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CHAPTER

periodic properties

The periodic table displays all chemical elements systematically in order of increasing atomic number i.e. the number of protons in the nucleus.

Historical models of periodic table

1. *Doebereiner's triads, 1829*

Doebereiner classified elements into a group of three, called triads. In the triads of element the atomic weight of the middle element was the arithmetic mean of the atomic weights of the other two.

Li	Na	K	Ca	Sr	Ba
7	23	39	40	88	137

2. *Newland's octet law, 1864*

If the elements are arranged in order of their increasing atomic weights, every eighth elements had similar properties to first one like the first and eight note is music.

sa	re	ga	ma	pa	dha	ni	sa
Li	Be	B	C	N	O	F	Na
Na	Mg	Al	Si	P	S	Cl	K

Inert gases were not discovered till then.

3. *Lothar Meyer's atomic volume curve, 1869*

Lothar Mayer plotted a graph between atomic weight and atomic volume (*i.e.* atomic weight in solid state/density). Elements with similar properties occupied the similar positions on the graph. Strong electropositive elements of IA except Li *i.e.* Na, K, Rb, Cs etc. occupied the top position on the graph. IIA group elements Be, Mg, Ca, Sr, Ba etc. occupied the positions on the ascending part of the graph. Inert gases except He occupied the positions on the descending part of the graph. Halogens also occupied the descending part of the graph.

4. *Mendeleev's periodic law*

The physical and chemical properties of elements are periodic functions of their atomic weights. If the elements are arranged in the order of their increasing atomic weights, after a regular interval elements with similar properties are repeated. The table is divided into nine vertical columns called groups and seven horizontal rows called periods.

Characteristics of periods

(a) First period is called shortest period and contains only two elements. Second and third periods are called short periods containing eight elements each. Fourth and fifth periods are long periods containing eighteen elements each. Sixth period is longest period with thirty-two elements. Seventh period is an incomplete period containing nineteen elements. Numbers 2, 8, 8, 18, 18, 32 are called magic numbers.

(b) Lanthanide and actinide series containing 14 elements each are placed separately under the main periodic table. These are related to sixth and seventh periods of IIIrd group respectively.

(c) Elements of third period from sodium (Na) to chlorine (Cl) are called representative or typical elements.

(d) Valency of an element in a period increases from 1 to 7 with respect to oxygen.

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O
1	2	3	4	5	6	7

(e) From left to right in a period generally

(i) Atomic weight, effective nuclear charge, ionisation potential, electronegativity and electron affinity of an element increases.

(ii) Atomic radius, electropositive character and metallic character of an element decreases.

(f) Diagonal relationship — Elements of second period Li, Be and B resemble closely with the elements Mg, Al and Si of third period in the next higher group.

Second period	Li	Be	B	C
Third period	Na	Mg	Al	Si

(g) Elements of second period are called bridge elements.

Characteristic of groups

(a) Mendeleef's periodic table contains nine groups. These are represented by Roman numerals I, II, III, IV, V, VI, VII, VIII and zero. Groups I to VII are divided into subgroups A and B, group VIII consists of three sets, each one containing three elements.

(b) Inert gases are present in zero group. These were not discovered till that time.

(c) The valency of an element in a group is equal to the group number.

(d) There is no resemblance in the elements of subgroups A and B of same group, except valency.

(e) The elements of the groups which resemble with typical elements are called normal elements. For example - IA, IIA, IIIA, IVA, VA, VIA, VIIA group elements are normal elements.

(f) Those elements of the groups which do not resemble with typical elements are called transition elements. For example- IB, IIB, IIIB, IVB, VB, VIB, VIIB and VIII group elements are transition elements.

(g) Hydrogen is placed in both IA and VIIA groups.

(h) In a group, from top to bottom in general,

(i) Atomic weight, atomic size, electropositive character and metallic character of an element increases.

(ii) Ionisation potential, electron affinity and electronegativity of an element decreases.

