
Pt	0·09	2093	2·09	0·019	0·039

It will be seen that there are twenty-two elements having values between 0·03 and 0·06 in the last column of this table. The agreements between similar elements in the column giving the value of $T\alpha$ are better, but still they are by no means perfect.

The formula $T\alpha \sqrt[3]{V} = \text{constant}$ fails entirely for Na, K, Mg, P, As, Sb, Bi, S, Te.

Formula $T\alpha = \text{constant}$ is restricted to groups of elements, and we notice that it holds fairly well but fails for Pb and Sn, also Mg and Hg when compared with Zn and Cd, and further for Te compared with S and Se.

The expression $T\alpha = $ constant means that the total expansion from absolute zero to the melting point of similar elements is constant, and hence α is a periodic function of the atomic weight.

If we plot the values of α against the atomic weight we do actually obtain portions of periodic curves on joining the points thus found.

But lack of reliable data, or even any data at all, prevents our finding out any relation so definite as that of the atomic volumes.

Thermal Conductivities.

The thermal conductivity of a substance is defined as the quantity of heat that flows in unit time through unit area of a plate of unit thickness when the temperature difference of the faces is 1°. Expressed in symbols this would be

$$k = \frac{Qd}{A(t_2 - t_1)T}$$

where Q is the total amount of heat flowing through an area A of a plate whose thickness is d in a time T, one face being at a temperature t_2 and the other at temperature t_1.

To give some idea of the magnitude of k, the following determinations by Neumann may be quoted :—

	Conductivity in C. G. S. units.
Copper	1·108
Zinc	0·307
Iron	0·164

It is usual, however, to express the conductivities in terms of Ag = 100.

The following is a list of the few known data, which are, however, none too reliable, in terms of this unit:—

Na 36·5	K 45		
Cu 73·6	Ag 100	Au 53·2	
Mg 34·3	Zn 28·1	Cd 20·06	Hg 5·3
Ca 25·4			
Al 31·33			
Sn 15·2	Pb 8·5		
Sb 4·03	Bi 1·8		
Fe 11·9	Co 17·2	Pt 37·9	

Even here we can notice a tendency towards periodicity, the maxima falling on the elements Cu, Ag and Au, and apparently also on Na and K. The minima seem to be with the elements of the sixth group—S, Se, Te, all of which are very bad conductors. Farther than this we cannot go until more data are at our disposal.

Latent Heats of Fusion.

The data at our disposal are very meagre and, in most cases, none too reliable.

The following is a list of the latent heats as far as these are known :—

Na 32·7	K 15·7	
Cu 43·0	Ag 24·7	Au 16·3
Zn 22·6	Cd 13·6	Hg 2·8
Al 100	Tl 5·1	Ga 19·2
Sn 14·5	Pb 5·4	
P 5·0	Bi 12·5	
S 11·8		
Br 16·2	I 11·7	
Pd 36·3	Pt 27·2	

In 1897 Richards[1] gave a relation between the atomic volumes, melting points and latent heats of the elements. This was that $L = 2{\cdot}1T$, if L be the latent heat and T the absolute melting point. Then as Pictet had concluded that $T = \frac{4{\cdot}5}{\alpha \sqrt[3]{V}}$ where V is the atomic volume, it followed that

$$L = \frac{4{\cdot}5 \times 2{\cdot}1}{\alpha \sqrt[3]{V}} = \frac{9{\cdot}5}{\alpha \sqrt[3]{V}}.$$

L denotes the latent heat of fusion of an amount equal to the atomic weight.

Now Deerr shows that Pictet's relation did not hold, and therefore neither could Richards'. However, the differences are never very great, as shown by the following short table :—

Element.	$L = \frac{9{\cdot}5}{\alpha \sqrt[3]{V}}$.	$\frac{L}{\text{At. Wt.}}$	Experimental L. H.
Cu	3006	46·2	43
Zn	1561	24·6	22·6
Pd	3832	36·1	36·3
Ag	2541	23·5	24·7
Cd	1253	11·1	13·1
Sn	1712	13·7	14·5
Pt	5106	26·3	27·2
Au	3035	15·5	16·3
Hg	654	3·3	2·8
Pb	1284	6·2	5·4
Bi	2777	13·4	12·4

Richards ventures to predict some values of the latent heat from the values of α. They are Mg 58, Fe 69, Co 68, Ni 68, Se 13, Ru 46, Rh 52, In 8, Sb 16, Te 17, Os 35, Ir 28, Tl 5·8.

Deerr suggests[2] that $\frac{TS}{L}$ is a constant for the

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[1] *C.N.* 75, p. 278

[2] *Proc. Chem. Soc.* 17, 695.

elements of the same periodic group. Here T is the melting point on the absolute scale, S the mean specific heat from $-273°$ to T, and L is the latent heat of fusion.

He also proposed the formula $\frac{LC}{S} = \text{constant}$ where C is the mean coefficient of expansion from $-273°$ to T. The following table shows the comparison between the two expressions and also their constancy.

Element.	I. $\frac{TS}{L}$.	II. $\frac{LC}{S}$.
Sodium	3·27	0·0078
Potassium	3·67	0·0079
Copper	3·25	0·0081
Silver	2·81 – 3·29	0·0074 – 0·0086
Magnesium	...	...
Zinc	2·35 – 2·92	0·0067 – 0·0081
Cadmium	2·51	0·0081
Mercury	2·57	0·0054
Aluminium	2·56	0·0094
Thallium	3·41	0·0050
Tin	1·90	0·0071
Lead	3·47	0·0047
Phosphorus	12·0	0·0003
Bismuth	1·15	0·0061
Sulphur	5·19	0·0037
Bromine	1·76	0·053
Iodine	1·78	0·051
Gallium	1·14	...
Gold	2·62	0·0074
Platinum	2·60	0·0077
Palladium	2·72	0·0069

If we take Deerr's relation $TC = \text{constant}$, then whatever applies to Column I. also applies to Column II., for the formula $\frac{LC}{S}$ follows then directly from $\frac{TS}{L}$; thus—

$$\mathrm{TC}=\text{constant, therefore } \mathrm{T}=\frac{\text{constant}}{\mathrm{C}}.$$

$$\frac{\mathrm{TS}}{\mathrm{L}}=\text{constant, therefore } \frac{\frac{\text{constant}}{\mathrm{C}}\cdot\mathrm{S}}{\mathrm{L}}=\text{constant.}$$

$$\text{Therefore } \frac{\mathrm{S}}{\mathrm{LC}}=\text{constant; hence } \frac{\mathrm{LC}}{\mathrm{S}}=\text{constant.}$$

We see that Na, K, Cu, Ag and Tl agree well, so do Zn, Cd and Hg. The closely-allied metals Pt, Pd, Au also agree. Ga and Bi, though not of the same family, are yet partly analogous. Br and I are particularly good. P and S are abnormal, and Pb and Sn give what might be expected, seeing that tin behaves so very much like a non-metal. Assuming these laws to hold, Deerr has predicted a number of latent heats, which are here collected together:—

Element.	From $\frac{\mathrm{TS}}{\mathrm{L}}$ formula.		From $\frac{\mathrm{LC}}{\mathrm{S}}$ formula.	
	L (calc.)	Constant used.	L (calc.)	Constant used.
Li	12·4	3·3 Mean of Na, etc.		
Mg	106·0	2·6 Mean of Zn, etc.	70·0	0·0077 Mean of Zn and Cd
In	7·0	3·3 Mean of Na, etc.	6·7	0·0055 Value for Tl
In	20·4	1·14 Mean of Ga and Bi		
Sb	32·0	Do.	32·0	0·0061 Value for Bi
As	50·0	Do.		
As	4·8	12·0 Value for P	4·6	0·0003 Value for P
Co	68·0	2·65 Mean of Pt, etc.	63·0	0·0075 Mean of Pt, Pd, Au
Fe	75·0	Do.	75·0	Do.
Ni	81·0	Do.	66·0	Do.
Rh	46·0	Do.	48·0	Do.
Ru	53·0	Do.	55·0	Do.
Os	35·0	Do.	35·0	Do.
Ir	33·0	Do.	33·0	Do.
Se	8·0	5·2 Value for S	8·4	0·0037 Value for S
Te	6·0	Do.		
Cl	20·0	1·77 Mean of Br and I		

Now since each of the formulæ $\frac{TS}{L}$ and $\frac{LC}{S}$ contains a periodic function of the atomic weight:—T and C, it follows that L must also be periodic. Hence by drawing up a table, in the same way as was done for the other properties, we at once see that 50 is the more probable value for the latent heat of arsenic and 7·0 for indium. The experimental value for aluminium is 100. Probably the calculated value 70·4 is nearer the truth, and similarly we might argue that 91 is nearer the value for magnesium. These are deduced from the general course of the curve, and this seems quite permissible, seeing that the latent heat does depend on some periodic function, and hence the curve formed by plotting the latent heats against the atomic weights must also show a periodicity.

The following table collects the observed and various calculated values of the latent heats:—

Li	Be	B	C	N	O	F			
12·4									
Na	Mg	Al	Si	P	S	Cl			
32·7	91	70·4		(5·0)	11·8	20			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
15·7							75	63	66
Cu	Zn	Ga	Ge	As	Se	Br			
43·0	28·1	19·2		50·0	8·4	16·2			
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd
Ag	Cd	In	Sn	Sb	Te	I	55	48	36·3
24·7	13·6	6·7	14·5	32·0	6	11·7			
Cs	Ba	La	Ce						
				Ta	W		Os	Ir	Pt
							35	33	27·1
Au	Hg	Tl	Pb	Bi					
16·3	(2·8)	5·8	5·4	12·6					

The observers of the experimental rules are given below.

Regnault. Br, I.

Person. Cd, P, Hg, S, Ag, Bi, Zn, Sn.

Berthelot. Ga.

Favre and Silbermann. I.

Violle. Pd, Pt.

Gruner has also determined the value of L for Iron, but the results vary so much with the kind of iron employed, that they need merely be quoted without paying further attention to them. He finds for white iron 33, for grey iron 23, for very impure cast-iron 50.

To summarise then, it appears that the latent heat is also a periodic function of the atomic weight, but the data are only sufficient just to indicate this without fully confirming it.

Refraction Equivalents.

The direct determination of the refractive index of a solid element is almost an impossibility. Where, however, the metal can be beaten out into extremely thin sheets, this could be done. Only three metals have been thus experimented on. They are gold, silver and platinum, and the indices obtained are respectively 0·2705, 0·2694, and 1·9493.

The refractivities of the gases can, however, be very accurately determined by an interference method devised and elaborated by Jamin.[1] The results obtained are as follows :—

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[1] *Ann. Chim. Phys.* (3), 52 (1858), p. 163.

Oxygen	1·000273
Hydrogen	1·000138
Nitrogen	1·000300
Chlorine	1·000772

This method has been largely turned to account very recently by Professor Ramsay and Dr Travers to determine the refractivities of the new gaseous elements of the atmosphere.

In 1858 Gladstone and Dale[1] showed that if n denote the refractive index of a liquid and d its density, then $\frac{n-1}{d}$ is constant for that liquid. Lorenz and Lorentz preferred the formula $\frac{n^2-1}{n^2+2}\ \frac{1}{d} =$ constant, for it was also valid when the substance was in the gaseous state. In this case Gladstone and Dale's formula failed altogether. However, in other cases, the formula of Gladstone and Dale is better than that of Lorenz and Lorentz.

Landolt found that the molecular refraction, *i.e.*, the product of the molecular weight (M) into the specific refractive index $\frac{n-1}{d}$ was an additive property, and this was further investigated by Brühl, who by a series of experiments derived the following values for the atomic refractions:—

Carbon	2·48
Hydrogen	1·04
Hydroxyl Oxygen	1·58
Carbonyl Oxygen	2·34
Chlorine	6·02

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[1] *Phil. Trans.* p. 887, and later (1863), p. 317.

Bromine	8·95
Iodine	13·99
Nitrogen (single bond)	3·02
Carbon (double linkage)	1·78
Carbon (treble linkage)	2·18

Since the molecular refraction of a compound is equal to the sum of the atomic refractions of its component elements, we can, by observing the index of refraction of a compound, knowing its composition, obtain the atomic refraction of any one unknown constituent.

Now, in inorganic chemistry, the indices of the elements are usually calculated from the index of refraction of the aqueous solutions of their salts, as Gladstone's formula also holds for solutions and takes the following shape :—

$$m\mathrm{R}=(18\rho+m)r-18\rho r'$$

Where R, r' and r are the reflective constants of salt, water and solution respectively $\left(\frac{n-1}{d}\right)$, m is the molecular weight of the compound and 18 that of water, whilst ρ denotes the number of water molecules to one of the salt. We are now, then, in a position to calculate the atomic refractions of the elements from the observed refractive indices of their solutions.

The following table of the refraction equivalents or atomic refractions includes all the known data, which are almost entirely due to Gladstone, and were determined for the red hydrogen line Hα, whose wave length is 656·2 millionths of a millimetre.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.		
Li	Be	B	C	N	O	F			
3·5	4·0		5·0	4·1 to 5·3	2·8	1·6			
Na	Mg	Al	Si	P	S	Cl			
4·4	6·7	7·7	7·4 ?	18·3	16·0	9·9 to 10·7			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co
7·85	10·0		24·6	24·8	19·9	12·2	12·0	9·9	10·4
Cu	Zn	Ga	Ge	As	Se	Br			
11·5	9·8	14·8		15·4	30·5	15·3 to 16·9			
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd
12·1	13·0		21·2					23·6	21·6
Ag	Cd	In	Sn	Sb	Te	I			
13·2	13·1	17·4	19·2	24·1		24·5 to 27·2			
Cs	Ba	La	Ce	Di					
19·2	15·8	23·0	20·0	23·1					
				Ta	W		Os	Ir	Pt
									24·7
Au	Hg	Tl	Pb	Bi					
23·1	19·4	20·4	24·3	38·2					
			Th		U				
					19·5				

The value for chromium is that in the salts of the formula $CrCl_3$, for chromates it is 23·0. Those for manganese and iron are in the "ous" state. Ferric iron has the value 20·1, and manganese in the permanganates has the value 26·2.

The lower values for chlorine, bromine and iodine are for organic compounds, the higher values are those which they possess in the salts.

Kanonnikoff[1] has also determined a few atomic refractions. His results, which do not differ much from those of Gladstone, are given on the next page.

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[1] *J. f. pr. Ch.* (2), 31, p. 339.

Lithium	3·16	Magnesium	7·03
Sodium	4·22	Calcium	9·32
Potassium	7·75	Zinc	9·80
Copper	11·6	Strontium	11·61
Rubidium	12·04	Cadmium	13·03
Silver	13·05	Barium	15·84
Cæsium	19·55	Mercury	19·20

The periodicity of the atomic refractions is unmistakable, the maxima falling on the elements of the fifth series, except in the case of arsenic. It is difficult to localise the minimum elements. They hover between groups seven, eight, one and two. Obviously, when we get better data, we shall arrive at more uniform results.

The Spectra of the Elements.

The study of spectra is of the utmost importance to the physical chemist, for it teaches more about the nature of the atoms than any other property of matter. Owing to the immense amount of work done in the domain of spectrum analysis, it will not be possible here even to give a short sketch of the subject, but only those portions which are of vital importance for our present consideration will be treated of.

There are three great classes of spectra :—

Emission Spectra,
Absorption Spectra,
Phosphorescence Spectra.

For our purpose we need only consider the first class—Emission spectra.

We have here again three great divisions :—

(1) Flame spectra; (2) Arc spectra; (3) Spark spectra.

The substances giving flame spectra are few in number. They are lithium, sodium, potassium, rubidium, cæsium, barium, strontium, calcium, indium, gallium, thallium, boron, and one or two more. The spark spectra are usually employed as all elements give them. For gases this is the only method possible. However, in some cases, the use of the arc spectrum is preferable, *e.g.*, carbon. The spectra obtained by these methods for any one substance are never identical, the flame spectrum or that produced at the lowest temperature is usually the simplest. The following examples will illustrate this point. Sodium in the bunsen flame gives a spectrum consisting of a pair of yellow lines very close together. The spark spectrum contains these two lines, also a close pair in the orange, another in the green, and a great many more lines. Thallium again gives one green line at the flame temperature. With the spark it gives a complex spectrum containing a set of bands in the violet. Lithium at a moderate temperature gives one red line. At a higher temperature there is also a faint orange line, and in the arc a blue line is further added. In the case of a gas both the pressure and the tension have a profound influence on the spectrum. The effect of pressure is well illustrated in the case of hydrogen. When the pressure is less than $\frac{1}{20}$-in. of mercury, there is a discontinuous spectrum of six green bands.[1] As the pressure is increased we get a temporary banded spectrum, and at $\frac{1}{20}$-in. the ordinary line spectrum

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[1] Possibly due to phosphorescence.

is produced. If the pressure be more than $\frac{1}{10}$-in., we have the bright line in the red and two in the green, and as the pressure is further increased the spectrum becomes more and more banded, but Hα and Hβ are the limits of the bright lines. At 8 in. the full brilliancy of the spectrum is retained, but at 16 in. it loses its intensity, the individual lines getting broader. As the pressure is further increased the spectrum becomes again brighter, the yellow and orange parts appear, Hα is very bright but blurred at the edges, and there is a continuous spectrum from the orange to the violet, which is brightest about Hβ. When the pressure is 32 in. or more the spectrum is continuous. We have therefore the following stages[1] :—

(1.) Spectrum of the six bands in the green.
(2.) Temporary banded spectrum.
(3.) Ordinary line spectrum.
(4.) More permanent and complete banded spectrum.
(5.) Pure continuous spectrum.

With regard to the effect of the tension, the gases hydrogen, nitrogen, oxygen, phosphorus, sulphur and selenium give the first order or banded spectrum at a moderate tension, whilst under a high tension the second order or line spectrum results. It is to be noticed that the gases under high pressure behave like solids and liquids, inasmuch as they give continuous spectra.

The Series Formations.

In a great many cases the spectral lines can be

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[1] Schellen's *Spectrum Analysis.*

sorted out into groups showing the most orderly rhythm, and such groups are spoken of as "series." As an example, mention may be made of the spectrum of the cleveite gases, which at first sight appears most irregular, but which, in the hands of Runge and Paschen, was resolved into six series, three of which belong to helium. However, Professor Ramsay maintains that all six belong to helium. Sir Norman Lockyer[1] has published the evidence in favour of the composite nature of the gases.

The intensity of the lines in a series decreases with the wave length. The wave frequency of such a series of lines is given by the formula $A+B/n^2+C/n^4$ where n represents the natural numbers from 3 upwards, whilst A, B and C are constants specific for each element. This formula is due to Kayser and Runge.

Balmer[2] showed that the hydrogen lines could be most accurately expressed by the formula $\lambda=A\frac{n^2}{n^2-4}$ where λ is the wave length, n one of the natural numbers from 3 to 15, whilst A is a constant, and has the value 3647·2 Ångstrom units according to Ames' measurements.

The following table illustrates this :—

[1] *Roy. Soc. Proc.* Vol. LVIII. p. 113, 193, Vol. LIX. p. 342, and Vol. LXII. pp. 55-58.

[2] *Wied. Ann.* (1885), 25, p. 8.

Line.	n.	Calculated.	Observed.	Diff.
Hα	3	6561·8	6562·1	+0·3
Hβ	4	4860·8	4860·7	+0·1
Hγ	5	4339·8	4339·5	−0·3
Hδ	6	4101·1	4101·2	+0·1
Hϵ	7	3969·5	3969·2	−0·3
Hζ	8	3888·4	3888·1	−0·3
Hη	9	3834·8	3834·9	+0·1
Hθ	10	3797·3	3797·3	0·0
Hι	11	3770·0	3769·9	−0·1
Hκ	12	3749·6	3750·2	+0·6
Hλ	13	3733·8	3734·1	+0·3
Hμ	14	3721·4	3721·1	−0·3
Hν	15	3711·4	3711·2	−0·2

The observed wave lengths are those of Cornu,[1] and are given in ten-millionths of a millimetre.

This is known as the first hydrogen spectrum, and is obtained in a Geissler tube, where the pressure is not too small. For the second hydrogen spectrum the formula does not apply at all.

It will be noticed that Balmer's formula is a particular case of that of Kayser and Runge. Rydberg also formulated an expression for the wave lengths of the spectral lines, which is as follows:—

$n = a - \frac{A}{(m+b)^2}$, where n is the frequency a and b are characteristic constants for a substance, m is one of the natural numbers 1, 2, 3 . . . . , and A is a constant for all series, and has the value 109721·6. In a great many cases a line, which appears to be single, is found, on using a greater dispersion, to be a double or even a triplet. Rydberg suggested that these might be remnants of flutings, the other lines of which are too faint to be seen. Kayser points

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[1] *Journ. de Phys.* [2], 5, p. 341.

out that the elements in the first vertical column of Mendeléeff's table give doublets, those in the second triplets, and the third doublets.[1] It appears, therefore, that elements with odd valency give doublets, whilst those with even valency give triplets, and this is confirmed by the triplets of oxygen, sulphur and selenium of the sixth group. The first elements of any group show the series strongest, and these get weaker and weaker with increase of atomic weight. The following examples will illustrate this point. Rubidium and cæsium do not show the weaker second series; gold gives no series; strontium shows a weak second series, and in barium it is absent.

There is only one known terrestrial element giving single lines, and it is helium, in the principal series. It might be noted here that Kayser and Runge distinguish three series :—

(1.) The Principal Series; their pairs are the strongest lines in the spectrum, and are easily reversible. Their vibration difference decreases as "m" increases.

(2.) The First Subordinate Series; strong, very hazy pairs of lines, having a constant vibration difference.

(3.) The Second Subordinate Series; weaker, but better defined pairs of line, with a constant vibration difference.

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[1] Each line of a doublet or triplet is connected with the corresponding lines in the other doublets or triplets by the usual formula $\frac{1}{\lambda} = A - Bn^{-2} - Cn^{-4}$.

The vibration difference is a most important constant, and seems to have a definite relation to the atomic weights. The principal series have as yet only been found in the alkali metals; all the other spectra seems to consist of secondary series, with, in some cases, a number of residual lines.

From the following table it appears that, for at least the first two groups of elements, the vibration difference (d) is proportional to the square of the atomic weight. In every case the spectrum advances towards the red with increase of atomic weight.

