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CHAPTER 4

CLASSIFICATION OF THE ELEMENTS

The 105 substances well-known as elements are the foundation of the study of chemistry. Attempts have always been made to discover an arrangement and order in a complex science such as chemistry comprising a vast number of experimental facts about all the 105 elements. In order to facilitate a systematic study of the vast facts we must classify them in a way that lays emphasis on similarities and differences between isolated and unrelated phenomena. The earlier attempts at such a classification have been attributed to many scientists and proved to be very useful in developing the modern system which is based upon the electronic arrangement of atoms. It is, therefore, worthwhile to trace the developments.

Early Attempts at Classification

1. ***Noble Metals and Base Metals*** **:** In one of the earliest attempts at the classification, the metals were divided into two groups. gold and silver were considered to be noble metals, whereas copper, iron, tin lead etc. were included among the base metals. When elements which are non-metals were discovered, a further classification into metals and non-metals were introduced and made it possible to anticipate the difference in the properties of hitherto unknown elements.

2. ***Dobereiner's Triads*** **:** In 1829, J. W. Dobereiner observed that several of the elements could be grouped together in sets of three, called *triads*, which have closely related properties. The triads are found to have either nearly the same atomic weights or differ by an almost constant difference. Using present-day atomic weights which are more accurate than those used by Dobereiner, the relationships among some triads may be shown as in Table 4.1.

Table 4.1 Dobereiner's Triads.

Triads	*Atomic weights*	*Difference between consecutive elements*
Li	6.940	
Na	22.997	16.057
K	39.100	16.103
Cl	35.457	
Br	79.916	44.459
I	126.91	46.994
Fe	55.85	
Co	58.94	Almost the same at. wts.
Ni	58.71	

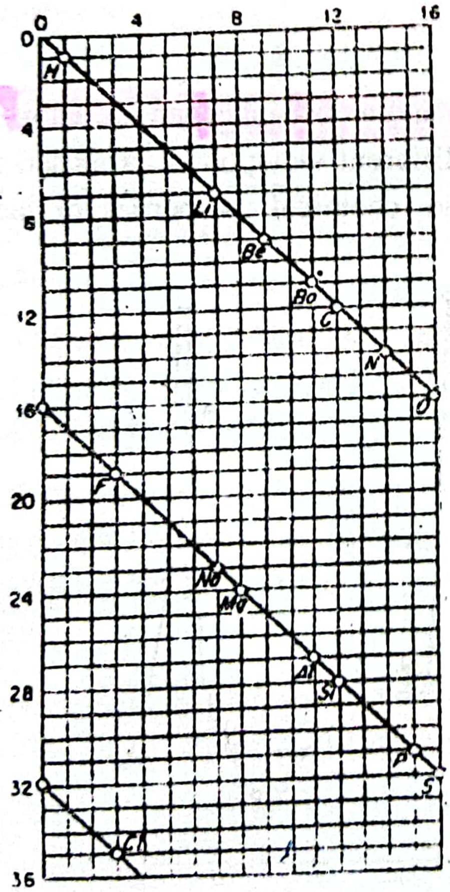

Fig. 4—1. A portion of the Telluric Screw on a flat surface

The triads of Dobereiner represent the first reported attempt at classification of elements on the basis of atomic weights. This observation stimulated further attempts to seek additional and wider numerical relationships. But most of the attempts did not meet with much success, largely because the atomic weights were not evaluated correctly. Mention may be made about Pettenkofer series which suggested that the atomic weights of chemically similar elements can be represented by arithmatic series. Thus oxygen, sulphur, selenium and tellurium could be classed as family of elements represented by the series $I+2n\times8$ where $I=$ at. wt. of O and $n=0, 1, 2, 3$. A French scientist, de Chancourtois, constructed a vertical cylinder on which he arranged the elements spirally at heights proportional to their atomic weights. It was found that similar elements appeared above one another on the cylinder. This arrangements is known as the Telluric Screw and this proved to be the forerunner of the modern classification of elements. A flat surface of the Telluric Screw is shown in Fig. 4—1.

3. ***Law of Octaves*** : In 1864, John Newlands arranged the elements in the increasing order of their atomic weights and observed that every eighth element in the list beginning from any given element showed a repetition of the physical and chemical properties of the first element. Because of its resemblance with the eight notes in musical scale this concept of the classification of elements was known as the Law of Octaves. Unfortunately this basically sound idea was not well received by scientists of Newlands' time. It may be pointed out that the inert gases were not then known and the discovery of the inert gases completely shelved the idea of the Law of Octaves.

Periodic Law :

In 1869, a German chemist, Lother Meyer, and a Russian scientist, Dmitri Mendeleeff, working independently and from different viewpoints, proposed a detailed relationship between the physical and chemical properties of the

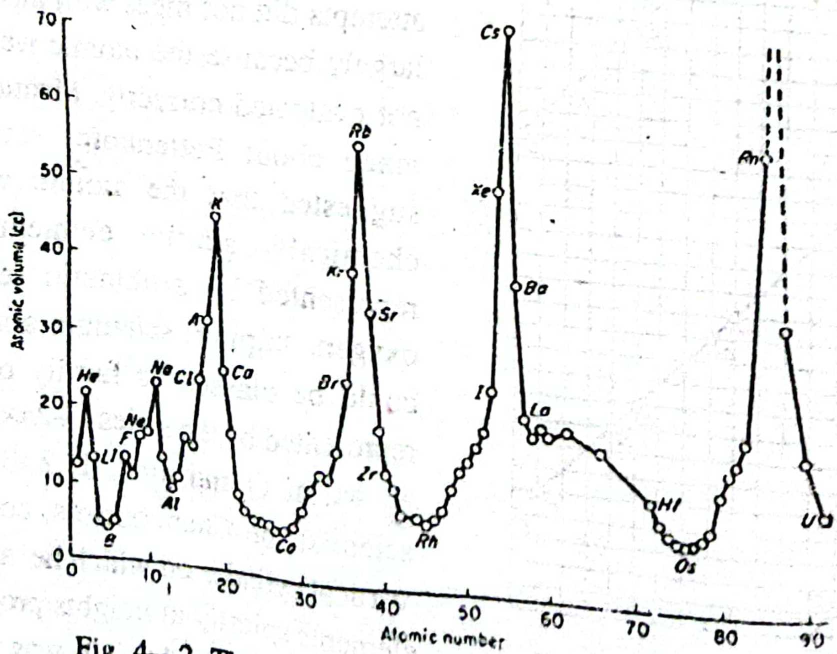

Fig. 4—2. The atomic volume curve of the elements.

