CCLXVII.—*The Electronic Structure of Atoms. Part I. The Periodic Classification.*

By J. D. MAIN SMITH.

THE outstanding feature of theories of the structure of atoms is their extensive and intimate relationship to the facts of chemistry summarised in the periodic classification of the elements. This relationship consists essentially in referring the periodicity in the properties of elements to a corresponding periodicity in the structural complexity of their atoms. The existence of this correspondence is readily deducible from a multitude of correlated chemical and physical experimental facts, but its precise nature has been variously interpreted, and diverging views have consequently been held as to the electronic structures attributable to the atoms of the elements.

Examination of the arrangement of the elements in the order of atomic weight shows that characteristic types of elements recur at fixed intervals or periods. The number of elements intervening in a period is always 8, 18, or 32. For example, if the noble gases be taken as points of reference, there are 8 elements from helium to neon and from neon to argon, 18 from argon to krypton and from krypton to xenon, and 32 from xenon to radon.

These sets of elements constitute Mendeléev's periods (see Table 1), the first two sets of 8 elements forming the first two "short"

TABLE 1.

Periodic Classification.

Group.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Valency.	+1	+2	+3	+4 −4	+5 −3	+6 −2	+7 −1	Zero or +8
Period.								
1	1H						(1H)	2He
2	3Li	4Be	5B	6C	7N	8O	9F	10Ne
3	11Na	12Mg	13Al	14Si	15P	16S	17Cl	18A
4	19K	20Ca	**21Sc**	**22Ti**	**23V**	**24Cr**	**25Mn**	**26Fe,27Co,28Ni,(Cu,Zn)**
	29Cu	**30Zn**	31Ga	32Ge	33As	34Se	35Br	36Kr
5	37Rb	38Sr	**39Y**	**40Zr**	**41Cb**	**42Mo**	**43Ma**	**44Ru,45Rh,46Pd,(Ag,Cd)**
	47Ag	**48Cd**	49In	50Sn	51Sb	52Te	53I	54Xe
6	55Cs	56Ba	**57La+** * 14 "Rare Earths"	**72Ct**	**73Ta**	**74W**	**75Re**	**76Os,77Ir,78Pt,(Au,Hg)**
	79Au	**80Hg**	81Tl	82Pb	83Bi	84Po	85—	86Rn
7	87—	88Ra	**89Ac**	**90Th**	**91Pa**	**92U**		

* 58Ce, 59Pr, 60Nd, 61Il, 62Sm, 63Eu, 64Gd, 65Tb, 66Dy, 67Ho, 68Er, 69Tm, 70Yb, 71Lu

periods, and the remaining sets of more than eight elements forming the "long" periods. The first two long periods of 18 elements fall into two series of eight valency groups, the "even" series consisting of 10 elements (three in Group VIII), and the "odd" series of 8 elements. The third long period, containing 32 elements, has been a subject of much discussion, but it is now generally agreed that it is divisible into two series or sub-periods like the other long periods, the even series, however, being of 24 elements, from cæsium to platinum, and the odd series as before of eight elements, from gold to the noble gas radon. It is assumed that in this period only one element, eka-iodine, belonging to the halogen group, remains to be discovered.

The Abridged Periodic Classification.

The history of chemical science has demonstrated clearly that the most useful method for the condensation and generalisation of data is that of classification by types. In organic chemistry, the method proceeds according to constitutional types, such as alcohols, ketones, aldehydes, etc., by reference to *structural* features possessed in common by *compounds*. In inorganic and general chemistry, the method proceeds similarly according to constitutional types, by reference to *valency* features possessed in common by *atoms*. The periodic classification is essentially classification by valency types, the elements being arranged into eight groups having valency from one to eight respectively. This supremely important octet classification is somewhat obscured by the detail introduced by the division of the long periods into the unequal sub-periods of the even and odd series. Modifications intended to simplify and increase the chemical utility of the classification must emphasise this octet arrangement. Many of those proposed in recent years, however, have had for their object, not the increase in the chemical utility of classification of detailed knowledge, but the facilitation of mathematical interpretations of atomic structure, and with this in view the number of groups is successively increased from 8 to 18 and 32 in passing from the short to the long periods. In all such systems, the essential chemical features of classification by valency and periodicity of properties are subordinated or suppressed, although the structure of atoms is fundamentally a chemical problem, profoundly interwoven with the periodic classification of the elements. It will be shown that abridgment, rather than expansion, clarifies the classification, and facilitates a more intimate and accurate interpretation of atomic structures, by throwing the chemically important octet arrangement into high relief.