Element.	d.	A.	$\frac{d}{A^2}$.
Na	17	23	321
K	57	39	375
Rb	234	85	324
Cs	545	133	308
Cu	248	63	625
Ag	921	108	789
Au	3877	196	994
Mg	41	24	717
Ca	104	40	645
Sr	394	87	517
Zn	388	65	921
Cd	1165	112	934
Hg	4633	200	1161

From group to group, however, the series advance towards the violet with increase of atomic weight. Kayser suggests that the melting points seem in some way to influence the series formation. The following table shows this:—

Element.	Melting Point.	Percentage of Series Lines.
Barium	1600°	0
Gold	1200°	4
Copper	1050°	6
Silver	960°	26
Strontium	700°	20
Calcium	700°	34
Magnesium	600°	64
Zinc	410°	80
Cadmium	320°	50
Lithium	180°	100
Sodium	90°	100
Cæsium	62°	100

It is obvious from what has been said that the farther we advance towards the violet, the closer do the lines approach each other, and hence the ultra-violet would seem to offer some fruitful object of research.

Professor Hartley[1] investigated the ultra-violet spectra of 22 elements, with most interesting results. By using prisms and unachromatised lenses of quartz or Iceland spar and dry photographic plates, he succeeded in obtaining the whole of the spectrum, from the blue to the ultra-violet, in focus at the same time. His measurements extend between λλ 4500 and 2000.

The elements examined were lithium, sodium, potassium; copper, silver, mercury; magnesium, zinc, cadmium; aluminium, indium, thallium; carbon, tin, lead; arsenic, antimony, bismuth; iron, cobalt, nickel; palladium, gold, platinum and tellurium. A summary of his results is as follows:—

The spectra of iron, cobalt, nickel and palladium, especially the two former, are very similar. There

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[1] *J. C. S.* 41 (1882), p. 84.

is a group of long lines of a sharp appearance at the less refrangible end of the spectrum. Rays more refrangible than Cd 17[1] are most numerous in the case of iron, then cobalt, and least so in nickel, and the dispersion and refrangibility of the rays increase in the same order.

The copper and silver spectra are very similar, consisting of fine but strong lines, and a scattered group of more refrangible short lines, stronger but less refrangible in the case of silver than in copper. Gold and platinum are very similar to these.

In the series magnesium, zinc and cadmium, similarity is shown in the number, shape and intensity of the lines. The refrangibility of the strong lines increases with atomic weight. There is also considerable similarity between tin and lead and the arsenic group. These spectra consist of pairs or groups of long lines with interspersed dots. The latter group—arsenic, etc.—are distinguishable by their nebulous short lines and dots.

The spectra of the alkalis are very simple. Lithium contains only 13 lines, of which 11 are long and well defined. In sodium there are 24 lines, of which 5 are long lines. In potassium we have 47 lines and only 3 long lines. The spectra of the aluminium group are characterised by dots.

Reference should be made to the original paper, where photographs will be found of the various spectra.

From a careful study of the spectrum of beryllium,

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[1] One of the reference lines in the cadmium spectrum.

Hartley was able to assign it to a place in the periodic table, which is the one it now occupies.[1]

Lecoq de Boisbaudran[2] found it possible, from a consideration of their spectra, to predict the atomic weights of certain elements. The method used will be illustrated in the case of germanium, for which it has received a most striking confirmation.

In the spark spectra of silicon, germanium and tin, there are two brilliant lines, and also in the spectra of aluminium, indium and gallium. The wave lengths (λ) of these lines in millionths of a millimetre are as follows:—

	Si	Ge	Sn	Al	Ga	In
1st line . .	λ=412·9	468·0	563·0	...	...	...
2nd line . .	λ=389·0	422·6	452·4	...	...	...
Mean . .	401·0	445·3	507·7	395·2	410·1	430·6

The atomic weights are Si=28, Ge=?, Sn=118, Al=27·5, Ga=69·9, In=113·5. Comparing the differences between the wave lengths and the differences between the atomic weights we get the following:—

Atomic Weights.		Δ	Variations.	λ (Mean).	Δ	Variations.
Si .	. 28	90	...	401·0	44·3	$\frac{40{\cdot}51}{100}$
Ge .	. ?			445·3	62·4	
Sn .	. 118			507·7		
Al .	. 27·5	42·4	$\frac{2{\cdot}8302}{100}$	395·2	14·9	$\frac{37{\cdot}584}{100}$
Ga .	. 69·9	43·6		410·1	20·5	
In .	. 113·5			430·6		

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[1] *J. C. S.* 43, p. 216.

[2] *C. N.* (1886), p. 4.

In the column "Variations" is stated the percentage of the first difference, which must be added to it to give the second difference, thus $44{\cdot}3+\frac{40{\cdot}51\times 44{\cdot}3}{100}=62{\cdot}4$. The following ratio gives a method for determining what the values of $\triangle$ for the atomic weights of silicon and germanium and for germanium and tin should be :—

$\mathrm{Al}-2\mathrm{Ga}+\mathrm{In}$	:	$\mathrm{Al}-2\mathrm{Ga}+\mathrm{In}$	=	$\mathrm{Si}-2\mathrm{Ge}+\mathrm{Sn}$	:	$\mathrm{Si}-2\mathrm{Ge}+\mathrm{Sn}$
(λ)		(At. Wt.)		(λ)		(At. Wt.)
37·584	:	2·8302	=	40·51	:	3·051

The number 3·051 is the percentage of the difference Ge – Si, by which this difference must be increased to make it equal to Sn – Ge, therefore first difference $=\frac{90}{2{\cdot}03051}=44{\cdot}32$.

Hence we get—

$$\begin{aligned}\mathrm{Si}&=28{\cdot}0\\ \mathrm{Ge}&=72{\cdot}32\\ \mathrm{Sn}&=118{\cdot}00\end{aligned}\begin{aligned}&>44{\cdot}32\\ &>45{\cdot}68\end{aligned}.$$

The atomic weight as subsequently determined by Winkler was 72·3.

We thus see that there is a close relation between certain lines in the spectra of allied elements and their atomic weights. The subject, although of great interest, presents many difficulties, owing to the complexity of spectra, and has at present been little investigated.

The absorption and phosphorescence spectra of the rare earths have been employed by Sir William Crookes in his laborious and beautiful researches on these substances. Nothing definite has, however, yet been arrived at, but it is to be hoped that it will be in the near future, when we shall be able to find the atomic weight of any element from an observation of its spectrum.

Magnetic Properties.

Faraday divided the elements into two great classes from a consideration of the manner in which they behaved when suspended between the poles of a large electro-magnet. Those which tended to set axially were called paramagnetic, whilst those which set equatorially were called diamagnetic elements. In this way he grouped the elements as follows :—

Diamagnetic—H, Na, Cu, Ag, Au, Hg, Zn, Cd, Pb, Sn, P, As, Sb, Bi, S, Se, Cl, Br, I, Tl, Si.

Paramagnetic—N, O, Fe, Ni, Co, Mn, Pt, Os, Pd, Ir, Rh, Cr, Ti, Ce, C, K, U.

As thus classed, the elements do not exhibit any general relationships. We notice that similar elements, *e.g.*, Cu, Ag, Au; P, As, Sb, Bi; Fe, Co, Ni, etc., have the same magnetic property. On the other hand, however, the closely allied elements, Na and K, O and S, N and P, Si and Ti, are of opposite properties.

In 1879 Carnelley[1] showed that if the properties of the elements be compared with their position in Mendeléeff's Table, then those elements which are in the even series are always paramagnetic, whilst those in the odd series are always diamagnetic. This is true for every case as yet tested, and is at once obvious if the magnetic property

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[1] *B.* 12, p. 1958.

of an element be put against it in the periodic classification.

In *Watt's Dictionary* (1st Edit.) it is stated that elements of low atomic volume are mostly paramagnetic, whilst those of high atomic volume are mostly diamagnetic. There are, however, some very important exceptions to this, *e.g.*, K is paramagnetic, whilst Ag, Cu, Au, Sn, Hg, Cd and Si are diamagnetic. In fact, the above statement cannot be regarded as true.

The following table gives a list of the few quantitative measurements made, with their observers. The sign + signifies paramagnetic and - diamagnetic.

This table gives the specific magnetic powers, that is to say the action exerted by a magnet on unit volume of the substance at unit distance, taking water = 1.

Element.	Observer.	Mag. Pow.
Cu	Becquerel	− 1·68
Ag	Do.	− 2·32
Au	Do.	− 3·47
S	Do.	− 1·14
Se	Do.	− 1·65
P	Do.	− 1·64
Sb	Do.	− 4·10
Bi	Do.	− 22·67
Bi	Faraday	− 20·37
Zn	Do.	− 0·772
Hg	Plücker	− 0·23
Pb	Becquerel	− 1·53
O	Faraday	+ 0·181
N	Do.	+ 0·003
H	Do.	− 0·001

Also—

S	Faraday	− 1·221
Zn	Becquerel	− 0·25

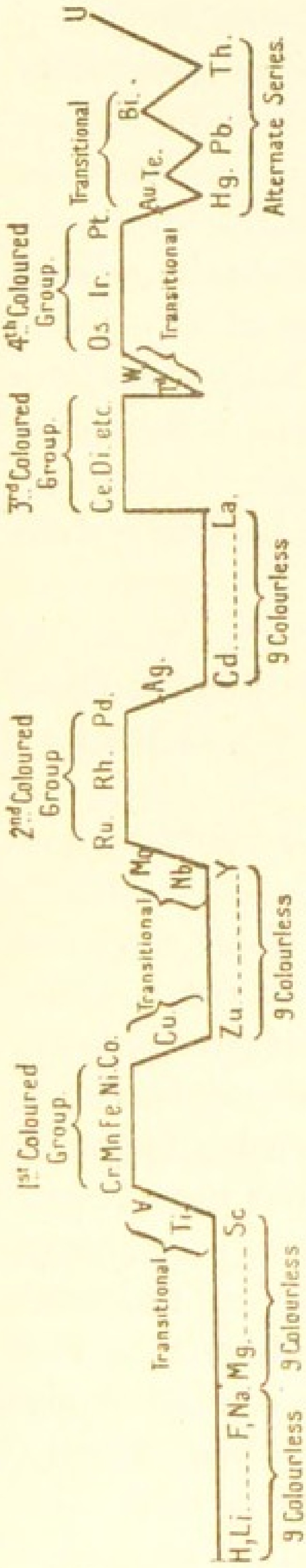
From these values it appears that the elements in the odd series get more and more diamagnetic with increase in atomic weight. Little more than this can be done.

It seems that in the eighth group the paramagnetism decreases with increase of atomic weight, for Fe, Co and Ni are strongly paramagnetic, whilst Ru, Pd, Pt, Os and Ir are only feebly so.

Electrical Conductivities.

The consideration of this property is rendered exceedingly difficult owing to the uncertainty of any data used. The electrical conductivity changes so much with the slightest trace of impurity, less than can be detected by chemical tests, that in many cases, where the substances employed were certainly not pure, the numbers expressing the conductivities are worthless. The electrical conductivity is usually stated to be a periodic function of the atomic weight, but the data seem only just sufficient to indicate this. No doubt, as time goes on, when we can obtain purer specimens than is possible at present, this property will be shown to be periodic like all the other well-defined properties of the elements. A list of conductivities, as yet determined, is given here, taking the value Hg = 1 at 0° as the unit:—

Li 10·69	Na 18·3	K 11·23	
Cu 53·0	Ag 60·0	Au 44·0	
Mg 22·84	Zn 16·1	Cd 13·46	Hg 1
Ca 12·5			
Al 20·97	Tl 5·2		
C 0·082	Sn 8·73	Pb 4·8	
As 2·7	Sb 2·05	Bi 0·8	
Te 0·05			
Fe 9·68	Ni 7·37	Co 9·68	
Pd 12·64 at 17·2	(Ag = 100 at 0°)	17·3 approx. when Hg = 1	
Pt 8·042 at 12·5	(Ag = 100 at 0°)	11·5 approx. when Hg = 1	



It appears that the elements Cu, Ag and Au lie at the maxima and the elements of the sulphur group at the minima of the curve. In fact, the thermal and electrical conductivities are, as a general rule, more or less proportional to one another.

Colour.

Owing to the great similarity in appearance of the various metals, it is not possible to find any periodic variations of this property with atomic weight of a sufficiently pronounced character.

However, when we come to the colour of the *ion* in solution, we can get more hopeful results.

Carey Lea investigated the question,[1] and showed that, at least for the elements up to the rare earths La, Ce, etc., there was a decided periodicity, and this is best shown by means of the appended arbitrary diagram.

We get first nine elements with colourless ions, then another nine followed by two elements, whose ions are sometimes coloured and sometimes not. After this we get the first coloured group, a transitional element, as those with both coloured

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[1] *C. N.* 73 (1896), p. 203.

and colourless ions are called, and then another group of nine colourless ions. The periodicity goes on in this way until we arrive at the lanthanum group, where we notice irregularities, owing, no doubt, to impure specimens and the number of missing elements. Leaving these, we get the two transitional elements tantalum and tungsten, another coloured group, the transitional element gold, and then finally the alternate series, as it is called, or colourless, transitional and coloured ions.

Here, then, we see that colour is a fairly well-defined periodic property.

General Physical Properties.

Under this heading it is intended to include those properties of the elements which are not, at least at present, quantitative.

These are best referred to the atomic volume curve in several cases.

It will be seen from the periodic table that the metallic elements, with the exception of the seventh group, are situated in the outer vertical columns, whilst the non-metals preponderate in the middle ones. Also, the metallic properties increase in each group with atomic weight in all cases except the first group.

The elements of the first series show a tendency to assume the characteristic properties of the next group, *e.g.*, lithium is very like the alkaline earths, by forming an easily soluble bicarbonate, a sparingly soluble carbonate and phosphate. Beryllium closely resembles the aluminium group. Boron is more like silicon than anything else.

The ductile metals are situated at or near the maximum or minimum points, whilst the brittle metals are to be found immediately before or after the minima on the atomic volume curve. This is, however, by no means well defined, and it would be uncertain to predict this particular property of any element from its position on the curve.

As regards the occurrence of the elements, we can again refer to the atomic volume curve, as shown by Carnelley.[1] Elements on the descending branches of the curve never occur free in nature or as sulphides, but always in combination with oxygen, and are reducible with difficulty. Elements on the ascending branches, on the other hand, occur more or less free in nature and as sulphides, either simple or mixed, and rarely in combination with oxygen, being also easily reducible.

Roberts-Austen[2] showed that there was a periodicity in the tenacity of gold alloyed with about 0·2 per cent. of other metals.

Sutherland[3] noted that the vibration periods of the elements at their melting points were also periodic functions. These vibration periods were obtained as follows:—Let M be the mass of a body and C the mean specific heat from absolute zero to the melting point (T). Then the heat received is MCT, and this is assumed proportional to the kinetic energy $\frac{1}{2}Mv^2$, where v is the vibration velocity of the molecule at the melting point. If there were no

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[1] *P. M.* (5), 18 (1884), p. 194.

[2] *Proc. Roy. Soc.* 43 (1887), p. 425.

[3] *P. M.* (5), 30, p. 318.

expansion this would be actually the case. Now since $MC=$constant, therefore v is proportional to $\sqrt{\frac{T}{M}}$. Let L be the length of the vibration, then $\frac{L}{v}$ represents the vibration period. Suppose d be the density of the body, then $\frac{M}{d}$ is volume occupied by the molecule, and if α be the mean linear expansion coefficient from absolute zero to the melting point, then $\alpha T\left(\frac{M}{d}\right)^{\frac{1}{3}}$ represents the increase in the linear dimension of the space occupied by the molecule when heated from absolute zero to T, and hence the amplitude of the vibration. The periodic time ρ of vibration of the molecule at its melting point is thus proportional to

$$\frac{\alpha T\left(\frac{M}{d}\right)^{\frac{1}{3}}}{\sqrt{\frac{MCT}{M}}}.$$

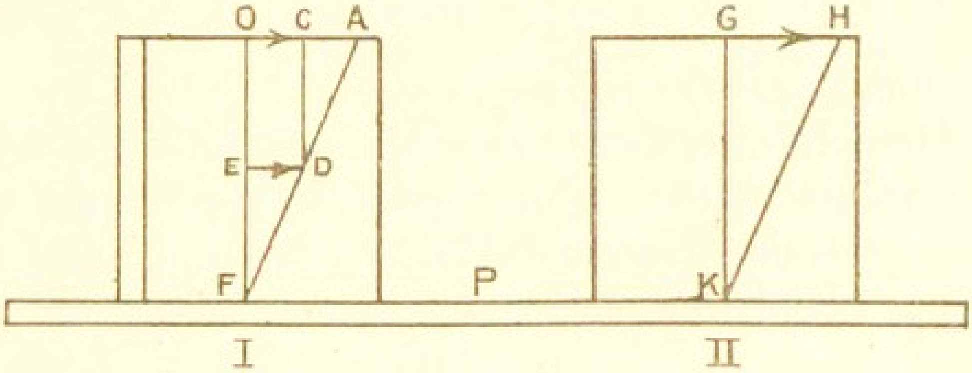
For the elements the atoms are considered and M is taken as the atomic weight.

As, however, α and C cannot be determined over the range required, the results arrived at do not actually represent the values of ρ. Also, in many cases α is not known at all. Sutherland finds that the empirical formula $\alpha TM\frac{1}{6}=$constant holds very well, and by introducing this into the above equation we get the simple result that $\rho=\frac{\left(\frac{M}{d}\right)^{\frac{1}{3}}M^{\frac{1}{3}}}{\sqrt{T}}\times$ some constant.

The author further applies these relations to similar compounds, and on the whole the results are fairly satisfactory.

Mechanical Properties.

We must not close this chapter without giving an account of the work of R. A. Fessenden on the mechanical properties of the elements.[1]



Let the two cubes I. and II. represent two cubic centimetres of different substances, of which the atoms of the one are twice the diameter of those of the other, or the distance between the centres of the atoms in the one case is twice as great as the other. Suppose I. to contain the smaller atoms. Assume one face of the cube made fast to a plank P, and then let both be sheared till they take up the positions denoted by F A and K H. Then the ratio of the work done in bringing an atom at G to H to that done in bringing an atom at E to D or at C to A is equal to the ratio of the force of attraction between K and G to that between F and E. This force varies inversely as the square of the distance and since GK = 2EF, therefore the work done in moving E to D

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[1] *C. N.* 66 (1892), pp. 206, 217.

is four times the work done in moving G to H. Again in (I.) there will be 2^3 times as many atoms as in (II.) to be displaced, and hence on the whole there will be $2^2 \times 2^3$ times as much work done in shearing cube (I.) as in shearing cube (II.). Therefore the rigidity should vary inversely as the fifth power of the distance between the centre of the atoms that is in symbols. $R \propto \frac{1}{(A)^{\frac{5}{3}}}$ where A is the atomic volume and R the rigidity.

The following table shows the comparison between the values of the rigidity given by Sutherland and those calculated from the above formula using the value 12960×10^9 for the constant, and thus the formula becomes $R = \frac{12960 \times 10^9}{(A)^{\frac{5}{3}}}$. This is obtained from the value for gold.

It will be seen that the agreement is fairly good.

		Rigidity.		
Element.	At. Vol.	Sutherland.	Calculated I.	Calculated II.
Iron	7·1	750×10^9	483×10^9	550×10^9
Copper	7·0	430	483	550
Zinc	9·4	350	314	340
Silver	10·2	280	270	270
Gold	10·2	270	270	270
Magnesium	13·9	150	154	143
Tin	16·2	136	122	100
Lead	18·2	84	100	83
Aluminium	10·4	250	250	260

Column I. gives the values from the formula $R = \frac{12960 \times 10^9}{(A)^{\frac{5}{3}}}$, and column II. the same from the formula $R = \frac{28 \times 10^{12}}{(A)^2}$, this being an arbitrary formula which seems to fit the results rather better.

If, then, the rigidity be proportional to some power of the atomic volume, it must naturally be periodic.

Young's Modulus.

Here we see that the moduli of elasticity can be fairly well calculated from the expression

$$Y=\frac{78\times 10^{12}}{(A)^2}.$$

Element.	Young's Modulus.	Calculated.
Iron	2000×10^9	1500×10^9
Copper	1220	1560
Zinc	930	920
Silver	740	750
Gold	760	750
Aluminium	680	690
Cadmium	480	465
Magnesium	390	395
Lead	190	235

Hence it is probable that Young's Modulus is also periodic.

Young's Modulus might be denoted by $\frac{1}{a}$, the Rigidity Modulus would then be $\frac{1}{2(a+b)}$, and the Bulk Modulus $\frac{1}{3(a-2b)}$, where b denotes the lateral shortening accompanying a longitudinal lengthening a.

Now if $\frac{b}{a}=$ constant, then both Young's and the Bulk Moduli would be each some fraction of the Modulus of Rigidity. Continental writers take $\frac{b}{a}=\frac{1}{4}$. Kelvin, Tait and Stokes, however, say there is no relation, and the fraction is *not* always equal to $\frac{1}{4}$.

We have $\frac{\text{Rigidity Modulus}}{\text{Young's Modulus}}=\frac{28}{78}$, therefore $\frac{a}{2(a+b)}=\frac{1}{2\cdot 7}$. Poisson gives 0·35. Hence the Bulk Modulus = 1·1 Young's Modulus. Wertheim for brass gives $\frac{10\cdot 2}{9\cdot 48}=1\cdot 08$.

We might thus expect the Bulk Modulus also to vary periodically.

Again, since the velocity of sound in a body is equal to the square root of the ratio of the elasticity to the density, or $V=\left(\frac{E}{D}\right)^{\frac{1}{2}}$, it might also be periodic.

$$\text{For } E = \text{Young's Modulus}$$

$$=\frac{\text{constant}}{(\text{at. vol.})^2}=\frac{k}{\left(\frac{\text{at. wt.}}{\text{dens.}}\right)^2}.$$

$$\text{Therefore } V=\left(\frac{\text{constant}}{\text{at wt.at . vol.}}\right)^{\frac{1}{2}}.$$

The value of the constant is 78×10^{12}. Let us see how calculated and observed values agree.

Element.	Obs. Velocity.	Calculated.
Silver . . .	$2\cdot 61\times 10^5$	$2\cdot 7\times 10^5$
Copper . . .	3·56	4·1
Gold . . .	1·74	1·9
Lead . . .	1·23	1·4

When we remember how much these various moduli depend on the purity of the metal used, the agreement between observed and calculated values must be considered fairly good. Of course such an acceptance would at once lead to the result that these mechanical properties are also periodic functions of the atomic weight.