elements and their atomic weights. Meyer selected some physical properties related to the atomic weights, namely atomic volume. Taking atomic numbers instead of atomic weights as the basis a graph of atomic volumes (the volume occupied by 1 g. atom of an element or at. wt. divided by the density) against atomic numbers is shown in Fig. 4—2. This graph does reveal a periodic variation of atomic volume when the elements are arranged in the increasing order of atomic weights or atomic numbers. It may be noted that a periodic variation repeats itself more or less at regular intervals or periods with the change of variables. Thus the change of seasons in a year is a periodic phenomenon. Night and day are periodic phenomena. The swing of a pendulum to and fro is a periodic phenomenon.

Mendeleeff gave a more detailed comparison of the physical and chemical properties of the elements and set up a periodic system in which the elements were arranged in horizontal ROWS (series) and vertical COLUMNS (groups) according to increasing atomic weights. This arrangement is the basis of our modern Periodic Table. Mendeleeff observed that when all the 65 elements (known at that time) were arranged according to increasing atomic weights, similarities and differences in their properties would be apparent. This was enunciated in the form of a PERIODIC LAW which stated that the physical and chemical properties of the elements are periodic functions of their atomic weights.

The discovery of rare gases during 1890—1900 did not produce any serious difficulty with regard to Mendeleeff's PERIODIC TABLE. Mendeleeff is usually given the principal credit for establishing the periodic system of the elements.

With the advancement of our knowledge about atomic structure and discovery of new elements, a modification in the definition of periodic law was proposed on the basis of atomic number. The modern statement of the periodic law is:

The physical and the chemical properties of the elements are periodic function of their atomic numbers.

There are various forms of the Periodic Table and a modern long form is given in Table 4.2. based on Aufbau Principle (building up of the atomic electronic configurations. As the nuclear charge increases, the electronic configurations become more complex.

n-1

The Modern Periodic Table

The original Periodic Table suggested by Mendeleeff has undergone many modifications, although the basic features have been maintained in all the modified forms.

No of elements electronic configuration

(2)

It is seen that the first short period (horizontal series) contains only two elements—hydrogen and helium. Helium has a complete energy level of two electrons ($1s^2$). The second short period consists of eight elements beginning with lithium and ending with neon. Neon has complete electronic arrangements of $1s^2 2s^2 2p^6$ and contains 8 electrons in the outermost level. The third short period again consists of eight elements beginning with sodium and ending with argon. Argon has the electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$ and the outermost energy level contains 8 electrons.

The fourth period is the first long period containing eighteen elements and this period starts from potassium (atomic number 19). Potassium has electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ and the next element calcium (atomic number 20) has one more election in 4s level, i. e., $4s^2$ and thereby making it complete. Scandium having atomic number 21 with the electronic arrangements $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$ starts building up the 3d energy level. The process of filling up of 3d level is completed until copper (atomic number 29). In copper the third quantum level contains 18 electrons. Each succeeding element in this period contains one more electron in the fourth quantum level. The fourth period comes to an end with the inert gas krypton (atomic number 36) containing eight electrons in the outermost energy level.

The fifth period begins with rubidium (atomic number 37). The last element is xenon (atomic number 54) and contains again eight electrons in the outermost energy level. The process of filling up of the energy levels follows the same pattern as in the fourth period and, therefore, the fifth period also contains eighteen electrons.

The sixth period consists of thirtytwo elements. This period starts from cesium (atomic number 55) having one electron in the 6s level, i.e., $6s^1$. The next element barium has two electrons in the 6s level. The next fifteen elements starting from lanthanum (atomic number 57) to lutecium (atomic number 71) contains 8 and 2, or 9 and 2 electrons respectively in the two outermost energy

How the elements are organized in a periodic table according to their atomic number

levels together with increasing number of electrons in the inner 4f orbital. 4 The fourteen elements starting from Ce (58) to Lu (71) have almost identical chemical properties and ~~all~~ are placed in the same position in the Periodic Table. They are known as ~~rare~~ earth elements and constitute the lanthanide series named after lanthanum. From cerium to lutecium each succeeding element has one more electron in the 4f energy level. Lutecium (atomic number 71) and above have a total of 32 electrons in the fourth energy level. The single electron in the 5d energy level in all the elements from lanthanum to lutecium starts building up with hafnium (atomic number 72) and becomes complete ($5d^{10}$) in gold (atomic number 79). From gold to the end of the period each such succeeding element has one more electron in the 6p energy level. The period ends with the inert gas radon (atomic number 86) containing 8 electrons in the outermost energy level ($6s^2 6p^6$). The seventh period is still incomplete. The first element francium (atomic number 87) has one electron in 7s energy level and after radium (atomic number 88) with $7s^2$ electrons the building up of 6d level starts but for all the elements upto the present element hahnium (atomic number 105) it remains constant, i.e., consists of only one electron. 4 From actinium (atomic number 89) a new series of elements starts which is known as actinides and may be considered to be complete at the element having atomic number 103 (Lr) placed along with lanthanides below the Periodic Table.

The elements actinium, thornium, protoactinium and uranium are naturally occurring radioactive elements in the actinide series. The eleven elements after uranium, known as transuranium elements, have been made artificially. Because of the filling up of the 5f energy level and identical electron arrangements in the 6d and 7s energy levels, the actinide series of elements have similar chemical properties. Like the lanthanides these are also placed in one position after radium in the Periodic Table. The recently discovered element kurchatovium (atomic number 104) is the beginning of the seventh period which is incomplete and will be considered to be complete at the element of atomic number 118. The next element (atomic number 105) has been named tentatively as hahnium (Ha).