5. *Long form of the periodic table or Mosley's periodic table*

Mosley (1909) studied the frequency of X-rays produced by the bombardment of a strong beam of electrons on a metal target. He found that the square root of the frequency of X-rays ($\sqrt{\upsilon}$) is directly proportional to the number of nuclear charge (Z) of metal. $\sqrt{\upsilon} = a\,(Z - b)$ where a and b are constants. Nuclear charge of metal is equal to the atomic number. So Mosley related the properties of elements with their atomic number and gave the new periodic law.

According to him, physical and chemical properties of elements are the periodic functions of their atomic number. If the elements are arranged in order of their increasing atomic number, after a regular interval, element with similar properties are repeated.

6. *Long form of periodic table or Bohr's periodic table*

With better understanding of the role of electrons in the properties of elements and the development of the nature of the electrons in atoms, a better understanding of the periodic properties of elements or the periodic table was possible. The long form of periodic table is also known as Bohr's periodic table.

The long form of periodic table offers the following advantages over the Mendeleev's classification.

(i) Sub-group A and sub-group B elements are placed separately. There is clear demarcation between metals and non-metals.

(ii) The nine elements of group VIII have been placed in separate groups corresponding to d^6, d^7 and d^8 configurations.

(iii) Fourteen lanthanones are not pushed together, but are assigned a separate group for each lanthanon in the *f*-block of elements.

(iv) The uniform trivalent state of the lanthanones can be explained due to the availability of only three electrons in the outer, high energy levels, the differentiating electrons going to the inner chemically inert orbitals.

(v) Uniform bivalence for the transition elements is due to the presence of outer ns^2 electrons, which makes them electropositive in nature.

(vi) The change from a highly electronegative to electropositive character through inert gas structure has been explained on the basis of the long form of periodic table.

Types of elements

Classification of elements on the basis of their electronic configuration

On the basis of electronic configuration, the elements may be divided into four groups:

(i) *s*-block elements

(a) These are present in the left part of the periodic table.

(b) These are IA and IIA *i.e.* 1 and 2 group elements.

(c) These are metals.

(d) In these elements last electron fills in the *s*-orbital.

(e) Electronic configuration of valence shell is ns^{1-2} (n = 1 to 7).

(ii) *p*-block elements

(a) These are present in right part of the periodic table.

(b) These constitute the groups IIIA to VIIA and zero groups *i.e.* groups 13 to 18 of the periodic table.

(c) Most of these elements are metalloids and nonmetals but some of them are metals also.
(d) The last electron fills in *p*-orbital of valency shell.
(e) The electronic configuration of valence shell is ns^2np^{1-6} ($n = 2$ to 7).
(f) ns^2np^6 is stable noble gas configuration. The electronic configuration of He is $1s^2$.

(iii) *d*-block elements

(a) These are present in the middle part of the periodic table (between *s* and *p* block element).
(b) These constitute IIIB to VIIB, VIII, IB and IIB *i.e.* 3 to 12 groups of the periodic table.
(c) All are metals.
(d) The last electrons fills in $(n-1)d$ orbital.
(e) The outermost electronic configuration is $(n-1)d^{1-10}\, ns^{1-2}$ ($n = 4$ to 7).
(f) There are three series of *d*-block elements as under
    3*d* series - Sc (21) to Zn (30)
    4*d* series - Y (39) to Cd (48)
    5*d* series - La (57), Hf (72) to Hg (80)

(iv) *f*-block elements

(a) These are placed separately below the main periodic table.
(b) These are mainly related to IIIB *i.e.* group 3 of the periodic table.
(c) There are two series of *f*-block elements as under
    4*f* series - Lanthanides - 14 elements - Ce (58) to Lu (71)
    5*f* series - Actinides - 14 elements - Th (90) to Lr (103)
(d) The last electron fills in $(n-2)\,f$-orbital.
(e) Their outermost electronic configuration is $(n-2)f^{1-14}\,(n-1)s^2\,(n-1)p^6\,(n-1)d^{0-1}ns^2$ ($n = 6$ and 7).