In the classification of the elements by valency types, the 16 light elements from lithium to argon fall naturally into two periods of eight groups with one element per group per period, each period ending with a noble gas. These two periods may, consequently, be regarded as simple or specific types for the heavier elements of the long periods. Consideration of the properties of these heavier elements shows that, in each long period, only a few elements approximate closely in properties to the simple types of the short

TABLE 2.

Abridged Periodic Classification.

Class.	Alkaline.		Amphoteric.		Non-Basic.			
Group.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Valency.	+1	+2	+3	+4 −4	+5 −3	+6 −2	+7 −1	Zero
Period.								
1	1H						(1H)	2He
2	3Li	4Be	5B	6C	7N	8O	9F	10Ne
3	11Na	12Mg	13Al	14Si	15P	16S	17Cl	18A
4	19K	20Ca*	31Ga	32Ge	33As	34Se	35Br	36Kr
5	37Rb	38Sr†	49In	50Sn	51Sb	52Te	53I	54Xe
6	55Cs	56Ba‡	81Tl	82Pb	83Bi	84Po	85—	86Rn
7	87—	88Ra§						

* 10 Elements, 21Sc to 30Zn
† 10 Elements, 39Y to 48Cd
‡ 24 Elements, 57La to 80Hg
§ All elements from 89Ac
relegated to Table 3.

periods, and that in any one period some of these kindred elements appear in the even and some in the odd series. Mendeléev suggested that the elements diverging most from the specific types were in the nature of " transition " elements bridging a gap between the typical elements of each long period, a view adopted later in a modified form by Bohr in his theory of atomic structure. Mendeléev's suggestion is virtually a recognition that the long periods can be short-circuited by excluding the transition elements, leaving an abridged classification constituted solely of elements closely related to the short period types, the periodic classification thus consisting only of simple periods each of eight elements.

In order to effect this short-circuiting or abridgment of the long periods, it is necessary to decide which elements are most closely related to the typical elements of the short periods, the remaining elements being relegated to transition series. In the first long period (see Table 1), it is evident that potassium and the elements from gallium to krypton are more closely related to sodium and the elements from aluminium to argon than are copper and the elements from scandium to nickel, and these last nine elements are therefore definitely transition elements. There remain only calcium and zinc for consideration. As one of the obvious features of the periodic classification is the increase in basicity with increase in atomic weight in each group, the element corresponding to magnesium, the oxide of which is feebly alkaline, should possess a strongly alkaline oxide, the heavier members of the group having still more alkaline oxides. This circumstance involves that the congeners of beryllium and magnesium are the alkaline-earth metals, calcium, strontium, barium and radium, whilst zinc, cadmium, and mercury are transition elements.

The transition elements of the first long period are consequently the ten elements from scandium to zinc (see Table 3). The remaining eight elements, potassium, calcium, and gallium to krypton, form an abridged period (see Table 2) with one element per periodic group, exhibiting extremely close resemblance to the typical elements of the short periods. Similar considerations apply to the second long period, the transition elements being the ten from yttrium to cadmium (see Table 3). The remaining eight elements, rubidium, strontium, and indium to xenon, form an abridged period with one element per periodic group. In the third long period, consisting of 32 elements, it is similarly possible to allocate the eight elements cæsium, barium, and thallium to radon to the abridged period. The 24 elements from lanthanum to mercury are in consequence relegated to the transition series.

In the fourth long period, the known elements come to an end with uranium in Group VI of the even series. The chemical and physical properties of actinium, thorium, protactinium, and uranium indicate decisively that they are analogues of yttrium, zirconium, etc., and therefore transition elements. The only remaining known element of the period is radium, which resembles barium so closely that it can be separated from it only with difficulty. Radium consequently is an alkaline-earth metal and must be regarded, not as a transition element, but as the Group II representative in the abridged classification. Similarly, eka-cæsium must, as an alkali metal, be postulated as the Group I representative of the abridged classification, not as a transition element. The existence of only one element, actinium, between thorium and radium renders it certain that the transition series of this last long period contains no transition sub-series similar to the anomalous 14 "rare-earth" elements (see p. 2035), and it is consequently probable that, if all the elements of this period were known, they would number only 18 as in the case of the first and second long periods.