The tensile strength also seems to depend on the atomic volume, but in a less satisfactory manner. In the following table are given the experimental values, and those calculated (I.) from the formula $T = \frac{6 \cdot 38}{(\text{at. vol.})^{\frac{4}{3}}}$, and (II.) allowing for the magnitudes of the melting point, and assuming that the flow is a *linear* function of the temperature.

Element.	Calculated (I.).	Calculated (II.).	Observed.
Iron	48	74	65
Copper	48	48	41
Platinum	36	48	35
Zinc	33	29	15·77
Silver	29	29	29·6
Gold	29	18	28·46
Aluminium	27	16	18
Tin	5	15	3·40
Lead	4	13	2·36

The numbers represent kilograms for a wire of 1 mm. cross section.

It is probable that in the future, when the metals have been obtained in a state of greater purity, that these hitherto little examined properties may eventually be shown to vary as periodically as even the atomic volumes, which are, up to the present time, the most regular of all the periodic functions as yet examined.

CHAPTER V

A DISCUSSION ON THE PERIODIC LAW—*continued*

(c) *Relations existing between the Properties of Typical Compounds.*

It is now necessary to examine the typical compounds of the elements and see whether they also show periodicity in their properties.

Halides.

The elements of the lithium group, as also sodium, form halides only of the general formula RX. The halides are soluble in water, and are not decomposed by it. The elements copper, silver and gold resemble more the metals of the eighth group than sodium. They form insoluble monohalides, and their dihalides are soluble in water, thus resembling the magnesium group; gold further forms trihalides. Of the beryllium group, all the elements form only dihalides, as do also those of the magnesium group, which are soluble in water. Mercury is an exception, it forms also an insoluble monohalide, thus resembling the copper group. Only trihalides are known in the boron group, and the elements of the aluminium group also form trihalides; however, a dihalide of aluminium is known in combination, also a dihalide of gallium. Indium forms both a di- and mono-halide, and thallium forms stable monohalides, but its dihalides are attacked by water, as are also those of gallium and indium.

In the carbon group only tetrahalides are known; however, cerium may form a trihalide, thus resembling the earths of the previous group. The silicon elements also form tetrahalides and dihalides in addition. Elements of the nitrogen group form several halides, nitrogen excepted. Vanadium forms at least four, niobium two, and tantalum one. In the phosphorus group the reverse is the case. Sulphur, selenium and tellurium furnish representatives of M_2R_2, MR_2, MR_4.[1] Iodine forms a mono- and trichloride. The halides of manganese and chromium resemble those of iron, cobalt and nickel, the formulæ of which are MX_2, MX_3, and MX_4. The palladium and platinum metals are similar.

Alkides.

These correspond to the halides in composition. Mendeléeff[2] pointed out that, excepting the second, elements of even series did not form alkyl compounds. Taking the ethyl compounds as typical, we have in the lithium group only the double compound $K(C_2H_5).\,Zn(C_2H_5)_2$, and the similar compound $Na(C_2H_5).\,Zn(C_2H_5)_2$ in the sodium group. The beryllium group is represented by $Be(C_2H_5)_2$, and the magnesium group by $Mg(C_2H_5)_2$, $Zn(C_2H_5)_2$,

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[1] Moissan has obtained a hexafluoride of sulphur (1900).

[2] *Ann. Chem. Pharm. Suppl.* (1872), p. 151.

$Cd(C_2H_5)_2$, and $Hg(C_2H_5)_2$. In the boron group only $B(C_2H_5)_3$ is known, with aluminium we have $Al(C_2H_5)_3$ and $Al_2(C_2H_5)_6$, and thallium is represented by $Tl(C_2H_5)_2Cl$, corresponding to $Tl(C_2H_5)_3$, which has, however, not yet been isolated. In the silicon group we have $Si(C_2H_5)_4$ and $Si_2(C_2H_5)_6$; $Ge(C_2H_5)_4$; $Sn(C_2H_5)_4$ and $Sn_2(C_2H_5)_6$; $Pb(C_2H_5)_4$ and $Pb_2(C_2H_5)_6$. In the nitrogen group we have $N(C_2H_5)_3$ and $N_2(C_2H_5)_4$, and in the phosphorus group $P(C_2H_5)_3$ and $P_2(C_2H_5)_4$; $As(C_2H_5)_3$, $As_2(C_2H_5)_4$ and $As(C_2H_5)_5$ (?); $Sb(C_2H_5)_3$, and lastly $Bi(C_2H_5)_3$.

This is as far as these interesting compounds are known.

Hydroxides.

Generally speaking, the hydroxides correspond to the halides, if the (OH) group be substituted for halogen. However, the compounds $C(OH)_4$, $P(OH)_5$, $S(OH)_6$ and $Cl(OH)_7$ are too unstable to exist; in fact, compounds of carbon containing only two hydroxyl groups on the same carbon atom are as a rule unstable. The derivatives of the above hypothetical compounds, namely, $(OH)_2CO$, $(OH)_3PO$, $(OH)_2SO_2$ and $(OH)ClO_3$ exist and show that the above compounds are possible.

Oxides.

In this category we can also include the sulphides, selenides and tellurides, and here the compounds known are more numerous and complex than has been the case hitherto.

In the elements of the lithium group, and also sodium, we have the normal oxides Li_2O, K_2O, Na_2O, etc., and sulphides Na_2S, K_2S, etc., together with a number of complex bodies of the type Na_2S_2, Na_2S_3, Na_2S_4, Na_2S_5, and oxides of the type K_2O_2, K_2O_3, and K_2O_4. In the case of copper, silver and gold we have representatives of the general formulæ M_2R, MR, M_2R_3 and MR_2, where M is the metal and R denotes either oxygen, sulphur, selenium or tellurium. In the beryllium group we have MR, together with CaO_2, SrO_2 and BaO_2, and also CaS_2, BaS_3, SrS_4 and CaS_5. In the magnesium group there are the compounds MR; and compounds of the formula ZnO_2, CdO_2 and ZnS_5 have been described, but their existence seems doubtful. Mercury gives M_2R and MR. In the boron group only B_2S_3 is known, and the oxides M_2O_3. However, lanthanum and yttrium seem also to form an oxide of the type M_4O_9. With the exception of thallium, which gives in addition Tl_2O, Tl_2S and Tl_2Se, the elements of the aluminium group only form sesqui compounds of the type M_2R_3. In the carbon group we have representatives of the formulæ MR, M_2R_3, MR_2, M_2R_5, MR_3 and M_2R_7. Except in the case of cerium the dioxides are the most stable. The elements of the silicon group give compounds of the types MR, M_2R_3 and MR_2. Here again the dioxides are the most stable, and as in the previous case are decidedly acidic in properties.

In the nitrogen group we have the representatives of M_2R, MR, M_2R_3, MR_2, M_2R_5 and MR_3. The compounds of M_2R_5 are the most stable. In the phosphorus group we have P_4O, P_4S_3, BiO, P_4O_6, P_2O_4, P_2O_5 as typical.

The elements of the oxygen group form MR, M_2R_3, MR_2, MR_3, whilst molybdenum further forms MoS_4 and uranium UO_4. The compounds of the type MR_3 are the most stable. In the sulphur group we have SO_2, SO_3, SeO_2, TeO_2 and TeO_3, SeS_3, TeS_2 and TeS_3, and also S_2O_2, S_2O_3 and S_2O_7 exist in combination. With manganese we have MnO, Mn_2O_3, MnO_2, Mn_3O_4, MnO_3 and Mn_2O_7. The most stable is MnO. The sulphides are similar, but fewer in number. The halogens give representatives of M_2O, M_2O_3, MO_2, M_2O_5 and M_2O_7. The sulphides range from SCl_4 to S_2Cl_2.

In the iron group we have representatives of M_2R (?), MR, M_2R_3, MR_2 and MR_3. The palladium group contains MO, M_2O_3, MO_2 and MO_3, whilst the platinum group has MO_4 in addition.[1]

The borides, nitrides, phosphides, carbides and silicides are too little known to be a profitable subject for investigation.

Of course, the formulæ of the salts of the oxygen acids depend upon those of the oxides, and need not be separately considered.

It is seen from what has been said that there is a certain definite order in the periodic classification, in which elements of similar chemical behaviour are grouped together, and we must leave it to the future to satisfactorily explain many of the apparent discrepancies to this classification.

We will now consider a few of the physical properties of the typical compounds, with special

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[1] A list of the oxides, etc., is given in the Appendix (*q.v.*).

reference to the atomic weights of the metals contained in them, and here again marked periodicity will in most cases be noticeable. Carnelley devoted a great portion of his life to the correct determination of some of these physical constants, and was, indeed, one of the most ardent workers in the field. A great many periodic relations were either pointed out or further demonstrated by him; but it must be remembered that some of his so-called experimental *values* were not really so.

Some of the properties of the typical compounds will now be discussed.

A.—PROPERTIES OF THE HALIDES.

Melting Points.

These were investigated by Carnelley in 1884, and shown to be periodic.[1] Reference should be made to the original memoir, in which a number of relations between the melting points of the halides are pointed out which are not suited for abstraction. By means of these relations, Carnelley was able, with, probably, a fair degree of accuracy, to calculate a number of unknown melting points.

The following table illustrates the periodicity in the case of the iodides. The melting points are those on the absolute scale. The values for the chlorides and bromides are collected together in the Appendix, as they follow a similar course to the iodides, and need not be separately considered.

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[1] *P. M.* [5], 18, p. 1.

Li 719	Be	B	C 373	N	O	F			
Na 901	Mg	Al 398	Si 393	P 328	S	Cl 298			
K 907	Ca 904	Sc	Ti 423	V	Cr	Mn	Fe	Ni	Co
Cu 874	Zn 719	Ga	Ge 417	As 419	Se	Br 309			
Rb 915	Sr 750	Y	Zr	Nb	Mo		Ru	Rh	Pd
Ag 800	Cd 677	In	Sn 419	Sb 438	Te 433	I 383			
Cs	Ba	La	Ce						
				Ta	W		Os	Ir	Pt
Au	Hg 514	Tl	Pb	Bi					
			Th		U				
RI	RI_2	RI_3	RI_4	RI_3	RI_2	RI			

Such are the experimental data at our disposal. It will be seen that the maxima fall on the alkalies and the minima on the elements of the chlorine group. Now that we have more accurate means of measuring high temperatures, largely owing to the researches of Professor Callendar on platinum thermometry, it would be very desirable to determine a number of these melting points again, and also others as yet unknown.

Boiling Points.

These were also shown to be periodic by Carnelley.[1] We will illustrate the periodicity in the case of the chlorides. The data for the bromides and iodides are to be found in the Appendix.

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[1] *P.M.* [5], 18, p. 1.

Li	Be	B	C	N	O	F			
		290	351	334	253				
Na	Mg	Al	Si	P	S	Cl			
		453	331	351	337	240			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
			563						
Cu	Zn	Ga	Ge	As	Se	Br			
abt.1273	953	493	359	405		286			
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd
Ag	Cd	In	Sn	Sb	Te	I			
	abt. 1173		388	496	600	373			
Cs	Ba	La	Ce						
				Ta	W		Os	Ir	Pt
Au	Hg	Tl	Pb	Bi					
	576			703					
			Th		U				
RCl	RCl_2	RCl_3	RCl_4	RCl_3	RCl_2	RCl			

If the calculated values of the melting and boiling points of the halides be also inserted in the periodic table, then the periodicity becomes more visible. It must be confessed that the experimental values do not show this any too satisfactorily.

Molecular Volume.

The molecular volumes are calculated from the expression $\left(\frac{A+nH}{s}\right)$ where A is the atomic weight of the metallic constituent, H is the halogen, and n the numbers of atoms of the latter in the molecule, s is the specific gravity of the halide.

We will consider the bromides as typical. The values for the chlorides and iodides will be found in the Appendix. The data are not very abundant, but, notwithstanding, periodicity is noticeable.

The values for the molecular volumes of the bromides are :—

Li 13·7	Na 19·0	K 28·6	Rb 35·9	Cs 37·7
Cu 30·8	Ag 23·0	...	...	...
Ca 33·4	Sr 39·8	Ba 49·2	...	...
Zn 37·4	Cd 38·2	Hg 47·2	...	...
B 43·6	Al 52·5	...	...	...
C 44·8	Si 60·3	Ti 73·0	...	...
P 47·0	As 49·5	Sb 54·6	Bi 58·2	...
Br 50·1	...	...	...	...

Heats of Formation.

These were investigated by Laurie[1] and later by Carnelley.[2]

For the chlorides they are as follows :—

Li	Be	B	C	N	O	F			
939		1040	210						
Na	Mg	Al	Si	P	S	Cl			
979	1510	1618		755					
K	Ca	Se	Ti	V	Cr	Mn	Fe	Ni	Co
1057	1706								
Cu	Zn	Ga	Ge	As	Se	Br			
657	974			715					
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd
	1846								
Ag	Cd	In	Sn	Sb	Te	I			
290	936		1298	898		58			
Cs	Ba	La	Ce						
	1947								
				Ta	W		Os	Ir	Pt
Au	Hg	Tl	Pb	Bi					
5·8	532			906					
			Th		U				
RCl	RCl_2	RCl_3	RCl_4	RCl_3	RCl_2	RCl			

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[1] *P. M.* [5], 15, p. 42.

[2] *P. M.* [5], 18, p. 1.

No further data are available. However, Laurie's curve shows periodicity.

The data for the other halides are to be found in the Appendix.

The elements of the 8th group will be left out of consideration in all cases owing to the difficulty of knowing which halides one is to select.

B.—Properties of the Alkides.

Carnelley[1] examined the boiling points of the methides, ethides, normal propides and normal butides, and also their specific gravities in the same way as the properties of the halides. Periodicity was here again displayed, the exceptions being those elements at or near the turning points of Lothar Meyer's curve.

The data are as follows for the boiling points on the absolute scale:—

Methides—

...	...	$Zn(Me)_2$ 319	...	$Hg(Me)_2$ 367
$B(Me)_3$ b257	$Al(Me)_3$ 403	...	...	...
$C(Me)_4$ 282	$Si(Me)_4$ 303	...	$Sn(Me)_4$ 351	$Pb(Me)_4$ 383
$N(Me)_3$ 281	$P(Me)_3$ 314	$As(Me)_3$ b373	$Sb(Me)_3$ 354	...
$O(Me)_2$ 249	$S(Me)_2$ 314	$Se(Me)_2$ 331	$Te(Me)_2$ 355	...
...	$Cl(Me)$ 249	$Br(Me)$ 277	$I(Me)$ 317	...

Ethides—

$Be(Et)_2$ 459	...	$Zn(Et)_2$ 391	...	$Hg(Et)_2$ 432
$B(Et)_3$ 369	$Al(Et)_3$ 467	...	...	...
...	$Si(Et)_4$ 425	$Ge(Et)_4$ 433	$Sn(Et)_4$ 454	$Pb(Et)_4$ 473
$N(Et)_3$ 362	$P(Et)_3$ 401	$As(Et)_3$ 413	$Sb(Et)_3$ 432	...
$O(Et)_2$ 308	$S(Et)_2$ 364	$Se(Et)_2$ 381	$Te(Et)_2$ b273	...
$F(Et)$ 283(?)	$Cl(Et)$ 285	$Br(Et)$ 312	$I(Et)$ 345	...

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[1] *P. M.* [5], 20 (1885), p. 259.

n Propides—

Be(Pr)$_2$ 518	...	Zn(Pr)$_2$ 432	...	Hg(Pr)$_2$ 464
...	Al(Pr)$_3$ 523	...	..	...
...	Si(Pr)$_4$ 486	...	Sn(Pr)$_4$ 498	...
N(Pr)$_3$ 429	...	...	...	...
O(Pr)$_2$ 357	S(Pr)$_2$ 405	...	...	...
...	Cl(Pr) 319	Br(Pr) 344	I(Pr) 375	...

n Butides—

N(Bu)$_3$ 486	O(Bu)$_2$ 413	S(Bu)$_2$ 455	Cl(Bu) 351
Zn(Bu)$_2$ 461	Br(Bu) 373	I(Bu) 403	Hg(Bu)$_2$ 479

C.—OXIDES.

Molecular Volumes.

The molecular volume is defined by the following formula $M=\left(\frac{2A+n16}{s}\right)$ where A is the atomic weight of the element, n represents the number of oxygen atoms in the highest oxide (R_2O_n), and s is the specific gravity of this oxide.

The periodicity was first shown by Brauner and Watts.[1]

The following table gives the molecular volumes of the oxides calculated from the above formula. That this property is periodic is unmistakable, as the number of data is considerable. The values are those given by Mendeléeff.

	I.	II.	III.	IV.	V.	VI.
1.	Li$_2$O 15	K$_2$O 35	Rb$_2$O	Cs$_2$O	...	...
2.	Be$_2$O$_2$ 16·3	Ca$_2$O$_2$ 36	Sr$_2$O$_2$ 48	Ba$_2$O$_2$ 60	...	...
3.	B$_2$O$_3$ 39	Sc$_2$O$_3$ 35	Y$_2$O$_3$ 45	La$_2$O$_3$ 50	...	...
4.	C$_2$O$_4$ <88	Ti$_2$O$_4$ 38	Zr$_2$O$_4$ 43	Ce$_2$O$_4$ 50	...	Th$_2$O$_4$ 54
5.	N$_2$O$_5$ 66	V$_2$O$_5$ 52	Nb$_2$O$_5$ 57	...	Ta$_2$O$_5$ 59	...
6.	O	Cr$_2$O$_6$ 73	Mo$_2$O$_6$ 65	...	W$_2$O$_6$ 67	U$_2$O$_6$ 80
7.	F$_2$O$_7$	Mn$_2$O$_7$	...	...	...	...

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[1] *B.* 14 (1881), p. 48.

	I.	II.	III.	IV.	V.	VI.
1.	Na_2O 24	Cu_2O 24	Ag_2O 31	...	Au_2O 33	...
2.	Mg_2O_2 22	Zn_2O_2 28	Cd_2O_2 31	...	Hg_2O_2 39	...
3.	Al_2O_3 26	Ga_2O_3 36	In_2O_3 38	...	Tl_2O_3 47	...
4.	Si_2O_4 45	Ge_2O_4 44	Sn_2O_4 43	...	Pb_2O_4 53	...
5.	P_2O_5 59	As_2O_5 56	Sb_2O_5 49	...	Bi_2O_5	...
6.	S_2O_6 82	Se_2O_6	Te_2O_6 68	...	...	...
7.	Cl_2O_7	Br_2O_7	I_2O_7	...	...	...

Affinity for Water.

The temperature of dehydration of the hydroxides, which would be a measure of the affinity of the oxides for water, was investigated by Carnelley and Walker.[1] The conclusions they arrived at were as follows:—

In the same group—

(1.) Even members show an *increase* in the temperature of dehydration with increase of atomic weight.

(2.) Odd members show a *decrease* in the temperature of dehydration with increase in atomic weight.

In the same series—

The temperature of dehydration diminishes to the middle member and then increases again.

These results may be summed up by saying that the stability of the hydroxides, or the affinity of the oxides for water, is a periodic function of the atomic weights of the electro-positive constituents.

The following table is given by the authors:—

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[1] *J. C. S.* 53 (1888), p. 59.

TEMPERATURES OF DEHYDRATION OF THE HYDROXIDES.

Series														
1	H_2O.		...		...		...		...		...		..	
2	Li_2O.	?	BeO.	High	B_2O_3.	Below 577	CO_2.	Below 100	N_2O_5.	About 260	...		...	
3	Na_2O.	Not at a red heat	MgO.	630	Al_2O_3.	About 850	SiO_2.	About 850	P_2O_5.	Not at a red heat	SO_3.	Decomposed on heating	Cl_2O_7.	?
4	K_2O.	Not at a red heat	CaO.	Red heat	Sc_2O_3.	?	TiO_2.	700	V_2O_5.	On evaporation	CrO_3.	On evaporation	Mn_2O_7.	?
5	Cu_2O.	360 (?)	ZnO.	585	Ga_2O_3.	?	GeO_2.	?	As_2O_5.	About 206	SeO_3.	Not at 265	Br_2O_7.	?
6	Rb_2O.	?	SrO.	Dull red heat	Yt_2O_3.	Red heat	ZrO_2.	About 550	Nb_2O_5.	Not at 100° red heat	MoO_3.	About 170°	...	
7	Ag_2O.	About 150	CdO.	385	In_2O_3.	655	SnO_2.	About 665	Sb_2O_5.	Below red heat	TeO_3.	At a red heat	I_2O_7.	160 (?)
8	Cs_2O.	?	BaO.	At a full red heat	La_2O_3.	?	CeO_2.	About 850	Di_2O_5.	?	..		...	
9	...		...		..		..		...		..		...	
10	...		...		...		...		Ta_2O_5.	At a low red heat	WO_3.	On ignition	..	
11	Au_2O.	Below 15	HgO.	About 175	Tl_2O_3.	?	PbO_2.	About 230	Bi_2O_5.	150	..		...	
12	...		..		...		ThO_2.	At a red heat	...		UO_3.	300	...	

Colour.

Carnelley[1] showed that in similar compounds with increase in atomic weight the colour changed in accordance with the following chromatic scale:—white, violet, indigo, blue, green, yellow, orange, red, brown and black. A great number of examples are given which bear out this suggestion. It is best demonstrated for the normal iodides by plotting a curve, the points of which have atomic weights for abscissæ and the arbitrary chromatic scale from black to white as ordinates. A periodic curve is thus obtained resembling somewhat that of the atomic volumes of the elements.

Prud'homme[2] showed that the shades produced by using the metallic oxides to fix one and the same colouring-matter varied periodically with the atomic weight of the contained metal.

Internal Friction.

J. Wagner[3] showed that the internal friction of aqueous solutions of a number of similarly constituted compounds also varied periodically. Among other workers in this field, mention must be made of Pribram and Handl.

In concluding this chapter, then, we can safely say that every well-defined property of an element that has been examined is a periodic function of the atomic weight; and the same holds for analogous compounds.

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[1] *P. M.* [5], 18, p. 130.

[2] *C. R.* 112 (1891), p. 236.

[3] *Zeit. Phys. Chem.* 5 (1890), p. 49.