Bohr's classification of elements

On the basis of electronic configuration of the incomplete shells, the elements are classified into five main categories-

1. Inert gases
2. Representative elements
3. Transition elements
4. Inner transition elements
5. Transuranium elements.

Although this classification is convenient for understanding of chemical properties of the elements, it overlooks the specific properties of the individual elements.

1. Inert gases

(a) *s* and *p*-orbitals of the outer most shell of these elements are completely filled. The outermost electronic configuration is $ns^2\ np^6$.
(b) He is also inert gas but its electronic configuration is $1s^2$.

2. Representative or normal elements

(a) Outermost shell of these elements is incomplete. The number of electrons in the outermost shell is less than eight.
(b) Inner shells are complete.
(c) *s*- and *p*-block elements except inert gases are called normal or representative elements.

3. Transition elements

(a) Last two shells of these elements namely outermost and penultimate shells are incomplete.

(b) The last shell contains one or two electrons and the penultimate shell may contain more than eight up to eighteen electrons.

(c) Their outermost electronic configuration is similar to *d*-block elements *i.e.* $(n - 1)d^{1-10} ns^{1-2}$.

(d) According to latest definition of transition elements those elements which have partly filled *d*-orbitals in neutral state or in any stable oxidation state are called transition elements. According to this definition, Zn, Cd and Hg (IIB group) are *d*-block elements but not transition elements because these elements have d^{10} configuration in neutral as well as in stable +2 oxidation state.

4. Inner transition elements

(a) In these elements last three shells *i.e.* last, penultimate and prepenultimate shells are incomplete.

(b) These are related to IIIB *i.e.* group 3.

(c) The last shell contains two electrons. Penultimate shell may contain eight or nine electrons and prepenultimate shell contains more than 18 upto 32 electrons.

(d) Their outermost electronic configuration is similar to *f*-block elements *i.e.* $(n - 2)f^{1-14} (n - 1)s^2(n - 1)p^6(n - 1)d^{0-1} ns^2$.

5. Transuranium elements

Elements of the seventh period after atomic number 93 (*i.e.* actinides) are synthetic elements and are called transuranium elements.

(a) In 1934, an Italian Physicist Enrico Fermi had observed that when an element is bombarded with slow neutrons, the element is transformed into a new element having next higher atomic number. First transuranic element, having atomic number 93 was identified by American Physicist Edwin Mcmilan and Philip H. Abelson. In the next year, element number 94 was discovered in uranium fission products by American Chemist Glenn T. Seaborg and coworkers. The elements 93 and 94 were named Neptunium (Np) and Plutonium (Pu) respectively for Neptune and Pluto, the planets discovered after Uranus.

$_{92}U^{238} + {_0n^1} \rightarrow {_{92}U^{239}} + \gamma$-rays

$_{92}U^{239} \rightarrow {_{93}Np^{239}} + {_{-1}e^0}$

$_{93}Np^{239} \rightarrow {_{94}Pu^{239}} + {_{-1}e^0}$.

(b) In 1944, Seaborg and coworkers at the University of California, Berkeley made new elements, 95 and 96 by bombarding uranium and plutonium with accelerated alpha particles. These elements were named Americium (Am) after America and Curium (Cm) after Curies.

$_{92}U^{238} + {_2He^4} \rightarrow {_{94}Pu^{241}} + {_0n^1}$

$_{94}Pu^{241} \rightarrow {_{95}Am^{241}} + {_{-1}e^0}$

$_{94}Pu^{239} + {_2He^4} \rightarrow {_{96}Cm^{242}} + {_0n^1}$.

(c) Seaborg and coworkers bombarded elements 95 and 96 to produce element number 97 in 1949 and element number 98 in 1950. These two elements were named Berkelium (Bk) and Californium (Cf) after Berkeley and California. For this work Seaborg and Mcmilan shared the 1951 Nobel Prize in chemistry.

$_{95}Am^{241} + _{2}He^{4} \rightarrow _{97}Bk^{245} + \gamma$

$_{96}Cm^{242} + _{2}He^{4} \rightarrow _{98}Cf^{246} + \gamma$

$_{96}Cm^{242} + _{2}He^{4} \rightarrow _{98}Cf^{244} + 2\ _{0}n^{1}$.