There remain for consideration only the two lightest elements, hydrogen and helium. Apart from hydrogen, no element lighter than helium is known, and many considerations, chemical and physical, render it improbable that any other element can exist. If it be admitted that electrons are the sole valency factors, the fact that helium contains only two electrons makes it certain that hydrogen with one electron is the only possible element lighter than helium. Despite the validity and utility of the octet classification, it is thus impossible to fill more than two of the eight groups of this primitive period. As the unit of valency and of atomic weight, hydrogen may be regarded as the type of all the valent elements and placed at the head of any of the Groups I to VII of the classification, helium being placed at the head of Group VIII as the type of all the non-valent and noble elements. It is not a matter of importance, in the classification of the elements, in which group hydrogen is placed, but from its univalency it may conveniently be placed in Group I *and* alternatively in Group VII.

The modification of the periodic classification derived from the foregoing considerations is shown in Table 2, and consists of a primitive period of two elements, two short periods each of eight elements, three abridged long periods each of eight elements, and a final abridged and incomplete period, or seven periods in all. Examination of these seven abridged periods reveals much greater regularities in the classification than are readily discernible in the extended form. Basicity, for example, *diminishes* regularly in each *period* from strong alkalinity in the first group to strong acidity in the seventh, and *increases* regularly in each *group* from the first to the seventh period. Further, all the elements which possess alkaline oxides are confined to Groups I and II. The alkaline thallous and plumbous oxides are only apparent exceptions to this rule, for in neither case does the metal exhibit the valency characteristic of the periodic group to which it belongs. This disappearance of alkalinity beyond Group II is of fundamental importance in the interpretation of the electronic structures of the atoms of all the elements, in Groups III to VIII no less than in Groups I and II, for, being a measure of electron mobility, it enables a differentiation to be made amongst the various sub-groups of electrons that constitute the exterior of atoms.

Comparison of Groups III and IV with Groups V, VI, and VII brings to light a further regularity relating to basicity. The whole of the elements of Groups III and IV possess amphoteric oxides, their basic tendencies being approximately equal to their acidic tendencies, and, where the elements exhibit lower valency, the lower oxides are never amphoteric but decidedly basic or even alkaline, as in the case of thallous and plumbous oxides. In Groups V to VIII, on the other hand, all the elements yield oxides which are strongly acidic, and, even where the basic properties are in any degree exhibited by the oxides, as in the case of bismuth and antimony, the derived salts are without exception hydrolysed by water to basic salts. Further, where the elements of Groups V to VII exhibit lower valency than that characteristic of the group, even the lower oxides are usually strongly acidic. Groups V to

VIII, moreover, include every known element which is gaseous below a red heat. The elements of Groups III and IV are consequently as sharply differentiated from those of Groups V to VII as from those of Groups I and II. The periodic classification can thus be divided, not only into groups, periods, and even, odd, and transition series, but also into classes of groups; the first class, Groups I and II, contains what may be termed the alkaline elements; the second class, Groups III and IV, the amphoteric elements; and the third class, Groups V, VI, VII, and VIII, the non-basic elements.

Variable Valency.

A further noteworthy feature of the abridged classification is that, without exception, every element exhibiting variable valency possesses valencies which differ by only 2, 4, or 6 units, iodine, for example, having valencies of 7, 5, 3, and 1. Apparent exceptions to this rule may be found in the case of gallium and indium : both metals, though normally tervalent, are stated to yield bivalent salts, while indium is stated to yield univalent salts in addition. The vapour density of indium " dichloride " slightly above its boiling point, however, proves the formula to be In_2Cl_4, not $InCl_2$. The dichloride has therefore no real existence, and it may be regarded as a double salt of the monochloride and trichloride, $InCl,InCl_3$ or $In(InCl_4)$. Gallium " dichloride " boils at 535°, but its vapour density has been recorded only at 1000° where it is normal. If, however, the formula is Ga_2Cl_4 and dissociation occurs on heating to a mixture of GaCl and $GaCl_3$, the vapour density of the mixture will be the same as that of $GaCl_2$. Fused gallium trichloride is a non-electrolyte, like aluminium chloride, whereas the alleged dichloride is a good conductor and readily yields metallic gallium on electrolysis, pointing to the formula $Ga(GaCl_4)$ or Ga_2Cl_4. A similar dimeric " dichloride " is obtained from thallium by mixing the monochloride with the trichloride, and it is definitely known that thallium does not exhibit bivalency. If gallium and indium " dichlorides " are, as suggested, really gallous gallichloride and indous indichloride, respectively, these two metals fall into line with thallium in the same group as possessing only tervalency and univalency, and the apparent exceptions to the rule of variation by two units of valency disappear from the abridged classification.