CHAPTER VI

APPLICATIONS AND USES OF THE PERIODIC CLASSIFICATION

When the periodic law was first formulated there were a number of instances in which the law and the then accepted atomic weights were not in harmony. Mendeléeff stated that the atomic weights, and not the law, were at fault, and subsequent experimenters have fully justified this statement. Indium, for example, was thought to be divalent, *i.e.*, that its oxide was InO and its chloride $InCl_2$. Its equivalent was 38. Hence the atomic weight would have been $2 \times 38 = 76$—that is, it would have had to come between arsenic and selenium. It showed no analogy to such a position, and, in fact, there was no room for it. Mendeléeff then assumed that the chloride was $InCl_3$ and the oxide In_2O_3. This would make its atomic weight 114. With this value the element falls in the aluminium group. Bunsen's determination of the specific heat gave 0·057, and hence the atomic weight deduced from Dulong and Petit's Law would be $\frac{6{\cdot}4}{0{\cdot}057} = 112{\cdot}3$. This, then, confirmed Mendeléeff's views.

Beryllium is another case in point. It was assumed to be trivalent, and hence its atomic weight was supposed to be $3 \times 4{\cdot}6 = 13{\cdot}8$—that is, it should come between carbon and nitrogen, where there is no room for such an element. If its oxide be BeO, then the atomic weight would be $4{\cdot}6 \times 2 = 9{\cdot}2$, and it would find its place between lithium and boron. A determination of the specific heat gave 0·45, and this would give 14 as the atomic weight. However, Mendeléeff still regarded 9·2 as correct, and a suggestion was made that perhaps the specific heat of beryllium was at ordinary temperatures abnormally low, like those of carbon and boron. A subsequent determination by Humpidge showed this to be actually the case. At 500° the specific heat was 0·6206. This gives 10 as the atomic weight. A further confirmation of the value 9·2 was given by Nilson and Petterssen,[1] who determined the vapour density of the chloride. The result was 40·42 (at. 812°), thus showing a molecular weight of 80·84, and hence the compound could not possibly contain more than two atoms of chlorine in the molecule.

Another example is furnished by uranium. The uranyl compounds were thought to contain the group (U_2O_2), and the formula of the most stable oxide was put down as U_2O_3. This gave uranium the atomic weight 120. There was no room for such an element in the table, and hence it was decided to double the atomic weight. This made the uranyl group (UO_2) and the oxide UO_3, and the element

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[1] *C. R.* 98 (1884), p. 988.

would be in its true place as an analogue of tungsten and molybdenum.

Cl. Zimmermann (1882 and 1886) subsequently confirmed this view by determining the atomic weight (1) by reducing U_3O_8 to UO_2 in a stream of hydrogen, and (2) by converting sodium uranyl acetate into sodium diuranate. The result was U = 239·4.

Osmium, iridium and platinum were given the atomic weights 200, 197 and 197-8 respectively. These were also put in their correct places, and they were later confirmed by Seubert.

The case which is at present unsettled is that of tellurium. This was discussed in a previous chapter (III.).

In the hands of Mendeléeff the classification was further utilised to predict the properties of undiscovered elements. He predicted with a most remarkable degree of accuracy the properties of the elements which we now know as scandium, gallium and germanium, but which he denoted as eka-boron, eka-aluminium and eka-silicon respectively.

The following comparison will show the remarkable agreement between theory and experimental results:—

Predicted Properties of Eka-Aluminium.

(1.) Should have an atomic weight about 69.
(2.) Will have a low melting point.
(3.) Its specific gravity should be about 5·9.
(4.) Will not tarnish in the air.
(5.) Will decompose water at a red heat.

(6.) Its chloride, oxide and sulphate will have the formulæ $ElCl_3$, El_2O_3, $El_2(SO_4)_3$.

(7.) Will form a potassium alum, which will probably be more soluble and less easily crystallisable than the corresponding aluminium alum.

(8.) The oxide should be more easily reducible to the metal than aluminium. The metal will probably be more volatile than aluminium, and hence its discovery by means of the spectroscope may be expected.

Four years later (1875) Lecoq de Boisbaudran discovered an element in a specimen of blende by means of its spectrum, which was characterised by a brilliant line in the violet, which he named *Gallium*. Its properties showed that it was the eka-aluminium of Mendeléeff, and are—

(1.) Atomic weight 69·9.

(2.) Melting point 30·15°.

(3.) Specific gravity 5·93.

(4.) Only slightly oxidised at a red heat.

(5.) Decomposes water at high temperatures.

(6.) Oxide is Ga_2O_3, chloride $GaCl_3$, and sulphate $Ga_2(SO_4)_3$.

(7.) Forms a well-defined alum.

(8.) Is easily obtained by electrolysis.

The properties of *eka-boron* should be oxide R_2O_3, without any marked tendency towards combination; sulphate should be sparingly soluble, difficult to separate from yttrium; the oxide will be soluble in alkalies; it will give gelatinous precipitates with potassium or sodium hydroxide and carbonate, sodium phosphate, etc.

Ten years later (1879) Nilson discovered scandium, having these identical properties.

Eka-silicon was not discovered till 1886. It is germanium, and was found by Winkler in argyrodite. It should easily form alkyl compounds, and this was confirmed by Winkler. Mendeléeff predicted that the germanium ethyl would have a boiling point at 160°, and a specific gravity about 0·96. Actual determination confirmed these values exactly.

From what has now been said, it is obvious that the periodic classification of the elements is one of the finest generalisations in the whole domain of chemistry.

It will now be well to say a few words about the rare earths. Amongst the investigators who have devoted a great portion of their lives to the study of these bodies are to be found Crookes, Lecoq de Boisbaudran, Nilson, Krüss, Clève, Brauner, and many other distinguished chemists. Having once found that these rare earths were not simple, definite bodies, it was necessary to try and separate them into their components. The method need not be described here. Suffice it to say that it consists in a process of either fractional precipitation or solution repeated many hundreds, nay, thousands, of times.

The elements (?) of the didymium group—neodymium, praseodymium and samarium—have been investigated by means of the absorption spectra of their aqueous solutions. By fractionally crystallising the double nitrates of the "old didymium" with ammonium nitrate, Carl Auer von Welsbach succeeded in obtaining two new bodies. One of these had pink salts and the other green. To them he gave the names neo- and praseo-dymium respectively. The joint spectra of these, however, do not make up the didymium spectrum. There are still two bands unaccounted for, which might be due to some other element.

It must be remembered that any one reagent can only effect a separation into two groups; and it was shown by Crookes that by different methods of fractionation quite different results could be obtained.

Krüss and Nilson[1] believe the old didymium to contain at least nine constituents. However, Brauner has shown that it is dangerous to draw any definite conclusions from such results, for he showed that, by mixing dilute solutions of samarium and didymium, three of the bands disappear from the didymium spectrum, whilst the samarium bands do not make their appearance until a large percentage of a salt of the latter has been added. The original erbium has similarly been resolved by the investigations of Brauner, Marignac, Loret, Clève and others into at least six different earths, three of which—scandia, ytterbia and terbia—give no absorption spectrum, the others—thulia, holmia and the new erbia—give an absorption spectrum. Roscoe showed that philippia was a mixture of terbia and yttria.[2]

Elements of the yttrium group give no absorption spectra. They have been investigated by means of

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[1] *B.* 20, p. 2134.

[1] *J. C. S.* 41 (1882), p. 283.

their phosphorescence spectra by Crookes, and by Lecoq de Boisbaudran using the spark spectra.

The old yttria has been separated into a number of portions. The spectra of the extreme ends of the fractions differ from the original yttrium by the appearance of new bands, and by the disappearance of some of the old ones. Some of the substances have been named by Crookes, and are known as samarium, mosandrium, yttrium and yttrium α. Boisbaudran considers that there are three characteristic earths, $Z\alpha$, $Z\beta$, and $Z\gamma$; and further than the oxide of $Z\beta$ may be identical with that obtained from terbium. Again, one must be exceedingly cautious, for Crookes has shown that the addition of lime or alumina greatly affects the phosphorescence spectra.

We see, then, that these rare earths are evidently not elementary substances, but mixtures.

Crookes concludes that these are capable of being resolved into an almost infinite variety of others. We are therefore unable to reconcile such a state of affairs with the periodic classification.

Since, however, this latter has stood the test of severe examination, and even predictions, it seems very probable that the rare earths consist of some few elements which are very similar to one another in properties, and hence difficult to separate, but for all of which places will be found in the periodic classification. Time alone will be able to definitely settle the question.

Modifications of Mendeléeff's Arrangement.

Almost from the time that the periodic classification was first formulated, numerous rearrangements and alterations have been proposed, which were thought better to account for facts than the original one of Mendeléeff.

We will here only consider four of these, namely, those of Crookes, Richards, Walker and Horsley.

Crookes showed that a spiral curve to represent the elements was inadmissible, inasmuch as any curve must pass through a point neutral as to electricity and chemical affinity twice in a cycle. Reynolds suggested a zigzag; however, this is not continuous. Now a figure of eighth will foreshorten into both a spiral and a zigzag, and is moreover continuous. It would result from (1) an oscillation to and fro, (2) an oscillation perpendicular to this, and (3) a motion at right angles to both (1) and (2), which in its simplest form would be of constant velocity. Any figure of eighth is chosen, and each loop divided into eight parts, and ordinates corresponding to the atomic weights of the elements of the first cycle are dropped from these. The whole vertical *height* is divided into 240 divisions. The coil crosses the neutral line at points which get lower and lower.

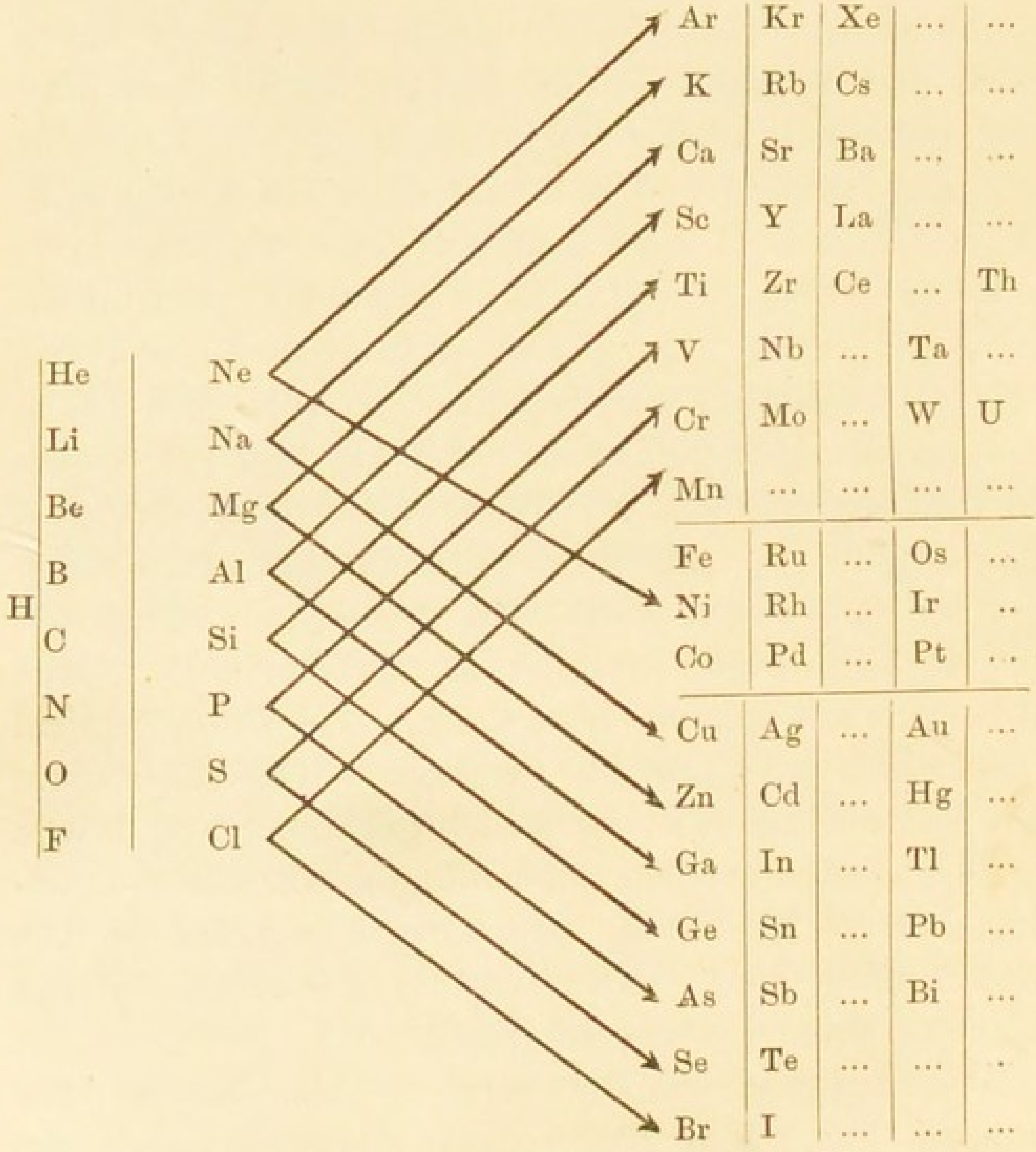
The electro-positive elements are on the retreating half of the swing, the electro-negative on the approaching half. Atomicity is governed by the distance from the central point.

Paramagnetic elements are on the left of the neutral line, whilst diamagnetic elements are on the right.[1] The table which accompanies the figure of eight diagram is appended below.

Crookes' Table.

H	He	Li	Be	B	C	N	O	F		Ne		Na	Mg	Al	Si	P	S
Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
Br	Kr	Rb	Sr	Yt	Zr	Nb	Mo	...	Rh	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
I	...	Cs	Ba	La	Ce	...	...	...		...		...	...	...	...	...	..
. .	...	...	...	...	...	Ta	W	...	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	...
...	...	...	...	...	Th	...	U	...		...		...	...	..	...	...	...

Richards' Table.



Ar	Kr	Xe	...	...
K	Rb	Cs	...	...
Ca	Sr	Ba	...	...
Sc	Y	La	...	...
Ti	Zr	Ce	...	Th
V	Nb	...	Ta	...
Cr	Mo	...	W	U
Mn	...	...	...	...
Fe	Ru	...	Os	...
Ni	Rh	...	Ir	..
Co	Pd	...	Pt	...
Cu	Ag	...	Au	...
Zn	Cd	...	Hg	...
Ga	In	...	Tl	...
Ge	Sn	...	Pb	...
As	Sb	...	Bi	...
Se	Te	...	...	..
Br	I	...	...	...

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[1] For further details *v. C. N.* 78 (1898), p. 25.

Richards divides up the elements into two short and five long periods.[1] His table is given here. It will be seen that helium and neon head the two short periods, and then these bifurcate into argon, krypton, and xenon at the head of the long periods, and into the metals of Mendeléeff's eighth group, to which indeed they may in some measure be compared, inasmuch as they form the transition between the halogens and the alkalies. Hence we see that these new inactive elements really supply a missing link in the periodic classification, and by no means upset the classification, as was thought to be the case when they were first discovered. If we want to place them in Mendeléeff's Table the best position seems to be before the alkali metals as shown in the accompanying table. Of course these elements can only occur in such rows where the elements of the eighth group are not transitional.

0	1	2	3	4	5	6	7	8		
He	Li	Be	B	C	N	O	F			
Ne	Na	Mg	Al	Si	P	S	Cl			
Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co
	Cu	Zn	Ga	Ge	As	Se	Br			
Kr	Rb	Sr	Y	Zr	Nb	Mo	...	Ru	Rh	Pd
	Ag	Cd	In	Sn	Sb	Te	I			
Xe	Cs	Ba	La	Ce	Di	...	...	...	...	...
	...	...	...	...	...	...	...			
...	...	...	Yb	...	Ta	W	...	Os	Ir	Pt
	Au	Hg	Tl	Pb	Bi	...	...			
...	...	...	...	Th	...	U	...	...	...	...

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[1] *C. N.* (1898), p. 194.

We now come to Walker's scheme :—[1]

Even Series.

Groups.			4	6	8	10	12
I.			K	Rb	Cs		
II.			Ca	Sr	Ba		
III.			Sc	Y	La	Yb	
IV.			Ti	Zr	Ce		Th
V.			V	Nb	Di	Ta	
VI.			Cr	Mo		W	U
VII.			Mn Fe	Ru		Os	
VIII.			Ni Co	Rh Pd		Ir Pt	
I.	Li	Na	Cu	Ag		Au	
II.	Be	Mg	Zn	Cd		Hg	
III.	B	Al	Ga	In		Tl	
IV.	C	Si	Ge	Sn		Pb	
V.	N	P	As	Sb		Bi	
VI.	O	S	Se	Te			
VII.	F	Cl	Br	I			
	1	3	5	7	9	11	

Uneven Series.

We see that fluorine is placed with the halogens, oxygen with the sulphur group, the earths come together, lithium is close to magnesium, beryllium to aluminium, boron to silicon, to which they are closely related.

A line drawn as shown sharply separates the metals from the non-metals. Of course this is not an ideal classification, for it places the elements lithium and sodium with copper, silver and gold, instead of with potassium, rubidium and cæsium.

My friend, Mr G. F. Horsley, has also suggested an arrangement. The elements are split into groups, shown by the vertical lines, from a consideration of

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[1] *C. N.* 63 (1891), p. 251.

their melting points. The arrows indicate the direction in which the melting point increases. Thus in the series oxygen, sulphur, etc., the melting point increases with increase of atomic weight, in the alkali series the opposite is the case. The element denoted by X is probably the lighter constituent of the cleveite gases; however, this remains to be proved, for Professor Ramsay observes that there is no such lighter constituent, and that the whole spectrum is simply that of helium.

HORSLEY'S ARRANGEMENT.

						X	He	Li									
	Be	B	C	N	O	F	Ne	Na									
	Mg	Al	Si	P	S	C	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co
Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd
Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba	La	Ce	Di					
										Yb		Ta	W		Os	Ir	Pt
Au	Hg	Tl	Pb	Bi							Th		U				
		→			↓	←		↑		↓	→			↑	←		

No classification as yet proposed is perfect; in fact; in all probability this is impossible. However, Professor Palmer has suggested[1] that these facts should be emphasised, namely—(1) omitting hydrogen, the elements fall in natural series, each of which begins with an alkali and closes with a halogen (now we should say begins with one of the inactive elements); (2) each series has light elements at the ends and heavy ones in the middle; (3) there are two short

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[1] *Proc. Col. Sci. Soc.* 1891-93.

series and five long series; (4) the short series can be compared with each other, member for member, as can also the long series; (5) *only the ends* of the short series can be compared naturally with the long series; (6) intermediate elements have double affinities with the respective members of the long series.

Since in all probability each series was evolved independently, analogies should not be emphasised too much in the attempt to discover an ideal arrangement.

PART II

CHAPTER I

THE PROBLEM OF CHEMICAL EVOLUTION

Of all problems of general chemistry this is perhaps one of the most fascinating and least investigated, because of the difficulties which it presents. In 1815 Prout supposed all the elements to be polymers of hydrogen. This was later changed to a half hydrogen primary unit, owing largely to the one fact that chlorine turned out to have an atomic weight of 35·5.

However, Dumas again halved this unit, because there were a number of elements whose atomic weights were neither integers nor uneven multiples of 0·5. But there were still several elements whose atomic weights had been most accurately determined, which could not be made to fit in with this idea, and Prout's hypothesis was considered untenable, as also its modifications.

In 1887 Crookes, from a consideration of his researches on the rare earths, gave it as his opinion that the elements, or "elementary groups," as he preferred to call them, were built up of some primary material, which he called "protyle," together with a number of "meta-elements."[1] It is difficult to realise what these "meta-elements" really are, and the reader is referred to the papers cited for a partial explanation of the term. Crookes then advances his theory of chemical evolution, which is somewhat as follows. Suppose that at the birth of the elements the action of the *vis genatrix* might be diagrammatically represented by a motion to and fro in cycles along a figure of eight path, while simultaneously time flows on, and some circumstance, *e.g.*, temperature, by which the element forming cause is conditioned, is declining. Then the result of the first cycle may be represented by H, He, Li, Be, B, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, and Cl, supposing the unknown formative cause to have scattered these along its journey. But the swing of the pendulum is not arrested at the end of its first round; it proceeds on its journey, and had all the conditions remained the same, the first cycle H to Cl would be continually repeated. These conditions might be represented by two mutually rectangular horizontal components of motion, *e.g.*, electrical and chemical energy, which are not materially modified. However, that to which the vertical component corresponds has lessened, and so we arrive at argon, and start the next cycle.

It is to be noted that hydrogen is not repeated.

Mendeléeff pointed out in 1889 that this pendulum hypothesis could not hold, for there are not an infinite

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[1] *J. C. S.* 53 (1888), and 55 (1889).

number of elements which we should theoretically expect if we assume this theory, for why should not the pendulum go on swinging for ever?

Now it depends entirely on how we regard Prout's hypothesis as to whether we must discard it or not. If we take it to mean that the atomic weights of the elements are integers, and may therefore be regarded as multiples of unity, *i.e.*, of the atomic weight of hydrogen, then our exact experimental evidences show that the above supposition is incorrect. But if we take it as meaning that the elements are condensed polymers of the hydrogen atom, then we have no reason to say our assumption is incorrect. It will be attempted in these few pages briefly to sketch the problem of chemical evolution as far as it has been carried, and the writer thinks that the evidence put forward strongly points to hydrogen's claim to being the primary matter.

It will be convenient to divide the discussion into separate groups, thus:—

(1.) To show that the elements have a certain definite fixed structure.

(2.) The evidence supporting the view that the elements are complexes of some primary material.

(3.) The reasons for considering hydrogen as this primary material.

(4.) An attempt to explain various objections to the theory.

We will now commence the consideration of each of these branches separately.

1. To show that the Elements have a fixed Atomic Structure.

This question must be answered by reference to stereo-chemistry. The only element whose stereo-chemistry has been at all thoroughly worked out is carbon; but yet several facts exist which either require, or at least suggest, a definite structure for the atoms of some other elements. From these can be argued that the elements all have a definite structure, although, perhaps, the method of argument is not logically rigid. It will be convenient to consider each element, whose study is profitable from this point of view, separately.

A.—The Stereo-isomerism of Carbon.