(d) Elements number 99 and 100 were produced in the laboratory by Berkeley group by neutron bombardment in 1952. Element number 99 was named as Einsteinium (Es) and 100 as Fermium (Fm) after Albert Einstein and Enrico Fermi respectively.

$_{98}Cf^{252} + _{0}n^{1} \rightarrow _{98}Cf^{253} + \gamma$

$_{98}Cf^{253} \rightarrow _{99}Es^{253} + _{-1}e^{0}$

$_{99}Es^{253} + _{0}n^{1} \rightarrow _{99}Es^{254} + \gamma$

$_{99}Es^{254} \rightarrow _{100}Fm^{254} + _{-1}e^{0}$

$_{99}Es^{253} + _{2}He^{4} \rightarrow _{101}Md^{256} + _{0}n^{1}$.

(Mendelevium)

(e) Element number 102 was made in 1958 through a collaboration between university of California, Berkeley and the Nobel institute in Sweden. Using a complicated type of bombardment a small amount element 102 was produced. It was named as Nobelium (No) after Alfred Nobel. In 1961, the Berkeley group reported detection of very small amount element 103. Element 103 was named Lawrencium (Lw or Lr) after E. O. Lawrence.

$$_{96}Cm^{246} + _{6}C^{12} \rightarrow _{102}No^{254} + 4\ _{0}n^{1}$$

$$_{98}Cf^{250} + _{5}B^{11} \rightarrow _{103}Lr^{257} + 4\ _{0}n^{1}$$

(f) Berkeley team also succeeded in making two elements 104 and 105. They named element 104 as Rutherfordium after Ernest Rutherford. Element 105 was named as Dubnium.

(g) For elements beyond atomic number 106, it would require not only more powerful particle accelerator; but also highly sensitive detection and analysis system capable of identifying a few atoms of extremely short-lived elements.

- During 1981-1985 a team of scientists at institute of heavy ion research led by Peter Armbruster used the new technique with the new detector to synthesise and identify elements 107 to 109, which were named as

107 - Bohrium (Bh) after Niels Bohr

108 - Hassium (Hs) after German State of Hasse

109 - Meitnerium (Mt) after Austrian Physicist Lise Meitner.

Elements 110, 111 and 112 are also named as ununnilium, unununium and ununbium.

PERIODICITY IN PROPERTIES

- The term periodicity in properties in the classification of elements means that same properties of the elements reappear at definite intervals when the elements are arranged in order of their increasing atomic numbers. In modern periodic table, these intervals are 2, 8, 8, 18, 18 and 32, *i.e.,* similar properties are observed with elements belonging to the same subgroup which have been arranged in subgroups after the difference of either 2 or 8 or 18 or 32 in atomic numbers as similar valency-shell electronic configuration recur after certain regular intervals of atomic number. **This is the cause of periodicity in properties.**

Electronic configurations of alkali metals

Element	At. No.	Electronic configuration
Li	3	$1s^2\,2s^1$
Na	11	$1s^2\,2s^2\,2p^6\,3s^1$
K	19	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$
Rb	37	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,5s^1$
Cs	55	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,5s^2\,5p^6\,6s^1$
Fr	87	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,5s^2\,5p^6\,6s^2\,4f^{14}\,5d^{10}\,6p^6\,7s^1$

Thus, the **cause of periodicity** of the properties of elements is the repetition of similar electronic configuration of their atoms in the outermost energy shell (or valence shell) after certain regular intervals.

- **Atomic radii**

– It is usually defined **as the distance between the nucleus and outermost shell where electron or electrons are present.** Three types of radii are commonly used, i.e., (a) covalent radii (b) crystal radii (c) van der Waals' radii. **Covalent radius is defined as half of the distance between the two nuclei of two like atoms bonded together by a single covalent bond.**

– Considering a homonuclear diatomic molecule A_2, bonded together by a single covalent bond, it is assumed that electron clouds of each atom touch each other. Let the bond length be d_{A-A}.