5 The vertical arrangements of elements in the Periodic Table are called groups. It may be seen that the groups are numbered IA, IIA IIIB, IVB VB, VIB, VIIB, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA and 0. The elements in sub-

group A show some similarities to the corresponding elements in the B sub-group of the same number. The sub-grouping of elements was originally empirical, but now it is based on the electronic arrangement of the atoms. The division into the sub-groups A and B is based on the fact that the penultimate energy levels (last but one quantum level) of electron in these groups contain the arrangement s^2p^6 and $s^2p^6d^{10}$ respectively. It may be noticed that the similarities between A and B sub-groups of the same group of elements sometimes are confined only in the oxidation states and some of their compounds. Thus manganese in group VIIB is a metal and chlorine in VIIA is a non-metal and a gas. However, oxidation states of +7 for Mn in $KMnO_4$ and Cl in $KClO_4$ is common for both and these compounds have similar crystalline form, solubility and oxidizing action.

The elements in group VIII have no sub-groups, instead these consist of three elements in one single group of the Periodic Table and occur in the middle of each long period. These have striking horizontal similarities. This group contains iron, cobalt and nickel in the fourth period' ruthenium, rhodium and palladium in the fifth period; and osmium, iridium and platinum in the sixth long period. The group VIII elements may be called bridge elements, because they form bridge between the hard, high melting metals of group VIB and VIIB and the softer metals of group IB and IIB. The inert gases, having elements of completed electronic levels, are placed at the end of the period where they fit excellently and are termed as elements of group 0.

Electronic Structure and the Periodic Law

Types of Elements : According to the electronic configurations, the elements may be divided into four types. Mention has already been made regarding the four types of atoms on the basis of electronic arrangement. The four types of elements are :

(1) The Inert Gases. (Elements of 0 group).

(2) The Representative Elements (s and p book elements).

(3) The Transition Elements (d block elements).

(4) The Inner Transition Elements (f block elements)

The Inert Gases : The zero group elements have been placed at the end of each period in the Periodic Table. It appears that these elements having s^2p^6 electronic arrangements in the outermost level are very stable. Helium has $2s^2$ stable arrangement and all other inert gases have s^2p^6 outer configurations. It may be noted that no atom has a complete energy level except helium and neon. This is one reason that discontinuities in the building up of energy level take place. These elements are colourless gases.

The Representative Elements (s and p block elements) : These elements generally belong to A sub-group of the Periodic Table. These elements have the outermost energy level incomplete just after the complete or stable groupings of s^2p^6. The chemical behaviour of these elements depends upon the valence electrons and these are both metals and non-metals. Thus the alkali metals, alkaline earth metals are s block or s orbital elements. Group IIIA elements under boron have a single electron in their valence **p** orbitals. The valence electrons of all the elements from boron to halogens (groups IIIA to VIIA vertically) occupy **p** orbitals. Hence these elements are called **p** block or p orbital elements. They generally form colourless compounds.

The Transition Elements (d block elements) : These elements are generally heavy metals of sub-group B and contain two incomplete energy levels because of the building up of the inner **d** electrons. The chemical properties of these elements depend upon the electrons from the two outermost levels (s and d electrons). These elements generally form coloured compounds.

As the atomic number increases each successive electrons enters the outermost energy level of the atom. But sometimes the additional electron enters one of the inner levels, such as the 3**d** on account of its lower energy than 4p, although this is not attained until 4s levels is completed. When 4s has got its 2 electrons, the next electron now goes to 3d instead of 4p and as the atomic number increases, it is the 3**d** level which is being filled up. The 4s continue to have 2 electrons and the properties of the successive elements do not appear to change much. Elements which have normally the same number of electrons in the outermost level but have a progressively greater number of electrons in an inner level (such as **d** level) are called "Transition Elements". In the Periodic

Table 4.2. The Periodic Table of elements (Long form).

Period→ s block elements; d block elements (Transition elements); p block elements; s electrons

Group ↓	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
	H 1																	He 2
	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
	Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
	Fr 87	Ra 88	Ac 89	Ku	Ha	(106)	(107)	(108)	(109)	(110)	(111)	(112)	(113)	(114)	(115)	(116)	(117)	(118)
	(119)	(120)	(121)	(154)	(155)	(156)	(157)	(158)	(159)	(160)	(161)	(162)	(163)	(164)	(165)	(166)	(167)	(168)

Lanthanides	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
Actinides	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103
Superactinides	(122)	(123)	(124)											(153)

Table we come across four such transition series in which the additional electrons enter the 3d, 4d, 5d and 6d orbitals. some of these are shown in Table 4.3.

Besides the transition elements, there are the inner transition elements in which not only the d levels but also the 4f or 5f levels are being progressively filled up. These are generally called the Lanthanides (the rare earths) and the Actinides (mainly trans-uranium elements).

Table 4.3. Outer electron levels of the transition metal groups.

