

3. Classification of elements and periodicity in properties

Some Important Points and Terms of the Chapter

1. **Dobereiner's Triads:** In 1817 a German chemist Dobereiner identified certain groups of three elements. These groups of three elements having similar properties were called triads. When three elements were arranged in order of their increasing atomic masses, the atomic mass of the middle element was roughly the mean of the atomic masses of the other two elements.
2. **New Land's Law of Octaves:** When elements were arranged in order of their increasing relative atomic masses. The properties of every eighth element were similar to the first one, like the eighth note of a musical scale. This repetition in the properties of elements is just like the repetition of eighth note in an octave of music.
3. **Mendeleev's Periodic Law:** The physical and chemical properties of elements are the periodic function of their atomic masses.
4. **Mendeleev's Periodic Table:** When Mendeleev started his work, 63 elements were known at that time. He selected hydrogen and oxygen as they are very reactive and formed compounds with most elements. Mendeleev's periodic table contains vertical columns called groups and horizontal rows called periods. There were 7 periods and 8 groups. Noble gases were not known at that time. So there was no group of noble gases. The elements in each group of the periodic table are similar to one another in many properties. The similar properties of the elements are repeated periodically.

(a) **Merits of Mendeleev's classification**

- Mendeleev's periodic law predicted the existence of some elements that had not been discovered at that time.
- Could predict the properties of several elements on the basis of their position in the periodic table.
- Could accommodate noble gases when they were discovered.

(b) **Limitations of Mendeleev's classification :-**

- The correct position could not be assigned to the hydrogen in the periodic table.
- Wrong order of the atomic masses of some elements could not be explained.

- The position of isotopes could not be explained.
- Uncertainty in prediction of new elements was there.

5. **Modern periodic law:** Properties of elements are the periodic function of their atomic number.

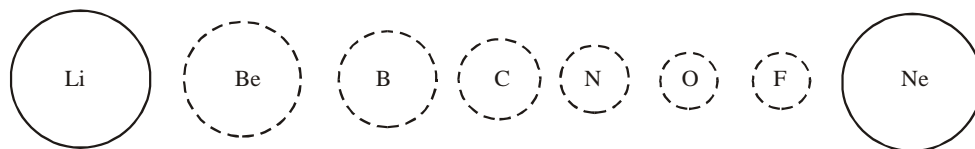
6. **Modern Periodic Table:** This table was prepared by Bohr and is based upon the electronic configuration of elements. The table consists of 18 vertical columns called groups. Elements having similar outer electronic configurations in their atoms are arranged in vertical columns, referred to as groups. According to the recommendation of International Union of Pure and Applied Chemistry (IUPAC), the groups are numbered from 1 to 18 and the table consists of 7 horizontal rows called periods. The first period contains 2 elements. The subsequent periods consist of 8, 8, 18, 18 and 32 elements, respectively. The seventh period is incomplete and like the sixth period would have a theoretical maximum (on the basis of quantum numbers) of 32 elements. In this form of the Periodic Table, 14 elements of both sixth and seventh periods (lanthanoids and actinoids, respectively) are placed in separate panels at the bottom.

group 1*	2	13	14	15	16	17	18
Ia	IIa	IIIb	IVb	Vb	VIb	VIIb	VIIIb
1	2	3	4	5	6	7	8
1 H	2 He	5 B	6 C	7 N	8 O	9 F	10 Ne
3 Li	4 Be	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
11 Na	12 Mg	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru
55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm
87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu

7. .Notation for IUPAC Nomenclature of Elements With $Z > 100$

Digit	Name	Abbreviation
0	nll	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