Then $d_{A-A} = r_A + r_A = 2r_A$

So $$r_A = \frac{d_{A-A}}{2}$$

– In a heteronuclear diatomic AB molecule if both atoms are linked by a single covalent bond and have nearly same electronegativity, the bond length d_{A-B} is equal to sum of covalent radii of the two atoms.

$$d_{A-B} = r_A + r_B$$

– If the covalent bond is formed between two elements of different electronegativity then we use the following relation:

$$d_{A-B} = r_A + r_B - 0.09\,(X_A - X_B)$$

where X_A and X_B are electronegativity of A and B respectively. This relation was given by **Stevenson** in 1941.

- **Crystal radii :** It is defined as one half of the distance between the nuclei of two adjacent metal atoms in the metallic closed packed crystal lattice in which metal exhibits a coordination number of 12.

- **van der Waals' radii :** It is half of the distance between the nuclei of two nonbonded neighbouring atoms of two adjacent molecules.

$$r_{\text{covalent}} < r_{\text{crystal}} < r_{\text{van der Waals}}$$

Atomic radius in the *n*th orbit is given by

$$r_n = \frac{n^2 a_0}{Z^*}$$

where n is principal quantum number (*i.e.*, number of shell), a_0, the Bohr's radius of H-atom (= 0.529Å) and Z^*, the effective nuclear charge.

- **The screening effect or shielding effect and Effective nuclear charge**

In a multielectron atom, the electrons of the valency shell (outermost shell) are attracted towards the nucleus and repelled by the electrons present in the inner shells. On account of this, the combined effect of this attractive and repulsive force acting on the valence electron is that the valence electron experiences less attraction from the nucleus. This decrease in the force of attraction exerted by the nucleus on the valency electrons due to the presence of electrons in the inner shells, is called screening effect or shielding effect.

Effective atomic number

Due to screening effect the valence electron experiences less attraction towards nucleus. This brings decrease in the nuclear charge (Z) actually present on the nucleus. The reduced nuclear charge is termed **effective nuclear charge** and is represented by Z^*. It is related to actual nuclear charge (Z) by the following formula :

$Z^* = (Z - \sigma)$ where σ is screening constant.

The magnitude of 'σ' is determined by the **Slater's rules.** The contribution of inner electrons to the magnitude of 'σ' is calculated in the following ways:

Slater's rule for Estimating Effective Nuclear Charges, Z^*

(1) Write out the electronic configuration of the element in the following order and grouping: (1*s*), (2*s*, 2*p*), (3*s*, 3*p*), (3*d*), (4*s*, 4*p*), (4*d*), (4*f*), (5*s*, 5*p*) etc.

(2) Electrons in any group higher in the sequence that the electron under consideration contribute nothing to the shielding σ.

(3) Then for an electron in an *ns* or *np* orbital

(a) all other electrons in (*ns*, *np*) group contribute $\sigma = 0.35$ each

(b) all electrons in the $n - 1$ shell contribute $\sigma = 0.85$ each

(c) all electrons in the $n - 2$ or lower shell contribute $\sigma = 1.00$ each

(4) For electron in an *nd* or *nf* orbital, all electrons in the same group contribute $\sigma = 0.35$ each; those in group lying lower in the sequence than the (*nd*) or (*nf*) group contribute $\sigma = 1.00$ each.

- Radius is also dependent on the extent of force of attraction which pulls outer shell inward.

Variation in Period

	Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
Z	3	4	5	6	7	8	9	10
σ	1.7	2.05	2.40	2.75	3.10	3.45	3.80	4.15
Z^*	1.30	1.95	2.60	3.25	3.90	4.55	5.20	5.85
n	2	2	2	2	2	2	2	2
r_n (pm)	123	90	80	77	75	74	72	160

In a period, left to right :

- Z (atomic no.) increases (by one unit)
- Z^* also increases (but by 0.65 unit)
- n (number of shells) remains constant

Thus $r_n \propto 1/Z^*$

In case of Noble gases (as in Ne) there is no covalent bond formation, hence only van der Waals radius is considered. Thus there is high jump in the value of radius from F (72 pm) to Ne (160 pm).