21	Sc	$3d^1 4s^2$	39	Y	$4d^1 5s^2$	57	La	$5d^1 6s^2$
22	Ti	$3d^2 4s^2$	40	Zr	$4d^2 5s^2$	72	Hf	$5d^2 6s^2$
23	V	$3d^3 4s^2$	41	Nb	$4d^4 5s^1$	73	Ta	$5d^3 6s^2$
24	Cr	$3d^5 4s^1$	42	Mo	$4d^5 5s^1$	74	W	$5d^4 6s^2$
25	Mn	$3d^5 4s^2$	43	Tc	$4d^5 5s^2$	75	Re	$5d^5 6s^2$
26	Fe	$3d^6 4s^2$	44	Ru	$4d^7 5s^1$	76	Os	$5d^6 6s^2$
27	Co	$3d^7 4s^2$	45	Rh	$4d^8 5s^1$	77	Ir	$5d^7 6s^2$
28	Ni	$3d^8 4s^2$	46	Pd	$4d^{10}$	78	Pt	$5d^9 6s^1$
29	Cu	$3d^{10} 4s^1$	47	Ag	$4d^{10} 5s^1$	79	Au	$5d^{10} 6s^1$
30	Zn	$3d^{10} 4s^2$	48	Cd	$4d^{10} 5s^2$	80	Hg	$5d^{10} 6s^2$

The first transition series of elements involving the completion of 3d level start from Sc (21) to Zn (30) which may be discussed as the elements of representative characters. The second series of transition elements start from Y (39) upto Cd (48) involving 4d energy level. The third group of transition metals starts from La (57) but with a break from Ce (58) to Lu (71) which are classified as inner transition metals and proceed upto Hg (80). Sometimes the metals of group IIB, namely, Zn, Cd, Hg, are not included in the transition metals. But for the sake of systematic study of chemistry they are included as transition metals on the basis of electron arrangement.

The properties of transition elements are summarized in the following points :—

1. All the elements are of high melting points, electropositive and heavy metals.
2. These metals have almost the same atomic and ionic sizes. There is only slight increase in the ionization energy of the formation of M^{+2} ions.
3. All these elements show positive oxidation states of +2 and +3 generally and form mostly ionic compounds. Higher oxidation states are also exhibited in some cases.
4. As a general rule, the transition elements form coloured compounds.
5. These elements are also effective catalytic agents.
6. All these form quite a large number of complex compounds.

These properties are due to the influence of the incomplete inner d orbitals in the transition elements. The properties are similar in the case of inner transition elements where f orbitals are being completed (see Chapter 18).

The Inner Transition Elements (f block elements) : These elements have three incomplete outer levels. The orbital in which the electron is added on increasing the atomic number is an f orbital. The series of 14 elements in which 4f level is being build up follows lanthanum (57) and are called Lanthanides. The series of elements in which 5f level is being filled follows actimium and is known as Actinides. The inner transition elements (lanthanides and actinides) are all metals and show variable oxidation states. Their compounds are highly coloured (see Chapter 18). Lawrencium (103) is the last element of the actinide series. The recently discovered element kurchatovium (104) is, therefore, the first element of the Transactinide series and should be chemically similar to lanthanum and hafnium. There is a report of the discovery of element 105 (Hahnium) by the Russian scientists and if the synthesis of the new elements continues, it is expected that elements 114 and 126 should possess increased stability. The most suitable means to achieve such a break-through towards the farther reaches of Periodic Table is evidently the bombardment of heavy nuclei. This requires more powerful cyclotrons and possibly a *superatinide* series of elements may be discovered.

Periodicity of Valence Electrons : When the elements are arranged in order of increasing atomic numbers, elements with similar physical and chemical properties repeat at definite intervals. In regard to atomic structure, it implies a periodicity in the number of valence electrons in the atoms of elements. If the elements containing the same number of valence electrons are grouped together, the elements within each group will be similar in properties. Table 4.4 gives the electron levels for the elements of atomic numbers in the beginning of the Periodic Table showing the periodicity as regards the number of electrons in the outermost energy level.

Table 4.4 Periodicity of valence electrons.

Element	H							He
Electron level	1							2
Element	Li	Be	B	C	N	O	F	Ne
Electron level	2,1	2,2	2,3	2,4	2,5	2,6	2,7	2,8
Element	Na	Mg	Al	Si	P	S	Cl	Ar
Electron level	2,8,1	2,8,2	2,8,3	2,8,4	2,8,5	2,8,6	2,8,7	2,8,8

It is seen that the elements in the vertical columns (groups) have the same number of electrons in the outermost energy level. The similarity in the chemical properties among the elements of the same group can be attributed to the number of electrons in the outermost energy level of an atom. Periodicity as regards valence electrons is reflected in the periodicity of oxidation states (the number of positive or negative charges of the atoms). This feature is shown in Table 4.5.

Table 4.5. Periodicity of Oxidation State.

+1 H							0 He
+1 Li	+2 Be	+3 B	+4,−4 C	+5,−3 N	−2 O	−1 F	0 Ne
+1 Na	+2 Mg	+3 Al	+4,−4 Si	+5,−3 P	−2 S	−1 Cl	0 Ar

Hydrogen, lithium and sodium have one valence electron each, and each shows an oxidation state of +1 when this electron is transferred to another atom in the formation of chemical bonds. Carbon and silicon atoms with four valence electrons may form four polar covalent bonds in which the shared electron pairs are shifted away (+4 oxidation state) or move towards (−4) oxidation state) of the carbon or silicon atom. Fluorine and chlorine atoms, each with seven valence electrons, normally assume completed octets by the addition of one electron giving them−1 oxidation states.

Variation of Properties within Periods and Groups

The physical and chemical properties of the elements are largely determined by their electronic structure. Differences in the properties within groups may be attributed primarily to three characteristics of atomic structures : (i) The nuclear charge and the number of electrons surrounding the nucleus (atomic number). (ii) The total number of electrons—particularly the number of valence electrons. (iii) The size of the atoms, i.e., the volume occupied by the electron in various energy levels.

1. Variation of Metallic Character of the Elements : Generally, it may be noticed that in the Periodic Table the metallic character of the elements decreases from left to right progressing in the series but increases in moving vertically from top to bottom in the groups.The term "metallic character" is a rough and qualitative combination of a number of specific properties, such as electrical and thermal conductivities, metallic lustre, reducing properties etc. Except the transition elements, the trend in the variation of metallic character of elements follows the above generalisation. For instance, the most non-metallic elements, fluorine, chlorine, oxygen, sulphur, nitrogen are found at the upper right of the Periodic Table whereas the most basic matals, the alkali and alkaline earth metals are at the lower left of the Table.