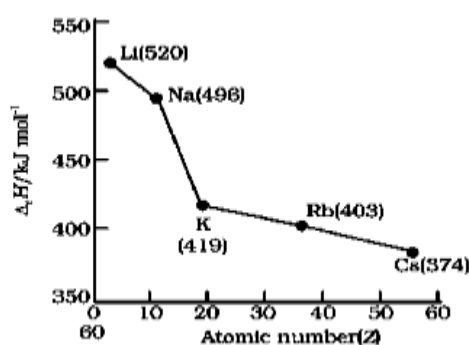
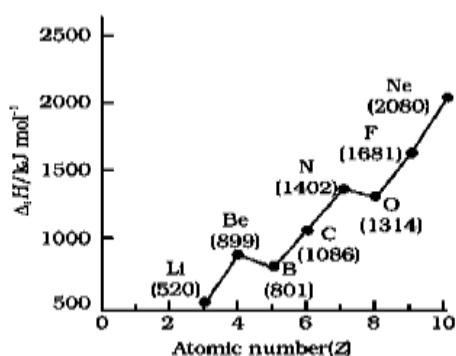
8. We can classify the elements into four blocks viz., s-block, p-block, d-block and f-block depending on the type of atomic orbital that are being filled with electrons.
9. **s-Block Elements** :The elements of Group 1 (alkali metals) and Group 2 (alkaline earth metals) which have ns^1 and ns^2 outermost electronic configuration belong to the s-Block Elements.
10. **p-Block Elements** The p-Block Elements comprise those belonging to Group 13 to 18 and these together with the s-Block Elements are called the Representative Elements or Main Group Elements. The outermost electronic configuration varies from ns^2np^1 to ns^2np^6 in each period.
11. **d-Block Elements** These are the elements of Group 3 to 12 in the centre of the Periodic Table. These are characterised by the filling of inner d orbitals by electrons and are therefore referred to as d-Block Elements. These elements have the general outer electronic configuration $(n-1)d^{1-10}ns^{0-2}$.
12. **f-Block Elements** The two rows of elements at the bottom of the Periodic Table, called the Lanthanoids, Ce($Z = 58$) – Lu($Z = 71$) and Actinoids, Th($Z = 90$) – Lr ($Z = 103$) are characterised by the outer electronic configuration $(n-2)f^{1-14} (n-1)d^{0-1}ns^2$. The last electron added to each element is filled in f- orbital. These two series of elements are hence called the Inner-Transition Elements (f-Block Elements).
13. **Variation in Atomic Radius in Period:** The atomic size generally decreases across a period It is because within the period the outer electrons are in the same valence shell and the effective nuclear charge increases as the atomic number increases resulting in the increased attraction of electrons to the nucleus.



14. **Variation in Atomic Radius in Group:** Within a family or vertical column of the periodic table, the atomic radius increases regularly with atomic number as). as we descend the groups, the principal quantum number (n) increases and the valence electrons are farther from the nucleus. This happens because the inner energy levels are filled with electrons, which serve to shield the outer electrons from the pull of the nucleus. Consequently the size of the atom increases as reflected in the atomic radii.
15. The **atomic radii of noble gases** are not considered here. Being monatomic, their (non-bonded radii) values are very large. In fact radii of noble gases should be compared not with the covalent radii but with the van der Waals radii of other elements.
16. A **cation is smaller than its parent atom** because it has fewer electrons while its nuclear charge remains the same. **The size of an anion will be larger than that of the parent atom** because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge. For example, the ionic radius of fluoride ion (F^-) is 136 pm whereas the atomic radius of fluorine is only 64 pm. On the other hand, the atomic radius of sodium is 186 pm compared to the ionic radius of 95 pm for Na^+ .
17. **Isoelectronic species** :Atoms and ions which contain the same number of electrons.. For example, O^{2-} , F^- , Na^+ and Mg^{2+} have the same number of electrons (10). Their radii would be different because of their different nuclear charges. The cation with the greater positive charge will have a smaller radius because of the greater attraction of the electrons to the nucleus. Anion with the greater negative charge will have the larger radius. In this case, the net repulsion of the electrons will outweigh the nuclear charge and the ion will expand in size.
18. **Ionization Enthalpy:** It represents the energy required to remove an electron from an isolated gaseous atom (X) in its ground state. In other words, the first ionization enthalpy for an element X is the enthalpy change ($\Delta_i H$) for the reaction depicted in equation. $X(g) \rightarrow X^+(g) + e^-$. The ionization enthalpy is expressed in units of $kJ\ mol^{-1}$. We can define the second ionization enthalpy as the energy required to remove the second most loosely bound electron; it is the energy required to carry out the reaction shown in equation $X^+(g) \rightarrow X^{2+}(g) + e^-$. Energy is always required to remove electrons from an atom and hence ionization enthalpies are always positive. The second ionization enthalpy will be higher than the first ionization enthalpy because it is more difficult to remove an electron from a positively charged ion than from a neutral atom.

In the same way the third ionization enthalpy will be higher than the second and so on. The term “ionization enthalpy”, if not qualified, is taken as the first ionization enthalpy.