It is not intended to give here a detailed or even partial account of the stereo-chemistry of carbon, but one or two typical confirmations of theory will alone be given. For an excellent account of this special subject, reference should be made to Van't Hoff's well-known treatise on *The Arrangement of the Atoms in Space.*

(α) *Formation of γ Lactones.*

The extraordinary readiness of carbon to form γ lactones from the γ oxyacids can be beautifully explained by assuming the hypothesis that the four valencies of the carbon atom are directed towards the angular points of a regular tetrahedron. Unless the tetrahedron be regular, the theory does not hold, and further, no cases of optical isomerism among carbon compounds can be explained unless we insert the one proviso, that the tetrahedron must be regular.

(β) *Stability of Rings.*

The varying stability of carbon rings containing different numbers of members is easily explained on the tetrahedron theory, together with Baeyer's Tension Theory. It explains the extraordinary stability of pentamethylene rings, and also the stability, in a less degree, of the benzene ring. For these points the reader is again referred to Van't Hoff's work mentioned above, and also to Meyer and Jacobsen's *Lehrbuch der organischen Chemie*, Vol. II.

Everything at present known about the carbon compounds can be explained on the tetrahedron hypothesis. It seems then justifiable to conclude that since the valencies represent points or areas of attraction on the atoms,[1] the carbon atom itself must have a fixed structure. As to what the actual shape of this or any other atom may be, we need not trouble, as it does not concern us here. All we require is that the shape is fixed and definite for the atom of any one element.

B.—STEREO-CHEMISTRY OF NITROGEN.

As the three hydrogen atoms of ammonia are

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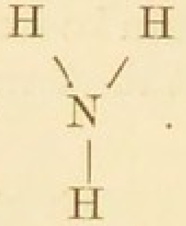
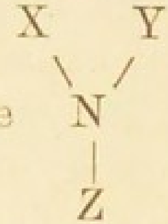
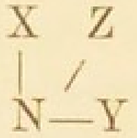
[1] At any rate, valency represents something definite and specific of the atoms.

identical, it would seem that they are in one plane with the nitrogen atom, thus:—  $\underset{H}{\overset{H\quad H}{N}}$. Obviously there can be no isomers of compounds having the formulæ  $\underset{Z}{\overset{X\quad Y}{N}}$;  $\underset{Z}{\overset{Y\quad X}{N}}$, for these are identical, and no isomers are found, although Miller and Plöchl[1] believe to have obtained two stereoisomers of the formula $NH(C_6H_3(CH_3)_2).\ CH(CH_3).\ CH_2.\ CHO$ which were inactive. This could be explained by assuming that the groups attached to the nitrogen atom are bunched together by their mutual attraction, and then  $\overset{X\quad Y}{N}{-}Z$ and  $\overset{X\quad Z}{N}{-}Y$ represent two different bodies. As the compounds contain an asymmetric carbon atom, the two isomers would probably be racemic mixtures, and hence inactive.

With doubly linked nitrogen, as in the oximes, etc., the case is different, and Hantzsch and Werner formulated the hypothesis that "The three valencies of nitrogen are, under certain conditions, directed towards the corners of a (probably irregular) tetrahedron, the fourth corner of which is occupied by the nitrogen atom itself." This easily explains the isomerism among the oximes, and the two forms have

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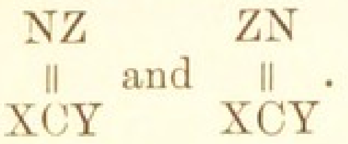
[1] *Ber.* 29 (1896), pp. 1462 and 1733.

been suitably written by Hantzsch and Werner thus:



$$\begin{array}{c}NZ\\ \|\\ XCY\end{array} \quad \text{and} \quad \begin{array}{c}ZN\\ \|\\ XCY\end{array}\ .$$

It must be noticed that no isomerism occurs unless the two groups attached to carbon are different, *e.g.*, methyl-aldoxime H_2CNOH exhibits no isomerism.

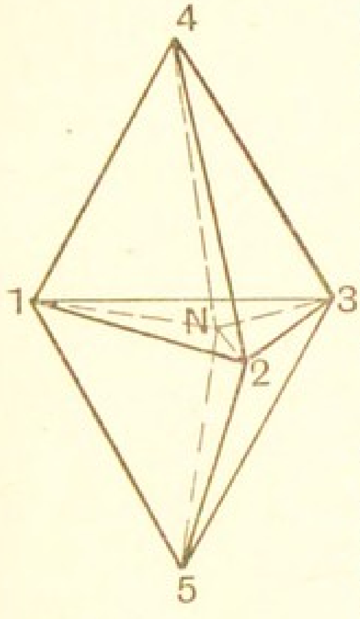


Fig. 1.

Le Bel has also made some important observations on ammonium compounds, in which, of course, nitrogen is pentavalent.

He advocates that the five valencies point towards the corners of a double tetrahedron, as shown in fig. 1. Van't Hoff suggests that the five valancies are directed towards five corners of a cube, as shown in fig. 2.

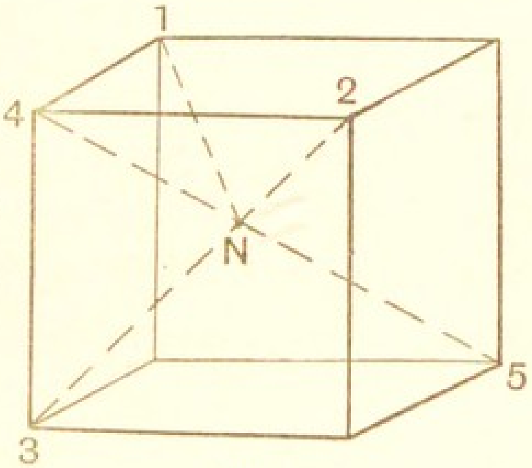


Fig. 2.

Until more is known about the stereo-chemistry of nitrogen it is impossible to say which of these two, or whether either, is correct. However, it seems pretty certain that the nitrogen atom has a fixed structure, or else the explanation of the formation of optical isomers would not be possible. For further details, see Van't Hoff's treatise.

C.—THE STEREOISOMERISM OF SULPHUR.

The work done on this subject is none too abundant or conclusive. The different observers have all busied themselves with the sulphines, in which sulphur is tetravalent. Sulphines are chosen which contain both asymmetric sulphur and carbon atoms,[1] and then if the four valencies of sulphur be not in one plane, we should expect to get two distinct racemic mixtures. All efforts to obtain these have failed, and it seems probable that four valencies of sulphur lie in one plane. The result of this would be that the six valencies are in the highest probability directed towards the corners of a regular octahedron. Experiments have been carried on in the laboratories of University College, London, by Messrs Smiles and Moritz, with the object of definitely settling the question whether the four valencies be in one plane, or whether they also possess a tetrahedral arrangement like those of carbon. The results obtained negative the latter suggestion.

D.—OTHER ELEMENTS.

Professor Werner of Zurich has treated in a re-

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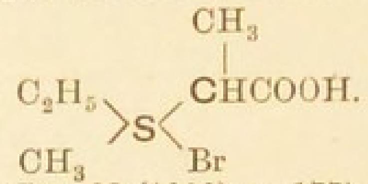
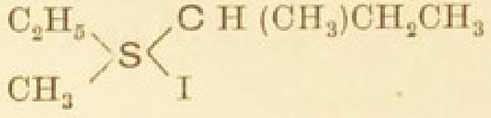
[1] For example, Vanzetti (*Gazz. ch. it.* 30 (1899) p. 175), employed the compound



$$\begin{array}{l} C_2H_5 \\ CH_3 \end{array} > S < \begin{array}{l} \overset{CH_3}{\overset{|}{C}}HCOOH. \\ Br \end{array}$$

Strömholm (*Ber.* 33 (1900), p. 177) employed the compound—



$$\begin{array}{l} C_2H_5 \\ CH_3 \end{array} > S < \begin{array}{l} CH\ (CH_3)CH_2CH_3 \\ I \end{array}$$

markable way the constitution of the complex platin- and cobalt-amines.[1]

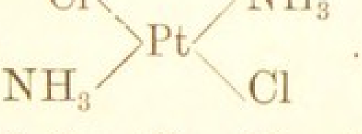
Those bodies are usually classed as molecular compounds, without any attempt being made to explain the manner in which the various elements and groups are linked together in the molecule. In fact, the ordinary ideas of valency are insufficient to be of service in representing these compounds. As is well known, several of these bodies have the same empirical formulæ, but quite different properties. For example, platinosamine hydrochloride and chloroplatinosodiamine hydrochloride both have the same empirical formula, $PtN_2H_6Cl_2$. The first crystallises in yellow rhombohedra, and silver removes all its chlorine. The second crystallises in yellow prisms, and silver removes only half the chlorine. The formula assigned to the former is $Pt(NH_2)_2 2HCl$, and that to the latter $ClPt(N_2H_5)HCl$.

Again, the chlorides of platosemidiammine and of platosamines both have the formula $Pt(NH_3)_2Cl_2$. The former is soluble in 387 parts of water at 0° and in 26 parts at 100°, the latter in 4472 parts at 0° and in 140 at 100°. Werner shows that the formulæ to be assigned to these must be as follows:—

For platosemidiammine hydrochloride

$$\begin{matrix}Cl\\Cl\end{matrix}>Pt<\begin{matrix}NH_3\\NH_3\end{matrix}$$

For platosamine hydrochloride



$$\begin{matrix}Cl\\NH_3\end{matrix}>Pt<\begin{matrix}NH_3\\Cl\end{matrix}.$$

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[1] *Zeit. anorg. Chem.* 3, p. 267, and *Zeit. Phys. Chem.* 12, p. 35, and 13, p. 506.

In fact, he shows that all the facts known about both platin- and cobalt-amines can be satisfactorily explained from stereo-chemistry; that is, by assuming a certain definite structure for both the atom of cobalt and the atom of platinum. Collecting our data, we find that the atoms of carbon, nitrogen, sulphur, cobalt and platinum have a definite structure. Now the elements in any one group of Mendeléeff's classification have very similar properties, and it seems highly probable that they should all have the same shaped atom. In this way we include in our list, besides those mentioned above, silicon, titanium, germanium, zirconium, tin,[1] lead, thorium, which belong to the carbon group, phosphorus, and the other members of the fifth group, those of the sulphur group, and those of Mendeléeff's eighth group. If, then, we conclude that all these elements have a definite structure for their atoms, then why not all elements?

It might be noted here that the periodic variation of valency with atomic weight is readily intelligible if we assume a definite structure for the atoms, which is the same for all elements of the same group in the periodic classification.

2. To show that the Elements are Complexes of some Primary Material or Protyle.

A.—THE VALUES OF THE ATOMIC WEIGHTS.

Chemists have again and again pointed out that

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[1] Pope and Peachey have obtained an optically active tin compound (*J. C. S.* 78 (1900)), containing an asymmetric tin atom, hence the valencies of tin must also be directed towards the corners of a tetrahedron.

the atomic weights do in a most unmistakable manner approximate to whole numbers. It will be subsequently shown that there is no reason for supposing that the atomic weights should have exactly integral values, or that the differences are in every case due to errors of experiment. The large percentage of these approximately integral values seems in a marked way to indicate the non-elementary structure of the atoms, and hence it shows that they are complexes of some primary substance.

B.—THE REGULARITIES SEEN IN THE INCREMENTS OF THE ATOMIC WEIGHTS.

The fact that the atomic weights of similar elements are in a great many cases simply related to one another, and also that similar elements recur at regular intervals, may also be viewed as evidence in support of the present view. It has been fully discussed in Chapter III., and no further mention need therefore be made of it here.

C.—STELLAR SPECTROSCOPIC EVIDENCE.

A number of astronomers, especially Sir Norman Lockyer and Professor Pickering, by their important spectroscopic researches on a large number of the fixed stars, have rendered great service to the problem of chemical evolution.

In the hottest stars, *e.g.*, ζ Orionis and γ Argus, only hydrogen, helium and an unknown gas were to any extent present. Even the lines of helium and the other gas are faint, whilst those of hydrogen are especially prominent. Further, in one of the stars in Argo—ζ Puppis—a system of lines was observed by Professor Pickering, which he thought to belong to a new element, but which were later shown by him to belong to a new series of hydrogen lines. This new series was observed in several other stars, and shows that they are the very hottest stars at present known (*v.* next chapter).

As cooler stars are observed, it is found that the lighter metallic elements, *e.g.*, calcium and magnesium, also make their appearance among the spectral lines, and then the heavier ones, such as iron and strontium; and finally, in our own sun, we find nearly all the terrestrial elements.

Starting, then, with these data, we can go a step further, and conclude that at a sufficiently high temperature helium would no longer exist. It does not seem probable that we shall ever be able to meet with any star in which this is the case, for its temperature would be simply prodigious, and hence its cooling at first very rapid. It is precisely this fact that would account for the presence of the first polymerisations, helium, etc.

D.—The Researches of Drs Preston and Zeeman.

Very recently—1897—a new field of research was opened by the labours of Dr Zeeman and of Dr

Preston. This was the behaviour of the spectral lines in a powerful magnetic field. In some cases a spectral line was converted into a triplet, in others into quartets, sextets, octets, or even more complicated types, whilst in many cases again the lines were not affected at all. It is unnecessary to go into the details of the results, but the chief point noted by Preston is that "these observations lend some support to the idea, so long entertained merely as a speculation, that all the various kinds of matter, all the various so-called chemical elements, may be built up in some way of the same fundamental substance."[1]

E.—THE RESEARCHES OF PROFESSOR J. J. THOMSON.

The researches of Professor J. J. Thomson on the properties of the cathode rays, especially their behaviour in a magnetic field, are also of importance for our present purpose. In offering an explanation for the facts observed, he writes: "The explanation which seems to me to account in the most simple and straightforward manner for the facts is founded on the view of the constitution of the chemical elements which has been favourably entertained by many chemists; this view is that the atoms of the different chemical elements are different aggregations of atoms of the same kind."[2]

Such, then, is the evidence we have in favour of the complex nature of the atoms, and it seems quite sufficient to entitle us to make the statement that

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[1] *Nature*, Vol. LX. p. 178.

[2] *Phil. Mag.* [5], 45 (1897), p. 311.

"the elementary atoms are complexes of some one primary material."

3. The Evidence in favour of Hydrogen being the Urstoff or Protyle.

A.—THE NATURE OF HYDROGEN.

It is obvious to the most youthful student of chemistry that, with regard to the remaining elements, hydrogen stands absolutely alone; in all its properties it is so very different from any other element. Among a number of its abnormal properties may be mentioned its extreme lightness, its very low boiling point, the extremely short range between melting and boiling points, its good thermal conductivity compared with other gases, its metallic behaviour, though quite different in appearance to metals, etc. Further, it must be noted that hydrogen is not repeated in Crookes' theory of evolution, it does not fit into Stoney's Spiral, neither can it be satisfactorily placed in the periodic classification. These remarkable properties are most suggestive of hydrogen's primary nature.

B.—ATOMIC WEIGHTS.

The very high percentage of approximately integral values of the atomic weights would be a natural consequence of hydrogen's being protyle. The only really important exception is chlorine 35·45. For a complete account and criticism of atomic-weight determinations, reference may be made to Ostwald's *Lehrbuch der Allgemeinen Chemie*, but more particularly to F. W. Clarke's *Constants of Nature*, and to his Annual Reports of the "Committee of Atomic Weights."

C.—Stellar Evidence.

The extraordinary importance of spectroscopic researches among the stars cannot be too strongly emphasised. Although no stars have yet been discovered consisting of nothing but hydrogen, yet the evidence, as far as it goes, seems most certainly to uphold hydrogen's claim to being the primary original matter. The reader is referred to the next chapter, and also to Lockyer's *Inorganic Evolution*, for a summary of the work done on the subject, and the conclusions which can be drawn from it.

It now remains to attempt an explanation to account for various objections to the theory. This, the fourth division, will conclude the chapter.

A.—The Actual Atomic Weights.

In the commencement of this chapter it was pointed out that there are two ways of viewing Prout's hypothesis. These are, first, that the atomic weights are multiples of unity or of that of hydrogen, and, secondly, that the atoms are polymers of hydrogen. If we give the hypothesis the first meaning, then obviously it is untenable; but if we interpret it in accordance with the second definition, then a careful consideration will show that there is no need to reject it, for the two are not identical, as is generally supposed.

We know that the atoms attract one another in the molecule; and if the atom be a complex system of protyles, then we must conclude that the protyles also attract one another in the atom. The cohesive force between the protyles is very great compared with the action of gravity on them, and therefore it may, and probably does, affect the weight of a system of protyles. With molar masses the attractions are not perceptible, and we have therefore no right, in our ignorance of the nature of gravitation, to assume that the weight, as we measure it, of n protyles is n times that of one protyle. For, as was pointed out by Professor Karl Pearson, it seems probable that, when we consider molecules, our laws which relate to molar masses no longer rigidly hold. No doubt the gravitation law will hold approximately, and hence the atomic weights must approximate to integral values, and this we find actually to be the case. The actual differences between experimental and integral values will in some measure depend on the structure of the atom. Probably, therefore, in the case of chlorine, the protyles are grouped together in some abnormal manner, which, in our ignorance, we are not in a position to discuss.

B.—The Rare Earths.

With regard to the assertion made by some that the rare earths have no place in the periodic classification, and therefore cannot be well reconciled to a protyle theory, it must be said that the perfect separation of these so-called elements is one of the most difficult problems of analytical chemistry. According to the method of fractionation resorted to, different results are obtained. No doubt, when a perfect means of performing this operation has been discovered, it will be found that the rare earths are made up of a few very similar elements, for all of which places will be found in the periodic classification. Until such a method has been discovered, it is scarcely fair to make any definite assertions regarding the nature of these elements.

C.—Lockyer's Dissociation Hypothesis.

If we accept the theory that the elements are complexes of some protyle, then we should expect the periodic classification to be in harmony with stellar evidence. This is, however, not the case, and to explain the phenomenon Lockyer has entered into a lengthy discussion of the chemical and astronomical evidence. The reader is referred to the next chapter for an account of this, but more especially to Lockyer's *Inorganic Evolution*, where all details will be found.

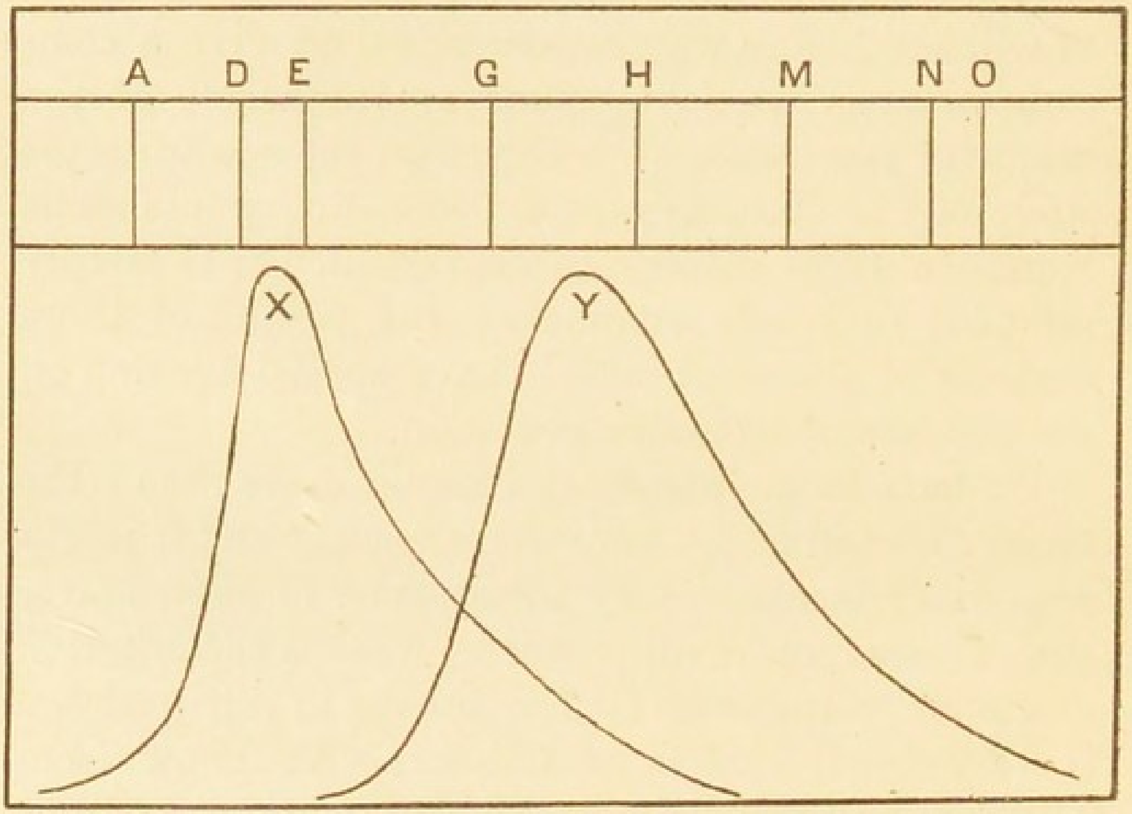
In conclusion, let us summarise what has been said in this chapter. Doing this, we can, with a great amount of certainty, say that the elements are condensation products of some one primary matter, which in all probability is hydrogen. By this is not meant hydrogen as we know it, but in that state in which its vibrations give rise to the principal series spectrum of which one line has been found by Rydberg in the very hottest stars. The others he calculated to be out of reach. The atomic weight of this form of hydrogen is thought to be the same as that of our terrestial hydrogen, the different spectra being simply caused by a resolution of the fundamental vibrations without any reference to dissociation of the atom. The actual law governing the polymerisations is no doubt a simple one, but different from any existing on our earth, which yet remains to be discovered.

CHAPTER II

THE WORK OF SIR NORMAN LOCKYER, K.C.B., F.R.S.

It will not in any way be attempted to give a complete or even partial account of the whole of the beautiful researches of Lockyer on the spectroscopic study of the stars, as such a proceeding would alone require a large volume to contain it. It is simply intended to briefly summarise the results of those portions of the work which have special bearing on the problem of inorganic evolution.

We have in the preceding chapter made use of the terms "hottest suns" and "cooler suns," and it might reasonably be asked why we consider one star hotter than another, or, in other words, what is the criterion of stellar temperature? The answer to this question is very simple, and is as follows:—We know from actual terrestrial observation that when a body is heated and examined with a spectroscope, at first only the red end of the spectrum is seen. On further heating, the orange and yellow portions of the spectrum appear, and finally, at a white heat, we have the whole visible spectrum from red to violet. But this is not all, for by the aid of photography further most important revelations are made. These are conditioned by rays of shorter wave length than the violet, which are known as ultra-violet rays. They do not leave any impression on the retina and are hence invisible, but their action on a photographic plate is considerable, and in this way they can be detected. The diagram here given is a rough curve showing the difference between the photographic and luminous effects of different parts of the spectrum.