2. Variation in Atomic Size : The atomic size in each succeeding element in a period decreases but the atomic radii of inert gases at the end of the periods, however, are larger than those of the elements of the preceding atomic number. The inert gases have completed outer energy levels, i. e., the p sub-level has been filled up with six electrons (p^6). As the nuclear charge increases in a period the electrons may occupy the same or different energy levels. When the succeeding electrons go into the same energy levels they are subject to greater attraction by the increased nuclear charge and hence the elements in a series show gradual decrease in the atomic size. Since the inert gases, such as argon, exhibit very weak binding force to hold the atoms together in a crystal lattice, the interatomic distances and atomic radii of these elements become greater than those of the preceding halogens.

The gradation from highly metallic sodium to highly non-metallic chlorine in the third period shown in Table 4.2 is explainable in terms of the smaller size of each succeeding element in the series. The tendency for each succeeding element to become less metallic results from the fact that the valence electrons are less readily lost as their distance from the nucleus becomes less, and the attraction for additional electrons from other atoms becomes greater.

Vertically in the groups the succeeding elements have increasing atomic radii. Thus, each alkali matal atom has a much greater atomic radius than that of the inert gas just before it. This is due to the fact that the additional electron occupies a new sub-level with a quantum number higher than those of the already filled energy levels. These elements become more metallic, i.e., lose valence electrons more readily as their size increases. This results from the fact that the valence electrons are held less strongly due to the increasing size of the atom.

A similar trend is noticed in the long periods but the gradation is less marked and also shows some exceptions, such as in Rh—1.24Å, Pd—1.28Å, Ag—1.34Å. Within a given group the heavier elements have the larger atomic size.

3. Variation in Ionic Radii : It is obvious that the size of a positive ion will be less than that of the atom from which it is formed. There is considerable decrease in size due to the loss of the outermost electron particularly in the case of alkali metals. In the cases of ions having inert gas electronic configurations, the contraction in size in a given period is well-marked. Thus in the series, Na^{+}, Mg^{+2}, Al^{+3} and Si^{+4}, which are isoelectronic with argon configuration, the decrease in their ionic sizes appears to be considerable as compared to the atomic sizes of the parent atoms. It will be seen that greater the nuclear charge, the smaller is the ionic radius in a series of isoelectronic ions. In a given group of the Periodic Table positive ions of succeeding elements have larger ionic radii.

A simple negative ion formed by the addition of one or more electrons to the outermost energy level of an atom, is expected to be much larger than the parent atom. In a given group the negative ions will have larger radii due to larger number of electron levels. The ionic sizes in a series also follow the same trend as in the case of the positive ions, i.e., the sizes decrease gradually from element to element. The trends are given in the Table 4.6 and Table 4.7.

Table 4.6. Trend in ionic sizes in a series.

Atom	Na	Mg	Al	Si	P	S	Cl	Ar
Radius(Å)	1.86	1.60	1.48	1.17	1.10	1.04	0.99	1.54
Ion	Na^+	Mg^{+2}	Al^{+3}	Si^{+4}	P^{-3}	S^{-2}	Cl^-	Ar
Radius(Å)	0.95	0.78	0.57	0.40	2.12	1.84	1.81	1.54

Table 4.7 : Trends in ionic sizes in a group(Å)

Atom	*Radius*	*Ion*	*Radius*
Li	1.52	Li^+	0.60
Na	1.86	Na^+	0.95
K	2.31	K^+	1.33
Rb	2.44	Rb^+	1.48
Cs	2.62	Cs^+	1.69
F	0.72	F^-	1.36
Cl	0.99	Cl^-	1.81
Br	1.14	Br^-	1.95
I	1.33	I^-	2.16

In the Long Periods, the ionic sizes of transition metals of the same charge (say, M^{+3}) show slight gradation with irregularities. The radii of the rare earth ions (M^{+3}) show regular decrease from lanthanum to lutecium. It is due to the relationship between ionic sizes and chemical properties that the pairs of elements, such as Zr and Hf, Nb and Ta, Mo and W, have almost identical chemical behaviour. These pairs of elements although placed widely apart in the

Periodic Table have almost identical ionic radii due to the trends in the variation of ionic sizes.

4. Variation in the Ionization Potentials : Ionization potential of an atom is the most important fundamental property of an atom and the metallic character is largely determined by its ionization potential, its atomic radius and its ionic radius. These three properties may be interdependent since the ionization potential is defined as the energy required to remove the outermost electron from an atom. In general, the greater the nuclear charge of atoms having the same number of electron orbit, the greater the ionization potential. Thus the elements in the same period have gradually increasing ionization potential. Slight irregularity within a period is due to building up of new sub-level for electrons. Metals generally have small ionization potentials and non-metals have large values. This indicates that metals give positive ions readily by the loss of electron and non-metals have no tendency to form positive ions during chemical reactions. The magnitude of the ionization potential to some extent gives a measure of the chemical activity of an element (particularly of metals). Thus the ionization potential increases in a series and shows decreasing tendency with a group in the periodic classification. In other words, the periodic variations are well-marked (see Fig. 3—1. page 111)

5. Variation in Electron Affinities : Electron affinity, as defined earlier, is a measure of the energy released when an electron is added to an atom to form a negative ion. Metals obviously have small electron affinities and non-metals, on the other hand, have large values of electron affinities and are therefore, good oxidising agents. In general, in a series of elements of a given period of the Periodic Table succeeding elements have higher electron affinities. Within a group having smaller electron affinities the metallic character becomes more prominent.

6. Variation in Electronegativities : The power of attraction that an atom shows for electron in a covalent bond (electronegativity) also shows periodic variations. The most electronegative elements are found towards the end of the periods. Metals having low electronegativities are found at the beginning of the periods. Thus the alkali metals show gradually decreasing electronegativity values within the group. The halogens are most electronegative elements and the values decrease from fluorine to iodine. It follows that elements at the extreme left of the Periodic Table form ionic bonds with, say, halogens. The elements adjacent to one another in a period generally form covalent bonds. The variations of electronegativities with the atomic numbers of elements are given in Fig. 4—3.