The Transition Series.

It has been shown, in connexion with the abridgment of the periodic classification, that 10 elements in each of the first two long periods, 24 in the third long period, and four of the six known elements of the last period show very considerable divergence from the properties of the typical elements of the two short periods, and are to be regarded as transition elements bridging a gap in each long period between elements most closely allied to the typical elements. In the first long period, these ten transition elements, from scandium to zinc, may be arranged in a sub-period or transition series consisting, like the abridged periods, of eight valency groups (see Table 3). The lightest member of the series, scandium, with an

TABLE 3.

All Transition Series.

Group.	III.	IV.	V.	VI.	VII.		VIII.		I.	II.
Valency.	+3 to 2	+4 to 2	+5 to 2	+6 to 2	+7 to 2		+8 to Zero		+1 to 3	+2 to 1
Period.										
4	21Sc	22Ti	23V	24Cr	25Mn	26Fe	27Co	28Ni	29Cu	30Zn
5	39Y	40Zr	41Cb	42Mo	43Ma	44Ru	45Rh	46Pd	47Ag	48Cd
6	57La*	72Ct	73Ta	74W	75Re	76Os	77Ir	78Pt	79Au	80Hg
7	89Ac	90Th	91Pa	92U						

* 14 Elements, 58Ce to 71Lu, relegated to Table 4.

invariable valency of three, naturally falls into Group III, the heaviest member, zinc, with an invariable valency of two, being proper to Group II, the transition period thus commencing with Group III and ending with Group II.

The set of ten transition elements from the second long period correspond so closely in chemical and physical properties to the ten transition elements from the first long period that, without further discussion, they may be allocated to the corresponding eight groups from III to II (see Table 3).

Owing to the fact that there are 24 transition elements in the third long period as against 10 in the other two long periods, no complete analogy exists, but the nine elements from celtium (hafnium) to mercury in this longest transition series present so close a resemblance to the nine elements in the preceding transition series, from zirconium to cadmium, that they may readily be allocated to the seven corresponding periodic groups from IV to II. There remain in this transition series only the 15 elements having atomic weights lying between barium in Group II and celtium (hafnium) in Group IV. These elements from lanthanum to lutecium (known as " rare-earth " elements) have characteristic tervalency, are relatively strong bases, and give rise to basic salts of the type $La(OH)CO_3$, and mixed salts of the type $LaFCO_3$. There can, therefore, be no doubt that these elements are completely analogous to yttrium and scandium, and are proper to Group III. This transition series of 24 elements may be short-circuited or abridged (see Table 3) by the omission of 14 of the 15 " rare-earth " elements in Group III, leaving an abridged transition series of 10 elements corresponding closely in every member to each of the transition series from the first two long periods. It is not a matter of great importance chemically which 14 "rare-earth" elements are relegated to a transition sub-series, but the relegation is of prime importance in the problem of the electronic structures of the atoms of this period. It is consequently necessary to make a decision, on chemical grounds if possible, as to the element presenting the closest resemblance to yttrium and scandium in the two preceding transition series, and to place the other fourteen in a transition sub-series. Scandium and yttrium have no valency higher than three, whilst yttrium (certainly) and scandium (probably) exhibit the valency of two in acetylenic carbides of the form YC_2. Both yield colourless, diamagnetic salts, while yttrium oxide is a stronger base than scandium oxide, the basicity of the former only just falling short of alkalinity. Consequently the element to be placed in Group III of the third transition series should have no higher valency than three, exhibit a valency of two in an acetylenic carbide, and possess colourless, diamagnetic salts and a strongly alkaline oxide. These properties are possessed only by the lightest of these elements, lanthanum, which must, accordingly, be regarded as the Group III representative in the transition series of the third long period, the remaining 14 from cerium to lutecium, being relegated to a transition sub-series (see Table 4). This transition sub-series

TABLE 4.

Transition Sub-series, Period 6.