The curve X shows the variation in intensity of the light, and the curve Y the intensity of the chemical action of the different parts of the spectrum.

The letters refer to the various lines of the solar spectrum, and may be used roughly as colour guides. Thus the A line, which is due to oxygen, is nearly invisible, and is situated in the extreme red. The

H line is in the extreme violet, and is due to calcium. The lines L, M, N and O are incapable of affecting the eye, but act on a photographic plate, and are all due to iron.

Now it is found that the hotter a body the further does its complete or continuous spectrum extend into the ultra-violet. We have thus a most valuable method for comparing stellar temperatures. And further, the hotter a body the less is its light, *cœteris paribus*, absorbed by the cooler vapours around it. Therefore by examining the photographed spectrum of a star with special reference to the character of the lines and the distance to which it extends into the ultra-violet, we can qualitatively compare the temperature of the star under consideration with that of some other star.

From a consideration of these points we arrive at the following relative temperature table :—

Hottest Stars.

Two in Argo (ε Puppis and γ Argus
Alnitam (ε Orionis).

Stars of Intermediate Temperature.

Ascending Series.—β Crucis, ε Tauri, Rigel, α Cygni [ ], Polaris, Aldebaran.
Descending Series.—Achernar, Algol, Markab [ ], Sirius, Procyon, Arcturus.

Stars of Lowest Temperature.

Ascending Series.—Autares (Condensing Nebulæ).
Descending Series.—19 Piscium (Dark Stars).

In the stars of gradually increasing temperature (Ascending Series) the metallic lines of the spectrum are thickest, whereas in those of decreasing temperature (Descending Series) the hydrogen lines are thickest.

The chemical characteristics of the various groups which the above stars represent are of the greatest importance, and are given in the next table :—

CHEMICAL DEFINITION OF THE VARIOUS STELLAR GROUPS.

Argonian.

Predominant.—Hydrogen and proto-hydrogen.

Fainter.—Helium, unknown gas (λλ 4451, 4457), proto-magnesium proto-calcium, asterium.

Alnitamian.

Predominant.—Hydrogen, helium, unknown gases (λλ 4089·2, 4116·0, 4649·2).

Fainter.—Asterium, proto-hydrogen, proto-magnesium, proto-calcium, oxygen, nitrogen, carbon.

Crucian.

Predominant.—Hydrogen, helium, asterium, oxygen, nitrogen, carbon.

Fainter.—Proto-magnesium, proto-calcium, silicium, unknown gas (λ4089·2).

Taurian.

Predominant.—Hydrogen, helium, proto-magnesium, asterium.

Fainter.—Proto-calcium, silicium, nitrogen, carbon, oxygen, proto-iron, proto-titanium.

Rigelian.

Predominant.—Hydrogen, proto-magnesium, proto-calcium, helium, silicium.

Fainter.—Asterium, proto-iron, nitrogen, carbon, proto-titanium.

Achernian.

Same as Crucian.

Algolian.

Predominant.—Hydrogen, proto-magnesium, silicium, helium, proto-calcium.

Fainter.—Proto-iron, asterium, carbon, proto-titanium, proto-copper, proto-manganese, proto-nickel.

Markabian.

Predominant.—Hydrogen, proto-calcium, proto-magnesium, silicium.

Fainter.—Asterium, helium, proto-iron, proto-copper, proto-titanium, proto-manganese, proto-nickel, proto-chromium.

CYGNIAN. *Predominant.*—Hydrogen, proto-calcium, proto-magnesium, proto-iron, silicium, proto-copper, proto-titanium, proto-chromium. *Fainter.*—Proto-nickel, proto-vanadium, proto-manganese, proto-strontium, iron (arc).	
	SIRIAN. *Predominant.*—Hydrogen, proto-magnesium, proto-calcium, proto-iron, silicium. *Fainter.*—The lines of the other proto-metals and the arc lines of iron, calcium, manganese.
POLARIAN. *Predominant.*—Proto-calcium, proto-magnesium, proto-titanium, hydrogen, proto-iron, and arc lines of calcium, iron and manganese. *Fainter.*—The other proto-metals and metals occurring in the Sirian stars.	PROCYONIAN. Same as Polarian.
ALDEBARIAN. *Predominant.*—Proto-calcium, arc lines of iron, calcium, manganese, proto-strontium, hydrogen. *Fainter.*—Proto-iron and proto-titanium.	ARCTURIAN. Same as Aldebarian.
ANTARIAN. *Predominant.*—Flutings of manganese. *Fainter.*—Arc lines of metallic elements.	PISCIAN. *Predominant.*—Flutings of carbon. *Fainter.*—Arc lines of metallic elements.

It will be seen that in the hottest stars hydrogen and proto-hydrogen are the only predominant elements, and that, as the stars cool, more and more of the elements make their appearance, until in our own sun, which is one of the coldest, we find nearly all the terrestrial elements.

The prefix proto was introduced by Lockyer, and when prefixed to the name of a metal signifies that the stellar spectral lines are coincident with those obtained when that metal is submitted to the highest temperature spark discharge. Such lines are said to be enhanced.

The term proto-hydrogen, however, has a special meaning, and is the name given to that form of hydrogen discovered by Professor Pickering in γ Argus and ζ Puppis. The lines of the proto-hydrogen spectrum fit in with those calculated from the usual formula by using even values for *m*, whereas the lines of the ordinary hydrogen spectrum are calculated from the same formula, with odd values for *m*.

The following table, given by Professor Pickering,[1] illustrates the agreement between observed and calculated values in both cases :—

Old Series.			New Series.		
m.	Calculated.	Observed.	*m*.	Calculated.	Observed.
6	6563·0	6563·0	5	10128·1	...
8	4861·5	4861·5	7	5413·9	...
10	4340·6	4340·7	9	4543·6	...
12	4101·9	4101·8	11	4201·7	4200·4
14	3970·2	3970·2	13	4027·4	4026·8
16	3889·2	3889·1	15	3925·2	3924·7
18	3835·5	3835·5	17	3859·8	3958·7
20	3798·1	3798·1	19	3815·2	3815·9
			21	3783·4	3783·4

Of course the agreement in the new series cannot be expected to be as good as in the old, for in the one case we are dealing with spectra produced many

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[1] *Astro. Journ.* Vol. V. p. 93.

billions of miles away, whilst in the other we have the gas in our laboratories.

A more general classification of the stars than the previous one is the following:—

Highest Temperature.

Gaseous stars	Proto-hydrogen stars	Argonian Alnitamian	
	Cleveite gas stars	Crucian Taurian	Achernian Algolian
Proto-metallic stars		Rigelian Cygnian ...	Markabian ... Sirian
Metallic stars		Polarian Aldebarian	Procyonian Arcturian
Stars with fluted spectra		Antarian	Piscian

Lowest Temperature.

From a combination of all the preceding we get:—

Gaseous stars	Longest spectrum	Highest temperature	Strong helium lines and faint enhanced lines
Metallic stars	Medium spectrum	Medium temperature	Feeble helium lines and strong enhanced lines No helium lines and strong arc lines
Carbon stars	Shortest spectrum	Lowest temperature	Faint arc lines.

Knowing now the effect of temperature on the chemical constitution of the stars, we can draw up the following colour relations to constitution and temperature:—

Colour.	Types.	Constitution.
White	Vega and Sirius	Hydrogen (strong), sodium and magnesium (weak)
Yellow	Capella and Aldebaran	Hydrogen and many metals
Orange or Red	α Orionis and α Herculis	No hydrogen, but many lines and bands

From this we infer that the white stars are the hottest, followed by the yellow, and finally the red. So that we see that the same sort of relation between the temperature and colour of the stars exists as between the temperature of a terrestrial object and its colour.

A comparison of the temperature ranges of the various spectral lines is very interesting, and also instructive, and for the purpose of showing this the following table was drawn up.

The very hottest stars known are those in which the proto-hydrogen lines, and also that of the principal series occur. They are δ, η, ζ and κ Orionis, γ Argus and ζ Puppis.

TABLE SHOWING THE TEMPERATURE RANGES.

GASES.

Gas.	Wave Lengths of Chief Lines.	Range of Temperature.	
		Ascending Series.	Descending Series.
Unknown .	4457·0 4451·0 3176·0	Seen only in γ Argûs	
New hydrogen	4544·0 4200·4	ζ Orionis to γ Argûs	No stars available
Unknown .	4089·2	α Crucis to γ Orionis	
Unknown .	4649·2	„	α Eridani
Helium . .	4471·6 4026·3	Rigel to ζ Argûs	α Eridani to γ Lyrae
Asterium .	4388·0 4000·9	„	„
Hydrogen .	Complete series	Aldebaran to γ Argûs	α Eridani to Arcturus
Oxygen . .	4070·1 4072·4 4076·3	α Crucis to ζ Orionis	About α Eridani
Nitrogen .	3995·2 4630·9	Rigel to ζ Orionis	α Eridani

PROTO-METALS.

Metal.	Range of Temperature.	
	Ascending Series.	Descending Series.
Magnesium .	α Ursae Min to γ Argûs	α Eridani to Procyon
Calcium . .	α Tauri to γ Argûs	α Eridani to Arcturus
Iron . .	α Tauri to ζ Tauri	β Persei to Arcturus
Titanium . .	,,	,,
Manganese .	α Ursae Min to α Cygni	β Persei to Procyon
Nickel . .	,,	,,
Chromium .	,,	γ Lyrae to Procyon
Vanadium .	,,	Sirius to Procyon
Copper . .	,,	β Persei to Procyon
Strontium .	α Tauri to α Cygni	Sirius to Arcturus

METALS (Arc Lines).

Metal.	Range of Temperature.	
	Ascending Series.	Descending Series.
Iron . .	α Tauri to α Cygni	α Canis Maj to Arcturus
Calcium .	α Tauri to α Ursae Min	,,
Manganese	,,	,,

NON-METALS.

Non-metal.	Range of Temperature.	
	Ascending Series.	Descending Series.
Carbon .	α Crucis	...
	Rigel to ζ Orionis	α Eridani to β Persei
Silicium .	α Ursae Min to α Crucis	α Eridani to Procyon

We now come to the most important part of the subject, namely, the bearing of stellar work on the periodic law. It has been shown in the previous chapter that the application of spectroscopic researches at high temperatures is of great moment for the problem of chemical evolution. We have now to consider whether the periodic law is in harmony with stellar observations, and if not, then we must see whether any plausible explanation can be made to account for the discrepancy.

If stellar evidence and the periodic classification were in harmony, we should expect every element to make its appearance after all other elements of lower atomic weights than that of the element under consideration. That is, we should expect magnesium to appear after sodium, and calcium after chlorine. But this is not found to be the case, the general order being calcium, magnesium, oxygen and sodium.

This Lockyer explains by assuming dissociation of the atom to have taken place, so that the atomic weights of the substances giving the enhanced lines or proto-metals are a simple proportional part of those determined by the ordinary methods of quantitative analysis. Hence we can get the following series of atomic weights:—

Proto-Calcium . . .	$10=\frac{\mathrm{Ca}}{4}$
Proto-Magnesium . .	$12=\frac{\mathrm{Mg}}{2}$
Oxygen	$16=\mathrm{O}$
Sodium	$23=\mathrm{Na}$

which would thus harmonise with their order of appearance in the stars. This seems very plausible, but by extending the idea a little further we are led to results which appear rather questionable.

The metals of low melting point, and also hydrogen, give three series of lines under different conditions:—one principal series and two subordinate. Oxygen, on the other hand, has six series of lines divided by Runge and Paschen into two normal sets of three, each containing one principal and two subordinate series.

At low temperatures Runge and Paschen measured 76 lines in the oxygen spectrum, of which 56 belong to the six series above referred to. This leaves us a surplus of 20 lines whose presence has to be accounted for. If, now, a powerful induced current be employed, a new spectrum is produced containing 114 lines according to Neovius, whilst the six series spectrum is practically extinguished. Of these new lines we know at present nothing, and only one of them corresponds to the table of Runge and Paschen. We have thus 113 new lines. The question now arises—Are these new lines due to the depolymerisations of the oxygen atom? If so, can we form any estimate of the number of such depolymerisations? A possible method is as follows:—Let us select a particular portion of the spectrum, say from λ260 to λ700, and find the number of recorded lines of the following elements, which give us three series:—Lithium, sodium, potassium, hydrogen, helium and asterium. We then get this result:—

	Maximum.	Minimum.	Average.
Principal series .	10 Ast	1 H	7
First subordinate .	17 He	6 Na	9
Second subordinate	12 He	4 Li	8
	39	11	24

therefore oxygen with $\frac{56}{2}=28$ lines per set is slightly above the average. The 113 new lines would then give us four more sets of three series, and hence we have the possibility of twelve depolymerisations. We can, in a similar manner, consider the case of hydrogen.

The number of lines in the above-mentioned region is 17. In the structure spectrum between $\lambda\lambda 642$ and 441, Hasselberg measured 454 lines.[1] Therefore we have the possibility of $\frac{454}{17}=27$ series, or nine sets of three each. This gives twelve depolymerisations. Since Hasselberg's work was limited, let us take six depolymerisations to be on the safe side. Clearly then we must arrive at very small atomic weights as shown by the table.

Spectrum.	Where Existent.	Series, etc.	Mass.
Line spectrum	Celestial	Principal	0·0019
		Subordinate	0·0039
	Terrestial	Subordinate	0·0078
Fluted spectrum	Set B Terrestial	Principal	0·0156
		Subordinate	0·0312
		Subordinate	0·0625
	Set A Terrestial	Principal	0·125
		Subordinate	0·25
		Subordinate	0·5
Continuous spectrum		Hydrogen weighed in the cold	1·0

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[1] *Bull. Acad. imp. St Péters.* (1880), p. 307.

Such, then, is Lockyer's reasoning. That is to say, he attributes these complex spectra to the dissociation of the atom.

There is, however, another line of argument which seems rather more plausible at least in this case.

We say that the atoms are continually in the state of a vibratory motion, and that the spectrum of a substance is considered by the specific character of its motion. This motion is communicated to the ether, which in its turn communicates it to the eye, giving rise to the various sensations of colour. Now we know that such motions are in many cases capable of resolution into simpler motions, or into more complicated ones, or even into motions of the same kind but of different amplitude. From this we may infer that it is the motion of the atom which is resolved and not the dissociation of the actual atom which causes the different spectra obtained under different conditions.

However, the latter state of affairs seems to be the case with the elements calcium, magnesium and the other proto-metals, but with oxygen and hydrogen it seems much more conceivable that the motion of the atom has been resolved.

Of course, until a little more is known about the production of spectra and the properties of the atoms, we can only speculate as to the cause underlying the production of the different sets of lines. The best compromise to make is to say that the spectra of elements at high temperatures are conditioned either by the dissociation of the atom or by the resolution of the motion of the atom, which it possesses at lower temperatures, into a system of more complicated, of simpler, or of similar motions. And in the present state of our knowledge, speculation and discretion can alone decide which of these causes is actually at work. The importance of stellar spectroscopy cannot be too strongly emphasised. It is of great moment to the evolutionist, and shows distinctly that at high temperatures a great number of our terrestrial elements cannot exist. And further, it most strongly points to the primary nature of hydrogen, for it alone exists to any predominance in the very hottest stars known. The actual temperature of these bodies must be something prodigious and quite beyond our conception. When such an incandescent mass of a primary material were launched into space, we should expect the cooling at first to be very rapid compared with the rate of cooling in later times owing to the enormous temperature difference between such a body and the surrounding space. It is precisely this very fact that would account for the presence, although only to a small degree, of the first polymerisations—helium and the proto-metals—in even those stars of the highest temperature.

Besides the cooling stars there is another set whose temperature is continually increasing. For an explanation of these ascending and descending series, reference should be made to Lockyer's *Meteoritic Hypothesis of the Origin of Cosmical Systems.* Before concluding this chapter, it might be suggested that possibly our method of analysing light vibrations is the cause of the complexity of some spectra. This is only a surmise, and has, as yet, no experimental proof to support it.

The following works by Sir Norman Lockyer are of importance for the study of chemical evolution :—

Contributions to Solar Physics,
Chemistry of the Sun,
Meteoritic Hypothesis,
Studies in Spectrum Analysis,
The Sun's Place in Nature,
Inorganic Evolution,

and also numerous papers read before the Royal Society of London, and recorded in the proceedings of the same.

CHAPTER III

THE CONSTITUTION OF MATTER

Definition.—Matter is usually defined as being that which occupies space. Its general properties are briefly impenetrability, divisibility, extension, porosity, and inertia. The discussion of these is to be found in all text-books on general chemistry and physics, to which reference may be made. It is intended here only to summarise the various theories proposed for the constitution of matter.

Democritus and Leucippus.—The idea that matter is composed of a great number of indivisible particles or atoms dates back to the time of Democritus and Leucippus, about 2400 years ago. These philosophers conceived the atoms to be hard masses, and Lucretius, in his famous poem, "De Rerum Natura," explains the fluidity of substances like water to be due to the fact that there are vacant spaces between the solid particles, and hence, though a substance is composed of solid ultimate atoms, it may yet, as a whole, be soft. Newton used this hypothesis to explain why sound travelled faster in air than it should, according to his calculations, which, although accurate in themselves, were yet founded on incomplete data.

Boscovich.—Boscovich conceived that the ultimate elements of matter were individual points, in accordance with the geometrical definition, surrounded by spheres of attractive and repulsive forces which alternate according to the distance of the points up to a certain degree of remoteness. This theory fails to explain the inertia of matter; and, further, since points have no real existence, it follows that the atoms cannot have any real existence—in fact, the idea is purely a mathematical fiction. Modern chemists consider matter to be composed of molecules and atoms. By molecules is meant the smallest part of a substance which can exist in a free state and preserve the properties of the entire substance. The molecules are thought to consist of a number of smaller indivisible particles or atoms which are capable of effecting chemical changes. Various physicists say that impenetrability is the essence of matter, but **Descartes** assumed extension as the criterion of matter.

Mills.—J. S. Mills considers matter to be the permanent possibility of sensation, and there are a great many other theories which have been proposed from time to time. The most plausible and most generally accepted one is the chemical theory regarding the existence of atoms and molecules. This, of course, involves the supposition that there is no infinite divisibility of matter possible, or, in other words, that it is discontinuous. The most weighty piece of evidence in favour of this is, that it alone can explain Dalton's Laws of Multiple and Constant Proportions, and further, that it is in harmony with spectroscopic researches.

Thales.—The first assumptions with regard to a primary matter were made as early as 600 B.C. by Thales, who considered all material substances to be states or stages of one primitive matter or element, which he took to be water. Anaximenes (about 550 B.C.) thought this element to be air or fire.

Prout.—Coming to more modern times, we have Prout's hypothesis in 1815, formulated from a consideration of the atomic weights of the elements. He supposed all the elements to be formed by peculiar condensations from a primary matter or protyle, which protyle was hydrogen. An apparent confirmation of this was laid before the British Association in 1889 by the late Professor Piazzi Smyth. He showed that after several years' use the gases enclosed in vacuum tubes gave no longer their characteristic spectra on passing an electric discharge through them, but that only hydrogen lines were visible. This was especially noticeable in the case of iodine and chlorine.[1] This has been lately explained by assuming that the gases were not perfectly dry, and on submitting the mixture to the electric spark the water had been decomposed into its component elements. However, the other gases have vanished, and this can hardly be explained by diffusion through the glass,

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[1] *Nature* (1889), p. 584.

for, according to Graham's Laws, the hydrogen would be the first to diffuse, whereas we find it remaining to the end; and further, we should expect to find, after a time, the air spectrum as well. But in most cases this is not present, so that a diffusion explanation does not seem to answer very well, and there is no other of any consequence.[1] We must therefore take the facts for granted, and form new speculations as to the cause of the phenomenon.

Now it is not absolutely impossible that matter is continuous; that is, that it is structureless, not composed of separate particles, but completely filling the space which the body inhabits. However, this theory seems very improbable, for it fails to explain the more simple phenomena of gases, especially compressibility. Nevertheless, this is hardly sufficient to justify the discardance of the theory, for when we speak of a supposition as inconceivable, we simply assert that no such case has ever yet come under our notice. Let us then accept the discontinuous theory of the constitution of matter and consider some of the suggestions made regarding the shape of the atoms. The most inconceivable is the theory of Boscovich, mentioned above, which supposed the atoms to be geometrical points.

Rankine.—In 1842 Rankine tried to explain the increase of pressure and the laws of expansion by heat of gases by his "hypothesis of molecular vortices," in which he assumes "that each atom of matter

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[1] Unless we tolerate the assumption that the other gases are absorbed by the negative electrode.

consists of a nucleus or central point enveloped by an elastic atmosphere, which is retained in its position by attractive forces, and that the elasticity due to heat arises from the centrifugal force of those atmospheres revolving or oscillating about their nuclei. For an account of this reference may be made to *Trans. Roy. Soc. Edinburgh* (1850), or *Phil. Mag.* (1851), and also to Preston's *Heat* (1894), p. 74.

Kelvin.—The most important idea of the shape of the atom is that of Sir W. Thomson (now Lord Kelvin) in 1867.[1] He supposes the atoms to be vortex rings, and the theory is usually known as that of the Vortex Atom.

Helmholtz.—Von Helmholtz in 1858 first showed that the rotating parts of a perfect incompressible fluid maintain their identity for ever, and are thus eternally differentiated from non-rotating parts. The rotating parts are arranged either in long, endless filaments, terminated only at the boundaries of the fluid, or else forming closed curves. The properties of such vortex motions may be summed up as follows:—(1) A vortex cannot be created nor destroyed; hence the indestructibility of matter. (2) A vortex is perfectly elastic. (3) Two vortices cannot intersect. (4) The rotating portions of the fluid composing the vortex maintain their identity for ever. (5) These motions must consist of an endless filament in which the rotation is always perpendicular to the axis of the filament unless this stretches to the boundary surface of the fluid. Since it can never be severed,

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[1] *Proc. Roy. Soc. Edin.* (1867).

it will form a true atom, and hence we get the vortex theory of the constitution of matter devised by Lord Kelvin. He assumes that space is filled with a substance called ether, and that an atom is a vortex in this medium. He explains the different kinds of atoms by assuming the vortices to be linked, and that the different atoms are distinguished by the number of such links.