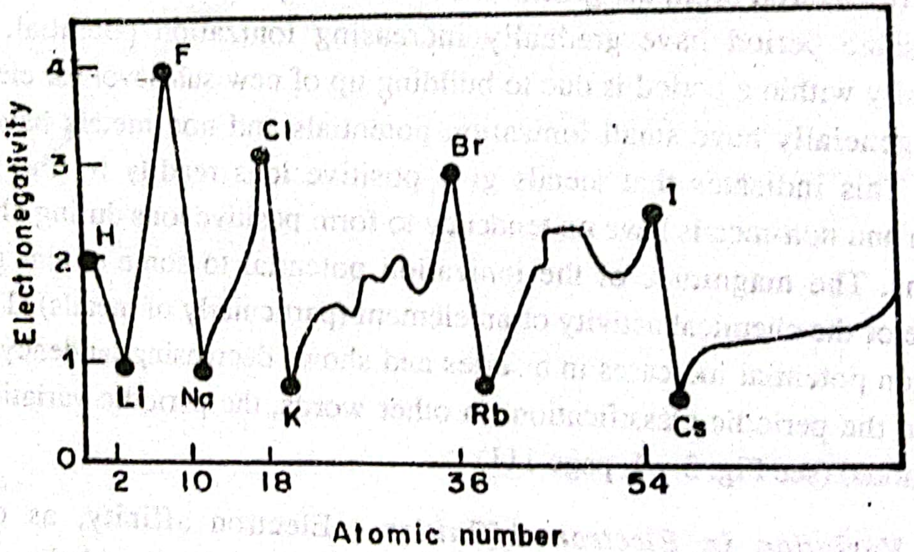

Fig. 4—3. Variation of electronegativities with atomic number of elements.

Table 4.8. Variation in electronegativities of some elements in series and groups.

Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na						Cl
0.9						3.0
K						Br
0.8						2.8
Rb						I
0.8						2.4
Cs						
0.7						

7. *Variation in the Stability of Oxidation States* : The transition elements generally exhibit more than one oxidation states. This is due to successive loss of electrons from the inner partially filled d sub-level. Thus, vanadium shows +3, +4 and +5 states and for chromium +2, +3 and +6. Those for manganese are +2, +3, +4, +6 and +7. It may be noted that the higher oxidation states become more stable near the bottom of each transition metal groups in the Periodic Table whereas the stability of +3 state decreases in the opposite order.

Among the families of post-transition metals having completely filled d levels if there are two possible oxidation states, it is found that the lower one is more stable than the higher ones. Thus in the case of tin having the electron configuration :

Sn	...	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 5s^2\ 4d^{10}\ 5p^2$
Sn^{+4}	...	... ... $4d^{10}$ ($5s^2$ and $5p^2$ lost)
Sn^{+2}	...	... ... $5s^2 4d^{10}$ ($5p^2$ lost)

$5s^2$ electrons in Sn occur after $4s^2\ 4p^6\ 4d^{10}$ completed levels and are inert in Sn^{+2}.

The inner $5s^2$ electrons are more inert and are referred to as "inert pair" of electrons. Hence Sn^{+2} is more stable than Sn^{+4}.

8. *Variation in the Oxidising and Reducing Powers* : Oxidising substances have tendency to accept electrons and are converted into lower oxidation states. The non-metals at the extreme right of the Periodic Table having high ionization potentials, electron affinities and eectronegativities tend to act as oxidising agents in chemical reactions with other substances. Similarly, reducing substances give up electrons and are converted into higher oxidation states during chemical reaction. The reducing power is the highest with the metals at the beginning of the periods, where the ionization potentials, electron affinities and electronegativities are low. Thus, alkali metals have the greatest reducing power. In general, the reducing power of the elements is progressively lower as we pass across the periods and higher, as we go down the groups. Francium should be the strongest reducing agent and fluorine, the strongest oxidising agent of all the elements.

9. Variation in the Basic Properties : The hydroxides of elements at the beginning of the Periodic Table dissociate in water solution giving OH-ions and show basic characters. The large positive ions form hydroxides which are strongly basic. On the other hand, elements of small positive ions at the end of the periods form hydroxides which in water give acidic behaviour. In general, the metals on the left of the Periodic Table form basic oxides and the non-metals on the right form acidic oxides. This accounts for the fact that the positive ions may exist in water solution with hydroxide ions (OH^-) and the negative ions may be found in water solution with a high concentration of hydronium ions (H_3O^+).

When an element exhibits two or more oxidation states, the ion of the element in its lowest state is less electronegative than in the higher state and the lowest state is the more basic than the higher one. Thus stannous ion is more basic than stannic ion.

10. Variation in Physical Properties : Almost any physical property of the elements, when plotted against the atomic numbers, shows periodicity and the curves obtained have remarkable similarity with the atomic volume curve. Thus the densities of the elements in the solid state vary periodically with their atomic numbers. The variation occurs in a regular manner within a period and shows a maximum in the central members.

Similarly, melting points and boilding points show periodic vaiations. The inert gases show minimum melting points and boiling points and occur at the bottom of the melting point curve against atomic number. The elements of groups IV and VI occupy the peaks as shown in Fig. 4—4.

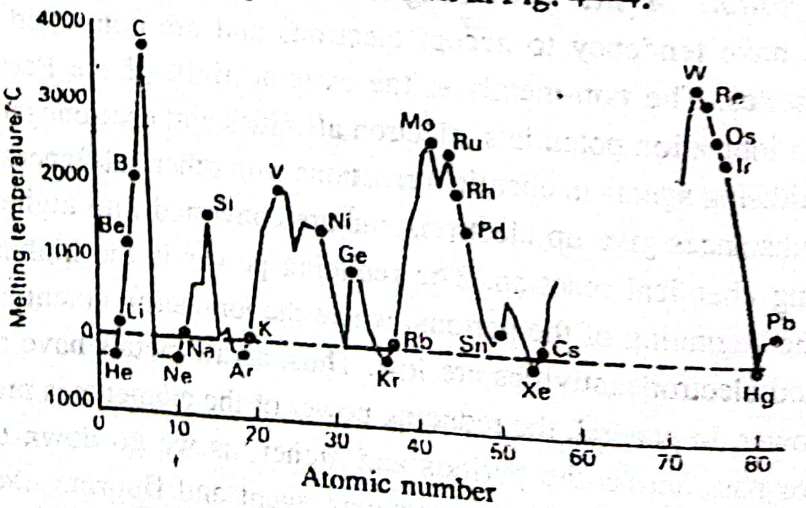

Fig. 4—4. Periodicity of melting points.