- 19. Variation in Ionization Enthalpy in Group:** As we descend in a group the first ionization enthalpy generally decreases. Because as we go down a group, the outermost electron being increasingly farther from the nucleus, there is an increased shielding of the nuclear charge by the electrons in the inner levels. In this case, increase in shielding outweighs the increasing nuclear charge and the removal of the outermost electron requires less energy down a group.
- 20. Variation in Ionization Enthalpy in Period:** The first ionization enthalpy generally increases as we go across a period. When we move from left to right in period, successive electrons are added to orbitals in the same principal quantum level and the shielding of the nuclear charge by the inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus. Thus, across a period, increasing nuclear charge outweighs the shielding. Consequently, the outermost electrons are held more and more tightly and the ionization enthalpy increases across a period.



- 21. Electron Gain Enthalpy:** When an electron is added to a neutral gaseous atom (X) to convert it into a negative ion, the enthalpy change accompanying the process is defined as the Electron Gain Enthalpy (Δ_{eg}H). Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion as represented by equation. $X(g) + e^- \rightarrow X^-(g)$. Depending on the element, the process of adding an electron to the atom can be either endothermic or exothermic. For many elements energy is released when an electron is added to the atom and the electron gain enthalpy is negative. For example, group 17 elements (the halogens) have very high negative electron gain enthalpies because they can attain stable noble gas electronic configurations by picking up an electron. On the other hand, noble gases have large positive

electron gain enthalpies because the electron has to enter the next higher principal quantum level leading to a very unstable electronic configuration.

22. Variation in electron gain enthalpies in Group & period: The variation in electron gain enthalpies of elements is less systematic than for ionization enthalpies. As a general rule, electron gain enthalpy becomes more negative with increase in the atomic number across a period. The effective nuclear charge increases from left to right across a period and consequently it will be easier to add an electron to a smaller atom since the added electron on an average would be closer to the positively charged nucleus. We should also expect electron gain enthalpy to become less negative as we go down a group because the size of the atom increases and the added electron would be farther from the nucleus. This is generally the case. However, electron gain enthalpy of O or F is less negative than that of the succeeding element. This is because when an electron is added to O or F, the added electron goes to the smaller $n = 2$ quantum level and suffers significant repulsion from the other electrons present in this level. For the $n = 3$ quantum level (S or Cl), the added electron occupies a larger region of space and the electron-electron repulsion is much less.

23. Electronegativity: A qualitative measure of the ability of an atom in a chemical compound to attract shared electrons to itself is called electro negativity Linus Pauling, an American scientist, in 1922 assigned arbitrarily a value of 4.0 to fluorine, the element considered to have the greatest ability to attract electrons. Electronegativity generally increases across a period from left to right (say from lithium to fluorine) and decrease down a group (say from fluorine to astatine) in the periodic table.

24. Anomalous Properties of Second Period Elements: The first element of each of the groups 1 (lithium) and 2 (beryllium) and groups 13-17 (boron to fluorine) differs in many respects from the other members of their respective group. For example, lithium unlike other alkali metals, and beryllium unlike other alkaline earth metals, form compounds with pronounced covalent character; the other members of these groups predominantly form ionic compounds. In fact the behaviour of lithium and beryllium is more similar with the second element of the Group 1, 2, 13, 14, 15, 16, 17. following group i.e., magnesium and aluminum, respectively. This sort of similarity is commonly referred to as **diagonal relationship** in the periodic properties. The anomalous behaviour is attributed to their small size, large charge/ radius ratio and high electronegativity of the elements. In addition, the first member of group has only four valence orbitals ($2s$ and $2p$) available for bonding, whereas the second member of the groups have nine valence orbitals ($3s$, $3p$, $3d$). As a consequence of this, the maximum covalency of the first

member of each group is 4 (e.g., boron can only form $[\text{BF}_4]^-$, whereas the other members of the groups can expand their valence shell to accommodate more than four pairs of electrons e.g., aluminum forms $[\text{AlF}_6]^{3-}$). Furthermore, the first member of p -block elements displays greater ability to form $p\text{--}p$ multiple bonds to itself (e.g., $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{N}=\text{N}$, $\text{N}\equiv\text{N}$) and to other second period elements (e.g., $\text{C}=\text{O}$, $\text{C}=\text{N}$, $\text{C}\equiv\text{N}$, $\text{N}=\text{O}$) compared to subsequent members of the same group.