The ether is considered to be a perfect fluid by some, an elastic, incompressible solid by others, whilst Larmor has suggested quite different properties. It is to be noted that, as light is produced by *transverse* vibrations in this ether, it cannot be frictionless. Sir G. G. Stokes has pointed out that although the ether may act as a perfect fluid for finite displacements, yet when these get very small and very rapid, as is the case in light, that for these the ether may behave as an elastic solid.

The vortex-ring theory possesses a number of recommendations. It shows the atom to be indivisible and indestructible. A vortex ring possesses kinetic energy when free from the influence of others, for it moves continually forward in a straight line. It may vibrate about a position of equilibrium, thus giving rise to motions in the ether which constitute light and radiant heat. The theory assumes nothing but the existence and properties of a hypothetical medium —the ether—and is thus more fundamental than any other one. However, the mathematical difficulties to be overcome in the further development of the theory are extremely great

Hill.—Professor M. J. M. Hill[1] has worked out the more fundamental mathematical considerations of his vortex sphere. The applications of it have been in part attacked by Professor Hicks.

Professor Hill does not think that this can be the ultimate atom, because the time taken by the particles to revolve once completely round is infinite. "This result does not constitute a difficulty,[2] for if a particle anywhere on the axis of the sphere could reach the extremity, then it would not be clear along which meridian of the sphere it should subsequently move."[3]

As regards the experimental work attached to the vortex rings, of course we can only produce vortices—at least at present—in the air, which is far from being a perfect fluid, or even far from answering to the fundamental properties of the ether. Professor J. J. Thomson has worked out some of the simpler problems connected with vortex motion, but it is only when the complete mathematical investigations have been carried out that a final acceptance or discardance of the vortex-atom theory can be definitely decided. The whole question rests on the assumed properties of the ether.

Fourlinnie.—Any theory regarding the shape of atoms must explain the valency of the elements, and recently there have been several suggestions made to this end. C. Fourlinnie, in 1896, proposed the following forms for the various atoms from mathematical considerations:—For the elements of the fluorine

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[1] *Phil. Trans.* 185 (1894), p. 213.

Mathematically.

[3] *Loco. cit.* p. 245.

group he proposes the hexahedron; for those of the oxygen group, the octahedron; for the nitrogen group, the dodecahedron; and for the carbon group, the icosahedron; whilst hydrogen is supposed to be a regular tetrahedron.

Addon.—W. L. T. Addon, in a paper read before the British Association in 1897, considers the question from a crystallographic point of view, and arrives at the following atom forms:—For the carbon group, the tetrahedron; for the nitrogen group, the bi-pyramidal hexahedron; for the sulphur group, the octahedron; for the chlorine group, the bi-pyramidal decahedron; for the boron group, a triangle having sides of a definite thickness; for the beryllium group, a cylindrical rod; and for the lithium group, a sphere. The elements of the iron group are thought to be probably tetrahedra. These two theories must be taken for what they are worth, and no criticism of them will be attempted here.

Dulk.—Dr L. Dulk[1] does not think the atoms are polymers of a primary material, but conceives them to be a system of geometric points or a collection of gyrating ether vibrations of equal weight arranged in some definite manner, generally represented by some plane geometrical figure inscribed in a circle. Here again the reader is left to form his own opinion on the subject.

Sperber.—Dr Joachim Sperber[2] explains valency in the following way from conclusions based on the parallelogram of forces. He considers (1) that atoms

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[1] *Ber.* (1898), p. 1865.

[2] *C. N.* (1898), 77, p. 87.

enter into combination at definite angles in such a way that the valency only indicates the value of the component which the atom contributes in the direction of the molecular movement in the resulting compound, and (2) that the valency (V) of an element is equal to the atomic weight (ω) multiplied by the cosine of the angle (θ) at which the atom enters into combination, *i.e.*, $V = \omega \cos \theta$. This presumes the components to be at right angles, a state of affairs which is spontaneously and frequently found in nature. The value of θ depends in some cases on the direction of the atom vibrations within the molecule, and in others on the direction of the molecular vibration itself. If $\theta = 90°$ then $V = 0$, *i.e.*, if an atom vibrates perpendicularly to the molecular vibrations, as, for example, in the case of an atom with transverse vibrations in the presence of gases, with a strong tendency to longitudinal vibrations, it has no valency, *i.e.*, it is chemically inactive. The theory, therefore, presumes the existence of non-valent elements. Such elements have been recently discovered by Lord Rayleigh and Professor Ramsay, and are known as helium, argon, neon, etc. To these Sperber also adds the cosmic ether, whose vibrations are transversal.

Crookes.—Regarding the genesis of the elements, we have the hypothesis of Sir William Crookes, which supposes the *vis genatrix* to act in a to and fro motion, like that of a pendulum, in a figure of eight path-forming cycles, which would be identical if all the conditions remained the same. However, one of these (*e.g.*, temperature) has declined, and hence a different cycle of similar properties to the first is arrived at.

Flawitsky.—Another hypothesis is that given by Flavian Flawitsky.[1] He supposes the atoms of an element to move in curves which are in planes parallel to one another. The atoms of different elements move in planes inclined at certain angles to one another. The character of the element is determined by the orientation of the motion, and might be regarded as due to the influence of a selective dualistic force, such as electricity, in the formation of an element.

It is useless to give any more of the theories propounded for the genesis of the elements or the constitution of matter, as they are all purely hypothetical and in many cases metaphysical, so that they do not appeal much to the minds of physical chemists. From what has been said, it would appear that practically nothing is known either of the ultimate shape of the atoms or of their genesis. We must be content to accept for the present the chemical theory which supposes all matter to be made up of certain elements, which are further built up from atoms by the intermediate formation of molecules. And it seems probable that the atoms are all polymers of some primordial substance, but regarding the actual arrangement of these protyles, as they are conveniently termed, in the atom we are at present ignorant.

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[1] *Zeit. anorg. Chem.* (1896), p. 182.

In conclusion, it might be noted that Professor Karl Pearson has also originated a theory regarding the constitution of matter, and known as the "Ether Squirt Theory," but the applications of this have not yet been fully worked out, so that no discussion of the theory will be attempted.

ERRATUM.

On page 189, ninth line from bottom, *for* Mills *read* Mill.

APPENDIX I

TABLE I.

A.	B.	C.	D.	E.	F.
Oxygen	O	8	100	8·01	100
Hydrogen	H	1	12·5	0·50	6·2398
Carbon	C	6	75	6·13	76·44
Boron	B	10·8	135	10·91	136·20
Phosphorus	P	31·4	392·5	15·72	196·14
Sulphur	S	16	200	16·12	201·17
Selenium	Se	40	500	39·63	494·58
Iodine	I	126	1575	63·28	789·75
Bromine	Br	78·4	980	39·20	489·75
Chlorine	Cl	35·4	442·5	17·74	221·33
Fluorine	F	18·7	233·75	9·37	116·90
Nitrogen	N	14	175	7·09	88·52
Potassium	K	39·2	490	39·26	489·92
Sodium	Na	23·2	290	23·31	290·90
Lithium	Li	6·4	80	6·44	80·33
Barium	Ba	68·6	857·5	68·66	856·88
Strontium	Sr	44	550	43·85	547·29
Calcium	Ca	20·5	256·25	20·52	256·02
Magnesium	Mg	12·7	158·75	12·69	158·35
Lanthanum	La	36·1	451·7	...	...
Cerium	Ce	46·3	578·8	...	...
Yttrium	Yt	32·2	402·5	32·25	402·51
Beryllium	Be	17·7	221·25	26·54	331·26
Aluminium	Al	13·7	171·25	13·72	171·17
Thorium	Th	59·6	745	59·65	744·90
Zirconium	Zr	22·4	280	33·67	420·20
Silicon	Si	14·8	185	22·22	277·31
Titanium	Ti	24·5	306·25	24·33	303·66
Tantalum	Ta	185	2312·5	92·45	1153·72
Tungsten	W	95	1187·5	94·80	1183·00

A.	B.	C.	D.	E.	F.
Molybdenum .	Mo	48	600	47·96	598·52
Vanadium . .	V	68·6	857·5	68·66	856·89
Chromium . .	Cr	28·1	351·25	28·19	351·82
Uranium . .	U	217	2712·5	217·26	2711·36
Manganese .	Mn	27·6	345	27·73	345·89
Arsenic . .	As	75·2	940	37·67	470·04
Antimony . .	Sb	129	1612·5	64·62	806·45
Tellurium . .	Te	64	800	24·25	801·76
Bismuth . .	Bi	106·4	1330	71·07	886·92
Zinc . .	Zn	32·2	402·5	32·21	403·23
Cadmium . .	Cd	55·8	697·5	55·83	696·77
Tin . .	Sn	59	737·5	58·92	735·29
Lead . .	Pb	103·8	1297·5	103·73	1294·50
Iron . .	Fe	27·2	340	27·18	339·21
Cobalt . .	Co	29·6	370	29·57	368·99
Nickel . .	Ni	29·6	370	29·62	369·68
Copper . .	Cu	31·8	397·5	31·71	395·71
Mercury . .	Hg	101·4	1267·5	101·43	1268·82
Silver . .	Ag	108·1	1351·25	108·30	1351·61
Gold . .	Au	199	2487·5	99·60	1243·01
Platinum . .	Pt	98·7	1233·75	98·85	1233·50
Palladium . .	Pd	53·4	667·5	53·36	665·90
Rhodium . .	Rh	52·1	651·25	52·2	651·39
Iridium . .	Ir	98·7	1233·75	98·84	1233·50
Osmium . .	Os	99·6	1245	99·72	1244·49

Remarks.—This table has been taken from Gmelin's *Handbuch der Chemie* (1843 Edn.).

In column A. are given the names of the elements and in B. their symbols.

Column F. gives Berzelius' values, and E. the same calculated to base H = 0·50.

In column C. are given the atomic weights which were considered most probable about 1840, and in D. the same values calculated to base O = 100·0.

In C. and D. the following relation holds between oxygen and hydrogen, viz., O = 8H.

In E. and F. the relation is O = 8·0083H.

TABLE II.

Stas' Atomic Weight Determinations.

Element.	Atomic Weight.	
	Stas.	Van der Plaats.
Silver . . .	107·9376±0·0037	107·930
Potassium . . .	39·1361±0·0032	39·144
Sodium . . .	23·0575±0·0041	23·049
Lithium . . .	7·0303±0·0042	7·024
Lead . . .	206·911±0·0090	206·91
Chlorine . . .	35·4529±0·0037	35·456
Bromine . . .	79·9628±0·0032	79·955
Iodine . . .	126·8640±0·0035	126·857
Sulphur . . .	32·0626±0·0042	32·06
Nitrogen . . .	14·0410±0·0037	14·05

Remarks.—The column headed "Stas" gives the values as obtained by that chemist. The probable errors are due to Ostwald. The column headed "Van der Plaats" gives the values calculated by him from Stas' original weights. It will be seen that the differences between the values of the two columns is always very small.

TABLE III.

Most Recent Atomic Weights and Specific Gravities of the Elements.

Element.	Atomic Weight.	Specific Gravity.	Temp. of Observation.
Aluminium	27·11	2·583	4, 4
Antimony	120·43	6·7	15, 4
Arsenic	75·01	4·7	14, 14
Barium	137·43	4·0	...
Beryllium	9·08	1·85	20, 20
Bismuth	208·11	9·76	4, 4
Boron	10·95	2·68	...
Bromine	79·95	3·18	0, 4
Cadmium	111·95	8·65	...
Cæsium	132·89	1·88	15, —
Calcium	40·07	1·57	...
Carbon	12·00	D 3·514, G 2·25, A 1·7	4, 4
Cerium	139·35	6·68	18, —
Chlorine	35·45	1·33	...
Chromium	52·14	7·0	...
Cobalt	58·99	8·9	...
Copper	63·60	8·95	...
Erbium	166·32	...	...
Fluorine	19·06	...	...
Gallium	69·91	5·96	24·5, 24·5
Germanium	72·48	5·47	20·4, 20·4
Gold	197·23	19·33	17·5, 17·5
Hydrogen	1·008	0·62	...
Indium	113·85	7·42	16·8, —
Iodine	126·85	4·95	40·3, —
Iridium	193·12	22·42	17·5, —
Iron	56·02	8·00	...
Lanthanum	138·64	6·163	...
Lead	206·92	11·35	0, —
Lithium	7·03	0·59	...
Magnesium	24·28	1·743	17, —
Manganese	54·99	7·39	22, —
Mercury	200·00	14·19	— 38·85, 4
Molybdenum	95·99	8·6	...
Neodymium	140·80	...	...
Nickel	58·69	9·0	...

Table III.—*Continued.*

Element.	Atomic Weight.	Specific Gravity.	Temp. of Observation.
Niobium	93·73	7·06	15·5, —
Nitrogen	14·04	0·885	B. P.
Osmium	190·99	22·48	17·5, —
Palladium	106·36	11·4	22·5, —
Phosphorus	31·02	2·22	17, —
Platinum	194·89	21·50	17·6, —
Potassium	39·11	0·865	15, —
Praseodymium	143·60	...	...
Rhodium	103·01	12·1	..
Rubidium	85·43	1·5	...
Ruthenium	101·68	12·26	0, 4
Scandium	44·12	...	...
Selenium	79·02	4·2	...
Silicon	28·40	2·48	10, —
Silver	107·92	10·57	...
Sodium	23·05	0·985	0, 4
Strontium	87·61	2·54	...
Sulphur	32·07	2·07	...
Tantalum	182·84	10·78	...
Tellurium	127·49	6·23	18·2, —
Thallium	204·15	11·9	...
Thorium	232·63	11·1	17, —
Tin	119·05	7·29	...
Titanium	48·15	3·59	0, 4
Tungsten	184·83	19·20	4, —
Uranium	239·59	18·68	13, 4
Vanadium	51·38	5·87	15, —
Ytterbium	173·19	...	...
Yttrium	89·02	...	...
Zinc	65·41	7·15	...
Zirconium	90·40	4·15	...

Remarks.—The atomic weights are those given by F. W. Clarke taking oxygen = 16·00.

The specific gravities are those given by Deeley (*J. C. S.* 63, p. 867).

The temperature column gives, first, the temperature of observation, and, secondly, the temperature of comparison of the water.

For specific gravities at other temperatures, *see* Bayley, *Chemist's Pocket Book*, 7th Edit. (1900), pp. 34-51.

TABLE IV.

Expansion Coefficients (linear).

Metal.	Exp. Coeff.	Temperature.	Authors.
Silver	·0000190868	0° to 100°	Laplace and Lavoisier
	1943	0° to 100°	Matthiessen
Thallium	3021	40°	Fizean
Sulphur	6413	40°	,,
Selenium	3680	40°	,,
Tellurium	1675	40°	,,
Lead	2848	0° to 100°	Laplace and Lavoisier
	2799	0° to 100°	Matthiessen
Iron	1220	0° to 100°	Laplace and Lavoisier
	1190	...	Calvert, Johnson and Lowe
Cobalt	1236	40°	Fizean
Nickel	1279	40°	,,
Copper	1722	0° to 100°	Laplace and Lavoisier
	1866	0° to 100°	Matthiessen
Ruthenium	0963	40°	Fizean
Rhodium	0850	40°	,,
Palladium	1176	40°	,,
	1104	0° to 100°	Matthiessen
Platinum	0886	0° to 100°	,,
	0899	40°	Fizean
Iridium	0700	40°	,,
Osmium	0657	40°	,,
Zinc	2976	0° to °100	Matthiessen
	2918	40°	Fizean
Cadmium	3159	0° to 100°	Matthiessen
	3069	40°	Fizean
Magnesium	2694	40°	,,
Indium	4170	40°	,,
Arsenic	0559	40°	,,
Antimony	1056	0° to 100°	Matthiessen
Bismuth	1316	0° to 100°	,,
Gold	1470	0° to 100°	,,
	1443	40°	Fizean
Carbon	0118	40°	,,
Silicon	0763	40°	,,
Tin	2173	0° to 100°	Laplace and Lavoisier
	2296	0° to 100°	Matthiessen
	2234	40°	Fizean
Aluminium	2220	0° to 100°	Calvert, Johnson and Lowe
	2313	40°	Fizean

Remarks.—The values in the text have been taken from *Chemiker Kalender* for 1899.

TABLE V.

Properties of the Halides, excluding Fluorides.

Substance.	Melting Point.	Boiling Point.	Specific Gravity.	Molecular Volume.	Heat of Formation in Large Calories.
	On the Absolute Scale.				
Cl_2	198	240	1·33	53·3	...
ClBr	...	286	...	...	25 K
ClI	298	373	...	...	58
Br_2	251	331	3·188	50·1	...
BrI	309	390	...	...	...
I_2	383	473	4·95	51·2	...
OCl_2	...	253	...	...	-178
SCl_2	...	337	1·62	63·5	...
$TeCl_2$	448	600	...	...	...
$TeBr_2$	553	612	...	...	...
TeI_2	433	...	...	...	...
NCl_3	...	334	1·65	72·9	...
VCl_3	...	...	3·00	52·57	...
PCl_3	...	351	1·61	85·1	755
PBr_3	...	444	2·92	47·0	448
PI_3	328	...	...	...	109
$AsCl_3$	244-5	405	2·205	51·2	715
$AsBr_3$	295	493	3·66	49·5	449
AsI_3	419	677	4·39	103·5	127
$SbCl_3$	345	496	3·064	74·1	898
$SbBr_3$	363	549	4·148	54·6	...
SbI_3	438	693	4·85	105·0	...
$BiCl_3$	503	703	4·56	68·9	906
$BiBr_3$	480	749	5·4	58·2	...
BiI_3	...	...	5·64	104·3	...
CCl_4	*a.* 248	351	1·632	94·2	210
CBr_4	364	462	3·42	44·8	...
CI_4	373	...	4·34	122·0	...
$SiCl_4$	...	331	1·524	111·6	...
$SiBr_4$	260	426	2·823	60·3	...

Table V.—*continued.*

Substance.	Melting Point.	Boiling Point.	Specific Gravity.	Molecular Volume.	Heat of Formation in Large Calories.
	On the Absolute Scale.				
SiI_4	393	...	...	...	...
$GeCl_4$	...	359	1·887	113·5	...
GeI_4	417	623-73	...	..	...
$TiCl_4$	...	563	1·76	107·8	...
$TiBr_4$	312	408	2·6	73·0	...
TiI_4	423	633	...	...	...
$SnCl_4$	...	388	2·38	109·6	1298
$SnBr_4$	303	474	...	...	...
SnI_4	419	568	4·696	133·2	...
BCl_3	...	290	1·35	86·9	1040
BBr	...	363	2·69	43·6	...
$AlCl_3$	...	453	...	...	1610
$AlBr_3$	363	533	2·54	52·5	1197
AlI_3	398	623	2·63	155·0	704
$GaCl_3$	346	487-92	2·36	74·6	...
$BeCl_2$	858-90	...	...	...	...
$BeBr_2$	858-90	...	...	...	...
$MgCl_2$	981	...	2·18	43·6	1510
$MgBr_2$	971	...	...	...	...
$ZnCl_2$	535	953	2·75	49·5	974
$ZnBr_2$	667	972	3·64	37·4	760
ZnI_2	719	...	5·7	70·0	492
$CdCl_2$	814	*a.* 1173	3·62	50·6	936
$CdBr_2$	844	...	4·8	38·2	752
CdI_2	677	...	5·7	64·5	488
$HgCl_2$	561	576	5·45	49·7	532
$HgBr_2$	517	592	5·73	47·2	160
HgI_2	514	622	6·30	72·3	243
$CaCl_2$	992	...	2·20	50·4	1706
$CaBr$	948	...	3·32	33·4	1409
CaI_2	904	...	...	...	1073
$SrCl_2$	1098	...	3·05	51·9	1846
$SrBr_2$	903	...	3·98	39·8	1577
SrI_2	750	...	4·41	77·4	...
$BaCl_2$	*a.* 1181	...	3·82	54·5	1947
$BaBr_2$	1085	...	4·23	49·2	1700
BaI_2	...	...	4·92	79·5	...
$LiCl$	870	...	2·00	21·24	939
$LiBr$	820	...	3·10	13·7	...

TABLE V.—*continued.*

Substance.	Melting Point.	Boiling Point.	Specific Gravity.	Molecular Volume.	Heat of Formation in Large Calories.
	On the Absolute Scale.				
LiI	719	...	3·48	38·4	...
NaCl	1045	...	2·16	27·0	979
NaBr	981	...	3·08	19·0	858
NaI	901	...	3·65	41·0	691
KCl	1007	...	1·98	37·4	1057
KBr	972	...	2·60	28·6	951
KI	907	...	3·01	55·1	801
RbCl	983	...	2·80	43·1	...
RbBr	956	...	3·36	35·9	...
RbI	915	...	3·57	59·4	...
CsCl	904	...	4·00	42·08	...
CsBr	...	...	4·46	37·7	...
CsI	...	...	4·54	57·2	...
CuCl	874	*a.* 1173	...	...	657
CuBr	777	...	4·72	30·8	500
CuI	874	...	5·70	33·3	325
AgCl	724	...	5·505	26·0	290
AgBr	700	...	6·215	23·0	227
AgI	800	...	5·67	41·4	138
AuCl	...	...	...	...	5·8
AuBr	...	...	...	...	1·0
AuI	...	...	...	...	−5·5

TABLE VI.

List of Oxides, Sulphides, Selenides and Tellurides.