Many other physical properties such as hardness, malleability, compressibility, coefficient of expansion, thermal conductivity and electrical resistance likewise show periodic variations.

Borderline elements mostly in the middle region of the Periodic Table exhibit both metallic and non-metallic properties and are known as metalloids. They usually act as electron donors with non-metals, and as electron acceptors with metals. It is not very well-defined as to which elements should be included in this class. But they generally occur near about the middle of the Periodic Table. Such elements are boron, silicon, germanium, tellurium etc. They are all solids at room temperature, somewhat brittle and poor conductors of heat and electricity.

Usefulness of the Periodic Table

The systematic arrangement of the elements found in the Periodic Table has greatly simplified the task of organising the extensive mass of knowledge relating to the chemistry of the elements as a whole. The following important applications of the Periodic Table may be mentioned :—

1. Classification of the Elements : The classification of elements of similar properties into groups simplified their study. For instance, sodium, a member of the alkali metals group reacts with water vigorously giving hydrogen gas and forming sodium hydroxide which is a strong base. The other alkali metals, lithium, potassium, rubidium, cesium and francium also react with water in a similar manner. Halogens, again, show properties which are all alike.

It may be noted that similarities of properties in a group actually show gradation. In some cases this gradation is very well-marked.

2. Prediction of Undiscovered Elements : At present all the elements from atomic number 1 to 105 have been discovered and their properties are more or less known. But a very remarkable use of the Periodic Table was made by Mendeleeff in predicting a number of undiscovered elements which were shown by a number of gaps in the then Periodic Table. It may be remembered that Mendeleeff's Table contained only 65 elements with a large number of vacant places. Mendeleeff predicted the existence and properties of 6 elements corresponding to the gaps. These elements have since been discovered and are scandium, gallium, germanium, technetium, rhenium and polonium. It is surprising that these elements have properties quite similar to those predicted by Mendeleeff.

Elements having atomic number 43, 61,85 and 87 were also missing from the Mendeleef's Table and discovered later.

3. Correction of Atomic Weight : Atomic weights of some of the elements at the time of Mendeleeff gave a wrong position to some of the elements in the Periodic Table. The properties of these elements required their placement somewhere else. These discrepancies have been a matter of great research by chemists and physicists. For instance, the element 'indium' was placed in a vacant place in the Periodic Table between Cd (112.4) and Sn (118.7) and indium with atomic weight of about 114 fitted very well in between Cd and Sn.

4. Periodic Table in Industrial Research : The Periodic Table has been found to be quite useful in industrial researches. Several of the light metals and their alloys used in modern mechanical equipments, jet engines and air-crafts were first studied in detail because of their position in the Periodic Table. The search for tetraethyl lead as an anti-knock compound to be added to modern ethyl gasoline, was found as the result of great need for such materials by looking through the Periodic Table for elements having such properties. Another classical example of the application of the Periodic Table to an industrial problem was in connection with the development of Freon, a non-toxic, non-inflammable refrigerant. It is easily visualized by a look at the Periodic Table that compounds of the non-metallic elements in the upper right-hand region of the table are volatile enough to act as refrigerant. Thus, fluorine compounds would possess such properties and as a result Freon, CF_2Cl_2, was discovered.

Limitation of the Periodic Table

There are certain inherent weakness in the Periodic Table although it has been immensely successful in producing a systematic classification of chemical knowledge.

1. Position of Hydrogen : The position of hydrogen in the periodic table is left undecided. It has similarities in properties with both the alkali metals and the halogens. According to the atomic number or atomic weight, hydrogen should occupy a position just before helium.

Hydrogen is a gas like fluorine and chlorine and forms compounds like CH_4, SiH_4 which are like CCl_4 and $SiCl_4$ respectively. Even solid hydrogen is a non-metal resembling iodine. The hydrogen molecule is diatomic like halogen.

On the other hand, hydrogen resembles lithium and other alkali metals in having one electron $1s^1$ which can be lost in forming the hydrogen ion. Under most conditions, however, hydrogen does not lose this electron, but shares it with other atoms. Again, sodium hydride and sodium fluoride are both crystalline ionic solids, a point which shows similarity of hydrogen with fluorine. But in most cases it assumes a +1 oxidation state. For this reason, hydrogen is usually included in group IA of the table. Actually, hydrogen shows no relationship with any other element.

2. ***Anomalies in the Mendeleeff's Table*** : When the atomic weights of the elements were adopted as a basis for periodic classification, a number of anomalies were observed with regard to the placement of some elements of similar properties. Thus potassium (39.1) should come before argon (39.94). Similarly, tellurium (127.5) comes before iodine (126.93) and cobalt (58.4) should be placed after nickel (55.69). These anomalies disapeared automatically when atomic number was adopted as the basis of periodic classification and these elements occupy positions justified by their atomic numbers.

3. ***The Position of Rare Earths*** : The rare earths are also known as lanthanides. These elements have the two outermost energy levels identically occupied by electrons which give them great similarity in properties. All of them are metals. Their compounds are very closely related to one another which involved tremendous difficulties in their separation. All these elements are, therefore, placed in one and the same group. Starting from lanthanum (57) to lutecium (71), these fifteen elements actually have only one place in the Periodic Table and they are generally omitted from the main table and placed by themselves at the bottom of the table starting from Ce(58). It may be assumed

that these elements form a sort of bridge between the preceding and the following elements, i.e. barium and hafnium.