Element.	Ce	Pr	Nd	Il	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Valency.	2	2	2		2	2				2			2	
	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4					4						

presents no analogy to the transition sub-period or to the main period, for these are real periods consisting of eight groups, whereas the elements of the transition sub-series do not exhibit valency less than two or greater than four, and thus cannot form a period. From time to time it has been proposed to place cerium in Group IV on the grounds of its quadrivalency and the isomorphism of some few of its salts with those of thorium and zirconium. These proposals have lost much of their point since the discovery of celtium (hafnium), properly allocated to Group IV because of its extraordinarily close resemblance to zirconium. It will, moreover, be shown, in discussing the electronic structure of atoms, that the allocation of cerium to Group III and to the transition sub-series on chemical grounds is fully justified, in that the electron responsible for the increase in the valency of cerium from three to four is probably structurally unrelated to any of the electrons responsible for the quadrivalency of celtium (hafnium) or indeed of any element in either the main or transition periods.

The transition sub-periods (Table 3), based upon the foregoing considerations, comprise two typical periods each of ten elements, an abridged period also of ten elements, and a final incomplete period, all the periods commencing with Group III and ending with Group II.

With the possible exceptions of scandium and zinc (although scandium possesses an acetylenic carbide of the probable formula ScC_2, in which the metal would be bivalent), all the transition elements exhibit variable valency, and this variation can and usually does occur by one unit, instead of by the invariable two units of the abridged classification. With very few exceptions, the transition elements give rise to coloured salts, whereas the elements of the abridged classification form only colourless salts. Unlike the abridged periodic classification, the groups of which are divisible into a class of two alkaline groups, a second class of two amphoteric groups, and a third class of four non-basic groups, the transition classification consists of only one strongly basic group, III, the other seven groups almost without exception comprising only elements with either amphoteric or strongly acidic properties in their highest oxides, although the acidic properties are feeble in Groups I and II.

The Complete Periodic Classification.

On recombining the transition classification (Table 3) with the abridged classification (Table 2), the full periodic classification including the whole of the elements is obtained (Table 1). This table differs from the commonly accepted forms in small but important features. Seven main periods suffice to include all the known elements, a primitive period of two elements, two simple periods each of eight elements, and four complex periods consisting each of two sub-periods. Each period comprises only eight groups, commencing with Group I and ending with Group VIII, the simple periods and the main sub-periods of the long periods terminating with noble gases and the transition sub-periods with noble metals. In order to indicate their close resemblance to the noble metals of Group VIII, the pairs copper and zinc, silver and cadmium, and gold and mercury, are alternatively included also in this group, just as hydrogen is alternatively included in Group VII to indicate its resemblance to the halogen elements.

The transition elements in each long period are shown in heavy type, the arrows between elements of Groups II and III indicating the position at which the transition elements create a gap between the typical elements of the periods. In order to preserve the symmetry of the octet classification, the 15 rare-earth elements, belonging to Group III and succeeding barium in atomic weight, are represented only by their most typical member, lanthanum, the other 14 being shown in detail in a footnote to the table. In order to facilitate the identification of the typical members of each group, which constitute the abridged classification, they are placed to the left and the transition elements to the right of the columns.

The abridged classification, the transition classification, the transition sub-series, and the complete periodic classification, shown in Tables 1, 2, 3, and 4, respectively, together with the experimental chemical evidence on which they are founded, will form the basis of subsequent papers on the interpretation of chemical evidence in terms of the distribution of electrons in atomic structures. The next paper will show primarily that the octet classification is due to the existence of from one to eight outer electrons in three sub-groups completed to 2, 2, 4 in the inert gases; that the transition classification is due to from one to eight more deeply seated electrons in two sub-groups completed to 4, 6 and forming part of a main group in five sub-groups of 2, 2, 4, 4, 6, completed in Group I; and that the transition sub-series is due to from one to fourteen still more deeply seated electrons completed to 6, 8, and forming part of a main group in seven sub-groups of 2, 2, 4, 4, 6, 6, 8, completed in lutecium. This scheme of atomic structure was first put forward by the author on incomplete evidence on March 9th, 1924 (*J. Soc. Chem. Ind.*, **43**, 323), and is now found to be fully justified in the light of additional evidence chiefly furnished by the foregoing periodic classifications.

The author desires to thank the Research Committees of Birmingham University and the Chemical Society, Gerald W. Kenrick, Esq., W. Byng Kenrick, Esq., Sir William Waters Butler, Bart., and Professor G. T. Morgan, F.R.S., for grants, laboratory facilities, and gifts and loans of rare metals and chemicals in aid of this series of researches.

THE UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, May 25th*, 1927.]