Element.	Oxides.	Sulphides.	Selenides.	Tellurides.
Hydrogen	H_2O, H_2O_2	H_2S, H_2S_3	H_2Se	H_2Te
Lithium	Li_2O, Li_2O_2 (?)	Li_2S ?		
Sodium	Na_2O, Na_2O_2	Na_2S, Na_2S_2, Na_2S_3, Na_2S_4, Na_2S_5	Na_2Se	
Potassium	K_2O, K_2O_2, K_2O_3, K_2O_4	K_2S, K_2S_2, K_2S_3, K_2S_4, K_2S_5	K_2Se	K_2Te ?
Rubidium	Rb_2O ?	Rb_2S ?	Rb_2Se ?	Rb_2Te ?
Cæsium	Cs_2O ?	Cs_2S ?	Cs_2Se ?	Cs_2Te ?
Beryllium	BeO	BeS ?	$BeSe$	
Calcium	CaO, CaO_2	CaS, CaS_2, CaS_5	$CaSe$	
Strontium	CrO Sro_2	SrS, SrS_4	$SrSe$	
Barium	BaO, BaO_2	BaS, BaS_3, BaS_5	$BaSe$	
Magnesium	MgO	MgS	$MgSe$?	$MgTe$?
Zinc	ZnO, ZnO_2 ?	ZnS, ZnS_5 ?	$ZnSe$	$ZnTe$?
Cadmium	CdO, CdO_2 ?	CdS	$CdSe$	$CdTe$
Boron	B_2O_3	B_2S_3		
Scandium	Sc_2O_3			
Yttrium	Y_2O_3, Y_4O_9			
Lanthanum	La_2O_3, La_4O_9			
Ytterbium	Yb_2O_3			
Aluminium	Al_2O_3	Al_2S_3		
Gallium	GaO (?), Ga_2O_3	Ga_2S_3		
Indium	In_4O_3 (?), In_2O_3	In_2S_3		
Thallium	Tl_2O, Tl_2O_3, TlO_2	Tl_2S, Tl_2S_3	Tl_2Se	
Chromium	Cr_2O_3, CrO_2	CrS, Cr_2S_3	$CrSe$, Cr_2Se_3	
Manganese	MnO, Mn_2O_3, MnO_2 MnO_3, Mn_2O_7	MnS		
Iron	FeO, Fe_2O_3	Fe_2S, FeS, Fe_2S_3, FeS_2	$FeSe$, Fe_2Se_3	$FeTe$?
Nickel	NiO, Ni_2O_3, NiO_2	Ni_2S, NiS, NiS_2	$NiSe$	
Cobalt	CoO, Co_2O_3, CoO_2	CoS, Co_2S_3	$CoSe$	
Carbon	CO, CO_2	CS, CS_2		
Titanium	TiO, Ti_2O_3, TiO_2, TiO_3	TiS, Ti_2S_3, TiS_2		
Zirconium	ZrO_2, Zr_2O_5	ZrS_2		
Cerium	Ce_2O_3, CeO_2, CeO_3	Ce_2S_3		
Thorium	ThO_2, Th_2O_7	ThS_2		
Silicon	SiO ?, SiO_2	SiS, SiS_2	$SiSe$?	$SiTe_2$
Germanium	GeO, GeO_2	GeS, GeS_2		

Element.	Oxides.	Sulphides.	Selenides.	Tellurides.
Tin . .	SnO, SnO_2	SnS, SnS_2, Sn_2S_3	$SnSe$, $SnSe_2$	
Lead .	PbO, PbO_2, Pb_2O_3	PbS	$PbSe$	$PbTe$
Nitrogen .	N_2O, NO, N_2O_3, NO_2, N_2O_5, N_2O_6	NS	NSe	
Vanadium .	VO, V_2O_3, VO_2, V_2O_5	VS_2, V_2S_5		
Niobium .	NbO, NbO_2, Nb_2O_5			
Tantalum .	TaO_2, Ta_2O_5	TaS_2 ?		
Phosphorus	P_4O ?, P_4O_6, P_2O_4, P_2O_5	P_4S_3, P_2S_4, P_2S_5	P_2Se_5	
Arsenic .	As_4O_6, As_2O_5	As_2S_2, As_2S_3, As_2S_5		As_2Te_2, As_2Te_3
Antimony .	Sb_4O_6, Sb_2O_4, Sb_2O_5	Sb_2S_3, Sb_2S_5	Sb_2Se_3	$SbTe$, Sb_2Te_5
Bismuth .	Bi_2O_2, Bi_4O_6, Bi_2O_4, Bi_2O_5	Bi_2S_2, Bi_2S_3	Bi_2Se_3	Bi_3Te, Bi_3Te_2, Bi_2Te_3
Sulphur .	S_2O_3, SO_2, SO_3, S_2O_7			
Selenium .	SeO_2	SeS_3 ?		
Tellurium .	TeO, TeO_3	TeS_2, TeS_3		
Molybdenum	Mo_2O_3, MoO_2, MoO_3	MoS_2, MoS_3, MoS_4		
Tungsten .	WO_2, WO_3	WS_2, WS_3		
Uranium .	UO_2, UO_3, UO_4, U_2O_9 ?, UO_6	US_2, US_3 ?		
Chlorine .	ClO, ClO_2	Cl_2S_2, Cl_2S, Cl_4S	Cl_2Se_2, Cl_4Se	Cl_2Te, Cl_4Te
Bromine .			Br_2Se_2, Br_4Se	Br_2Te, Br_4Te
Iodine .	I_2O_3 ?, I_2O_5	I_2S_2 ?		I_2Te, I_4Te ?
Rhodium .	RhO, Rh_2O_3, RhO_2, RhO_3	RhS, Rh_2S_3		
Ruthenium	RuO, Ru_2O_3, RuO_2, RuO_3, RuO_4	Ru_2S_3, RuS_2		
Palladium .	Pd_2O, PdO, PdO_2	Pd_2S, PdS, PdS_2	$PdSe$	
Osmium .	OsO, Os_2O_3, OsO_2, OsO_3, OsO_4	OsS, OsS_4		
Iridium .	IrO, Ir_2O_3, IrO_2, IrO_3	IrS, Ir_2S_3, IrS_2, IrS_3		
Platinum .	PtO, PtO_2	PtS, PtS_2		
Copper .	Cu_2O, CuO, Cu_2O_3, CuO_2	Cu_2S, CuS, CuS_2	Cu_2Se, $CuSe$	
Silver .	Ag_2O, AgO	Ag_2S	Ag_2Se, $AgSe$	Ag_2Te
Gold . .	Au_2O, AuO ?, Au_2O_3	Au_2S, Au_2S_3		Au_2Te
Mercury .	Hg_2O, HgO	HgS	$HgSe$	

TABLE VII.

Wave-lengths of the principal Solar Lines.

			Due to
Ultra-red—			
	A^{iv}	1220·0	Oxygen
	A^{iii}	1176·0	"
	A^{ii}	1050·0	"
	A^{i}	863·0	"
Visible Spectrum—			
	A	760·4	"
	B	686·7	"
	C	656·2	Hydrogen
	D_1	589·5	Sodium
	D_2	588·9	"
	D_3	587·6	Helium
	E_1	527·1	Iron
	b_1	518·3	Magnesium
	b_2	517·2	"
	b_3	516·8	Iron
	b_4	516·7	Magnesium
	F	486·1	Hydrogen
	d	438·4	Iron
	G_1	434·0	Hydrogen
	f	432·5	Iron
	G_2	430·7	"
	g	422·7	"
	h	410·1	Hydrogen
	H	396·7	Calcium
	K	393·3	"
Ultra-violet—			
	L	381·9	Iron
	M	372·9	"
	N	358·0	"
	O	344·0	"
	P	336·0	"
	Q	328·6	"
	R	317·9	"
	r	314·4	"
	S_1	310·0	Nickel
	S_2	309·9	Iron
	s	304·6	"
	T	302·0	"
	t	299·4	"
	U	294·8	"

These values for the wave-lengths are those given by Ångström.

APPENDIX II

THE KINETIC THEORY OF GASES AND ITS CONSEQUENCES

DAVID BERNOULLI, in 1738, in consideration of his work on the efflux of fluids, showed that the expansion of gases, and also their pressure, could be explained on the hypothesis of molecular motion. But it was left to Clausius and Maxwell to fully develop the Kinetic Theory of Gases.

The theory assumes gases to consist of an immense number of very elastic bodies, known as molecules, which are continually in a state of motion, colliding with one another and with the sides of the containing vessel.[1] These motions give rise to the pressure which a gas exerts, and to calculate this pressure we proceed thus :—

Consider a cube whose edge is l. Let n be the number of molecules, each of mass m, contained in it, and suppose them to be moving in all directions with the same average velocity, c.

Resolve c into three directions, at right angles to one another. Then the three components x, y, z are

---

[1] Van der Waals calculates that 1 cmm. of a gas at N. T. P. contains about $5 \cdot 4 \times 10^{16}$ molecules.

related by the equation $x^2+y^2+z^2=c^2$. Let these components be parallel to the faces of the cube. Consider the component x.

The change of momentum of a molecule on rebounding from the side of the cube is $2mx$. In unit time this action takes place $\frac{x}{l}$ times between two parallel faces. Therefore the total action is $\frac{2mx^2}{l}$ of one molecule in unit time, and of all the molecules it is $\frac{2mnx^2}{l}$. In the same way we can argue for the other components, and hence the total action of the molecules will be $\frac{2mn}{l}(x^2+y^2+z^2)=\frac{2mnc^2}{l}$. The total surface exposed is $6l^2$, therefore the pressure p is $\frac{2mnc^2}{6l^3}$, and as l^3 is the volume v, we get finally $pv=\frac{1}{3}mnc^2$. Since at any one temperature the right-hand members of the equation are constant, we have *Boyle's Law* at once.

Despretz, Regnault, Amagat and others showed that Boyle's Law was only an approximation to the truth, and various empirical formulæ were proposed which were thought more accurately to represent facts than the simple formula $pv=\mathrm{R}\theta$.

Regnault used the equation—

$$\frac{p_0 v_0}{pv}=1\pm \mathrm{A}\left(\frac{v_0}{v}-1\right)\pm \mathrm{B}\left(\frac{v_0}{v}-1\right)^2.$$

Rankine suggested the form—

$$pv=\mathrm{R}\theta-\frac{c}{v\theta},$$

and there are several others.

In 1879, J. D. van der Waals worked out the problem theoretically, and by allowing for the size of the molecules, and also for the effect of their attractions on one another, arrived at the well-known equation—

$$\left(p+\frac{a}{v^2}\right)(v-b)=\mathrm{R}\theta, \text{ where } a \text{ and } b \text{ are constants.}$$[1]

This formula was better than the simple one of Boyle, yet failed to accurately represent all known facts, and Clausius, on this account, constructed the equation—

$$\left[p+\frac{c}{\theta(v+b)}\right](v-a)=\mathrm{R}\theta \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a, b and c are constants.

As this was not satisfactory, he changed $\frac{c}{\theta}$ into a general function of the temperature. To do this, the equation (1) must be re-written thus—

$$\frac{p}{\mathrm{R}\theta}=\frac{1}{v-a}-\frac{c}{\mathrm{R}\theta^2}\left(\frac{1}{v+b}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$\frac{c}{\mathrm{R}\theta^2}$ in (2) is replaced by a general function $\frac{1}{\phi}$ of the temperature, and we get—

$$\frac{p}{\mathrm{R}\theta}=\frac{1}{v-a}-\frac{1}{\phi}\left(\frac{1}{v+b}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The form assigned to $\frac{1}{\phi}$ is $\frac{a}{\theta^n}-b$, and in this particular form the equation (3) gives a very fair agreement between calculated and observed values.

M. Sarrau put $ke^{-\theta}$ for $\frac{c}{\mathrm{R}\theta^2}$ in the general form (1) of Clausius' equation.

Another notable equation is that mathematically deduced by M. Violi. It takes the complicated form—

$$\left[p+\frac{a}{2\{v(1-b)(1+c\theta)\}^2}\right]v(1-b)=\mathrm{R},$$

where p is pressure in metres of mercury, v the volume reduced to 0° C., c the coefficient of expansion of a perfect gas, θ the temperature centigrade, a the molecular attraction constant, b the ratio of the volume of the molecules to the total volume of the gas.

However, up to the present, the complete solution of this problem is still unaccomplished.

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[1] b is usually known as the co-volume.

The heat in a gas is another name for its kinetic energy, and the absolute temperature has, by an elaborate mathematical investigation, been shown to be proportional to mV^2 where V^2 is the average value of c^2. We thus get the other form of the equation, namely, $pv = R\theta$ where R is the gas constant.

It was shown in Chapter II. how to deduce *Avogadro's Law*, and it now remains to obtain the laws of Graham and Dulong and Petit.

It is convenient in this investigation to make the unit of heat equal to the unit of energy, so that the quantity of heat in a gas is not only proportional, but also equal to $\frac{1}{2}\beta V^2 mn$, where β is the ratio of the total energy in the gas to the energy of translation.[1]

Further, it is convenient to employ a unit of temperature which will make absolute temperature *equal* to mV^2. Then if θ be the absolute temperature of a gas, and E the energy in unit volume, we have—

$$\text{(1.)}\quad V^2 = \frac{\theta}{m};$$

$$\text{(2.)}\quad E = \tfrac{1}{2}\beta V^2 mn = \tfrac{1}{2}\beta V^2 \rho = \tfrac{1}{2}\beta \frac{\rho}{m}\theta = \tfrac{1}{2}\beta N\theta,$$

where N is the number of molecules in unit volume and ρ is the density.

The thermal capacity of unit volume, at constant volume, is $\frac{dE}{d\theta}$, and therefore the specific heat is $\frac{1}{\rho}\frac{dE}{d\theta} = \frac{1}{2\rho}\beta N = \frac{\beta}{2m}$. We see therefore that the specific

---

[1] The total energy in a gas consists of (1) energy of rotation; (2) energy of vibration; (3) energy of translation. The first two are included under *interna* energy. β has the value 1·634 for the more permanent gases.

heat varies inversely as the atomic weight, and this is *Dulong and Petit's Law.*

Again, the velocity of diffusion through a porous partition will vary jointly as N and the mean value of u where u is the component of the velocity resolved at right angles to the partition. This latter can be shown to be proportional to $\sqrt{\frac{1}{3}V^2}$. Therefore the rate of diffusion is proportional to NV. Now, at any one temperature and pressure, N is the same for all gases, hence the diffusion velocity is proportional to V, and therefore to $\sqrt{\frac{1}{m}}$, or, what is the same thing, to $\sqrt{\frac{1}{Nm}}=\sqrt{\frac{1}{\rho}}$, where ρ is the density. This is *Graham's Law.*

We might introduce many more interesting deductions, but sufficient has been said to show that the kinetic theory of gases, although experience cannot actually prove it to be true, very well explains the more important phenomena connected with gases, and until any serious objection is brought forward, we can be content with this hypothesis.

The following bibliography may prove useful to those interested in this subject :—

R. Boyle . "Touching the Spring of Air and Its Effects." 1661.
D. Bernoulli . Hydrodynamica. 1738.
Despretz . Ann. Chim. Phys. (2), 34 (1827), pp. 335, 443.

Regnault	Relations des Expériences, Vol. II. p. 237.
	Memoires de l'Académie, Vol. XXI. p. 329.
Rankine	Phil. Trans. 1854, p. 336.
Clausius	Phil. Mag. 1870.
Van der Waals	Die Continuität des gasförmigen und flüssigen Zustandes.
Clausius	Wied. Ann. (9), 1880, p. 337.
	Do. (14), 1881, p. 279.
Sarrau	Compt. Rend. 101 (1885), p. 941.
Violi	Phil. Mag. 1889.
Leray	Ann. Chim. Phys. (6), 25 (1892), p. 89.
Preston	Theory of Heat. 1894.

APPENDIX III

In this appendix various additional notes to some portions of the text, which are thought to be of general interest and may prove useful, will be inserted.

Addition to Chapter I.

The following points should be noted regarding Prout's hypothesis:—

(1.) In the first paper, the important part is contained in the sentence, "I had often observed the near approach to round numbers of many of the weights of the atoms before I was led to investigate the subject."

(2.) The second paper contained the hypothesis couched in the following terms:—"If the views we have ventured to advance be correct, we may almost consider the protyle of the ancients to be realised in hydrogen; an opinion, by-the-bye, not altogether new."

Both papers were published anonymously, but their author soon became known, and the hypothesis seemed so delightfully simple that it received a number of distinguished adherents.

Additions to Chapter II.

Regnault, in his investigations, extending over more than twenty years, tested the accuracy of Dulong and Petit's Law, and found that most substances gave values ranging between 6·76 and 5·7, with a mean of about 6·38 for the atomic heat.

Leray[1] tried to show that for gases the product of the *absolute* specific heat and the molecular weight was constant. By absolute specific heat is meant the amount of heat required to change the mean energy of vibration of the molecules in unit mass, whilst the temperature increases by 1° C. Its value is less than that of the ordinary specific heat, and is calculated from an approximate formula.

Neumann and Woestyn.—Neumann's Law[2] states that for similar compounds the molecular heat is constant, *e.g.*—

Substance.	Mol. Wt.	Sp. Ht.	Product.
$CaCO_3$	100·0	0·2044	20·46
$MgCO_3$	94·3	0·2161	20·38
$ZnCO_3$	125·3	0·1712	21·45
$BaCl_2$	208	0·090	18·7
$SrCl_2$	158	0·120	19·0
$RbCl_2$	278	0·066	18·3

Woestyn's Law[3] states that the molecular heat of a compound is equal to the sum of the atomic heats of the constituents, or in symbols, $WS = \Sigma(nsw)$ where W and S are the molecular weight and specific heat of the compound, whilst n denotes the

---

[1] *Ann. Chim. Phys.* (6), 25 (1892), p. 89.

[2] *Pogg. Ann.* 23 (1831), p. 1.

[3] *Ann. Chim. Phys.* (3), 23 (1848), p. 295.

number of atoms of an element of atomic weight w and specific heat s in the molecule of the compound.

Kopp[1] carried out a number of researches on this subject, and derived the following values for the various atomic heats:—

C 1·8, H 2·3, B 2·7, Be 3·7, Si 3·8, O 4·0, P 5·4, S 5·4, Ge 5·5, and for the other elements 6·4.

As an example of the application of Woestyn's Law, let us calculate the molecular heat of Potassium Pyrophosphate $K_4P_2O_7$. We have—

$$\begin{array}{lll}
4K & = 4 \times 6{\cdot}4 & = 25{\cdot}6 \\
2P & = 2 \times 5{\cdot}4 & = 10{\cdot}8 \\
7O & = 7 \times 4{\cdot}0 & = 28{\cdot}0 \\
\hline
\multicolumn{2}{l}{K_4P_2O_7 \text{ (calculated)}} & = 64{\cdot}4 \\
\text{Do.} & \text{(found)} & \ 63{\cdot}1
\end{array}$$

The agreement is not always so good as this. Kopp further showed that, using this relation, the specific heat of water of crystallisation was the same as that of ice, *i.e.*, of solid H_2O.

Addition to Chapter III.

Stoney's Logarithmic Spiral (*p.* 65).

It might be observed that statement (2) on p. 66 was a natural consequence of the fact that a vacant space was left for every gap in Mendeléeff's Table.[2] Of course, this is not intended to be thus interpreted.

The method given is for drawing the spiral curve to see how smooth it really is. But in investigations

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[1] *Ann. Suppl.* 3 (1864), pp. 1 and 289.

[2] Page 65, line 3 from bottom.

of this kind one would naturally draw the mathematical spiral and radii, and then the circles representing the atomic weights, and note how closely to any particular radius the circles cut the curve.[1] Hence, by stating that similar elements fall on the same radius, is meant that the experimental circles cut the true spiral on, or very near to, the same radius.

ADDITIONS TO CHAPTER IV.

Wertheim's values for Young's Modulus are slightly different from those of Sutherland, and are given below.

Metal.	Young's Modulus.
Lead (drawn)	1803×10^8
,, (tempered)	1727
Gold (drawn)	8131
,, (tempered)	5585
Silver (drawn)	7274
,, (tempered)	7141
Zinc	8734
Copper (drawn)	12449
,, (tempered)	10519
Platinum (drawn)	...
,, (tempered)	15518
Iron (drawn)	20869
,, (tempered)	20794

The following works are useful to those wishing to find the properties of the elements and of a number of compounds:—

The Chemiker Kalender, edited by Biedermann;
The Chemist's Pocket Book, edited by Bayley;
The Text Book of Inorganic Chemistry, by Dammer; and the
Physico-chemical Tables of Buchka.

---

[1] The polar equation of a logarithmic spiral is $r = ae^{\theta \cot a}$.

Conductivities.

Thermal.

The values given below are those found in Buchka's Tables, and differ considerably from the values used in the text.

Sb	21·5	Cu	104·7
Pt	8·4	Hg	1·35

Electrical.

To the values given, add—

In 11·23 and Sr 3·77.

A glance at the different values obtained by various observers on different samples of metal is sufficient to show how difficult it is to obtain a metal pure enough for researches in that direction, *e.g.*—For iron, the following values have been given for the electrical conductivity, 8·3401, 7·861, 9·685; for sodium, 14·06, 21·05, and so on.

The variations of thermal conductivity are sufficiently indicated by comparing the above values with those in the text.

Relation between Valency and Atomic Volume.[1]

Traube[2] showed that "a charge of valency of an elementary atom is generally accompanied by a charge of atomic (solution) volume."

If ρ be the atomic or molecular latent heat of fusion, then $\frac{\rho}{T_0} = C\Sigma(V)$ where T_0 is the melting point on the absolute scale and C is a constant.

---

[1] Crompton, *C. N.* 72 (1895), p. 9.

[2] *Ber.* 27 (1894), p. 278.

Guldberg[1] showed that if p and p' are the vapour pressures of solution and solvent, and T and T_0 are the melting points of solution and solvent in absolute measure, then—

$$ln\frac{p}{p'}=\frac{\rho}{R}\cdot\left(\frac{1}{T}-\frac{1}{T_0}\right) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where R is the gas constant.

Nernst[2] showed that if P be the osmotic pressure of a solution in which a change of volume dv is effected by removing dx gms. of solvent, then—

$$P=\frac{dx}{dv}\cdot RT ln\frac{p}{p'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Eliminating $ln\frac{p}{p'}$ from (1) and (2) we get—

$$\frac{P}{T_0-T}\cdot\frac{dv}{dx}=\frac{\rho}{T_0}=C\Sigma(V).$$

Now $\frac{dv}{dx}$ is the volume occupied by one molecule of the solvent in the given solution.

Consequently, the molecular volume of a salt is a function of the valencies of the atoms forming the molecule.[3]

---

[1] *C. R.* 70 (1870), p. 1349.

[2] Nernst, *Theoret. Chem.* p. 126 (1895).

[3] *Ber.* 28 (1895), p. 148.

INDEX

SUPPLEMENTARY NOTE.—On page 190, mention was made of Piazzi Smyth's observation on gases in vacuum tubes. It ought to have been there remarked that those gases which show the effect best—iodine, bromine, chlorine—are *not* present in the sun. This looks very much as though they were comparatively unstable, and hence likely to be split up by the electric discharge into a simpler matter—hydrogen.

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