4. Position of the Actinides : This group of elements starting from actimium (89) include all the trans-uranium elements which have been discovered within the last few years. The electronic configurations of these elements have been found to be very similar to that of lanthanides. Both of these groups of elements contain f energy levels which are being systematically filled. Thus cerium to lutecium contains $4f^2$ to $4f^{14}$ and the actinide series of the $5f^2$ to $5f^{14}$ is being completed at lawrencium (103). For the same reason, as in lanthanides, the actinides are also placed in the same position of the Periodic Table and are tabulated at the bottom.

5. Oxidation states and the Periodic Table : The position of each element in the Periodic Table emphasizes only one oxidation number for each element. But most of the elements show more than one oxidation numbers.

6. Properties which are not Periodic functions : Certain properties have no relationship with the periodic classification : (i) The activities of the elements expressed in terms of electromotive series (e.m.f. series) do not show periodic variations although this is very useful in explaining many properties of the elements. Elements arranged in the e.m.f. series do not follow any order in the Periodic Table but are scattered throughout the table.

(ii) Some of the eleménts in the sub-group do not show any likeness in the properties with others. For example, group B copper, silver and gold (IB) have many properties different from those of the alkali metals (IA).

(iii) The specific heat of elements do nòt give periodic curve but a hyperbolic curve when plotted against atomic numbers.

(iv) Some of the elements in the same group of periodic classification do not belong to the same analytical scheme in qualitative analysis. There are elements widely scattered in the Periodic Table but are included in the same analytical group. For instance, Ba, Sr and Ca of group IIA of the Periodic Table are placed in the same group in the analytical scheme. On the other hand, Pb, Bi, Cu, Cd, Hg, As, Sb, which are widely separated in the Periodic Table, are included in the same group of qualitative analysis. This is mainly due to the different basis of classification. The analytical scheme is based upon the formation of insoluble compounds under identical conditions by group reagents.

(v) Isotopes and Periodic Table : Isotopes are elements possessing the same atomic numbers but different atomic weights. There are over 1000 isotopes of all the elements occurring in nature or made artificially. Obviously, all these isotopes cannot be accommodated in their respective places. However, the classification based on atomic number has solved this problem.

7. ***Diagonal Relationships*** : Lithium, a member of the alkali metal of group IA, in some respects respects resembles magnesium of group IIA. Thus, lithium salts usually occur in hydrated form unlike other alkhali metal salts. Moreover, unlike other alkali metal carbonates and phosphates Li_2CO_3 and Li_3PO_4 are insoluble in water, as are the corresponding magnesium carbonate and phosphate. Lithium is the only alkali metal to form ionic lithium nitride, Li_3N, like magnesium nitride. Thus, Li of group IA resembles Mg of group IIA in many respects contrary to its group properties. Similar relationship exists between the three elements, beryllium of group IIA, aluminium of group IIIA. Boron of group IIIA shows likeness with silicon of group IVA. Thus, the light elements of one group shows similarity in properties with the second elements of the following groups. This similarity is generally referred to as *diagonal relationship* in the Periodic Table as shown below.

I	II	III	IV	V	VI	VII	O Group
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar

The diagonal relationship between the elements may be explained in terms of the electropositive character of the elements. Although an element present in a given group is more electropositive than the corresponding element of the next higher group, the elements become more electropositive in passing down the group. Thus, Li in group IA is more electropositive than Be in group IIA, but Mg is also more electropositive than Be. Thus, both Li and Mg are more electropositive than Be and less electropositive than Na.

The other explanation is based on the sizes of the ions formed by the removal of valence electrons. Thus, Li^{+} ion is almost of the same size as Mg^{+2} ion. Similarly, H^{+}, Be^{+2} and Al^{+3} ions have approximately the same ionic size. B^{+3} and Si^{+4} also present the same situation. Compounds having similar properties of the elements showing diagonal relationship are formed due to the effect of ionic sizes and their distorting influence on the same anions.

QUESTIONS AND PROBLEMS

1. Write an essay on the periodic classification of the elements.
2. Write a note on transition elements.
3. Write a note on periodic law.
4. Discuss the general feature of the Periodic Table and show that these are in conformity with the atomic structure of the elements.
5. Give a brief account of the periodic classification of the elements and discuss how this has systematised the vast informations regarding the chemistry of the elements.
6. Discuss some of the limitations of the Mendeleeffs's periodic classification of the elements.
7. Explain the usefulness of the Periodic Table.
8. Discuss the Periodic Table in terms of the electronic structure of the elements.
9. Discuss the variation of properties of elements in groups and also in periods in the periodic classification of the elements.
10. Write notes on :—(a) Diagonal relationships between elements. (b) The position of rare earth elements in the Periodic Table. (c) Periodic variation of valence electrons. (d) The position of hydrogen in the Periodic Table.
11. Discuss the so-called diagonal relationships in the Periodic Table, with particular reference to the elements Li and Mg, B and Si, O and Cl
12. (a) Discuss briefly the arrangement of extra-nuclear electrons in the different atoms and hence explain the terms "transition" and "inner transition element."

    (b) Describe the properties of rare earths and the position of these elements in the Periodic Table.
13. Write a brief note on diagonal relationship in the Periodic Table.
14. Write detailed notes on group properties of elements.

15. Discuss the following :—

(a) Alkali metals are highly reactive.

(b) Elements of zero group are inert.

(c) Properties of B and Si are similar in many respects.

16. Write explanatory notes on :

(a) Transition elements.

(b) Periodic Law.

(c) Variable oxidation states.

17. Explain the anomalous properties of Li in relation to other alkali metals.

18. Explain why alkali metals react vigorously with water and chlorine.

19. Plot the quantities of the reciprocal values of the first ionization potential for each of the first 18 elements. What is the significance of this graph.

20. Find the relationship between the atomic weights of the following triads of elements :

[illegible], Na, K

[illegible], Cl, Br

Fe, Ru, Os