Variation in a Group

Element	***Z***	**σ**	***Z****	***n***	**Radius (pm)**
Li	3	1.7	1.3	2	123
Na	11	8.8	2.2	3	157
K	19	16.8	2.2	4	203
Rb	37	34.8	2.2	5	216
Cs	55	52.8	2.2	6	235
Fr	87	84.8	2.2	7	—

In a group, top to bottom :

- Z increases
- Z^* almost remains constant
- n increases

Thus $r_n \propto n^2/Z^*$

Hence atomic radius in a group is dependent on the value of n.

- **Ionic radii**

It is defined as the distance between the nucleus and outermost shell of an ion or it is the distance between the nucleus and the point where the nucleus exerts its influence on the electron cloud.

Metal ions are smaller than the atoms from which they are formed.

When a positive ion is formed, the number of positive charges on the nucleus exceeds the number of orbital electrons, and the effective nuclear charge (which is the number of charges on the nucleus to the number of electrons) is increased. This results in the remaining electrons being more strongly attracted by the nucleus. These electrons are pulled in further reducing the size.

A positive ion is thus always smaller than the corresponding atom, and the more electrons which are removed, the smaller the ion becomes.

Thus $Mg > Mg^+ > Mg^{2+}$

$Fe > Fe^{2+} > Fe^{3+}$

The negative ion is always larger than that of the corresponding atom.

– Negative ion is formed by gain of one or more electrons in the neutral atom and thus number of electrons increases but magnitude of nuclear charge remains the same.

– Due to decrease in nuclear charge per electron, there is expansion of outer shell. Thus size of anion is increased.

$O^{2-} > O^- > O$

$I^- > I > I^+$

These can be explained on the basis of Z/e ratio $\left(\frac{\text{Nuclear charge}}{\text{No. of electrons}}\right)$. When Z/e ratio increases, the size decreases and when Z/e ratio decreases, the size increases.

	Na	Na^+	Cl	Cl^-
Z/e	$\frac{11}{11}=1.0;$	$\frac{11}{10}=1.1;$	$\frac{17}{17}=1.0;$	$\frac{17}{18}=0.95;$
So	$Na^+ < Na$	$Cl^- > Cl$		

For isoelectronic species the size decreases with an increase of atomic number. This is illustrated in the following table:

Atom or Ion	Atomic Number Z	No. of electrons e	Z/e ratio	Size in Å
O^{2-}	8	10	0.8	1.40
F^-	9	10	0.9	1.30
Ne	10	10	1.0	1.12
Na^+	11	10	1.1	0.95
Mg^{2+}	12	10	1.2	0.65

H^+ and Cs^+ are the smallest and largest cations respectively.

H^- and I^- are the smallest and largest anions respectively.

Ionisation potential or Ionisation energy

The minimum amount of energy required to remove the most loosely bound electron from an isolated atom in the gaseous state is known as ionisation potential or ionisation energy or first ionisation potential (I_1) of the element.

$$M \xrightarrow{\text{energy}} M^+ + e$$

$$\text{Ionization potential (eV)} = \frac{\text{Ionization energy in Joule}}{\text{Charge of electron } (1.6\times10^{-19})}$$

The energy required to remove the second electron from the monovalent cation is called second ionisation potential (I_2).

$$M^+ + I_2 \rightarrow M^{2+} + e$$

Similarly, we have third, fourth . . . ionisation potentials.

$$M^{2+} + I_3 \rightarrow M^{3+} e$$

$$M^{3+} + I_4 \rightarrow M^{4+} + e$$

It is observed that I_2 is higher than I_1, I_3 is higher than I_2 and so on, *i.e.*, $I_1 < I_2 < I_3 < I_4$. The increase in the values of successive ionisation potentials can be explained on the basis that effective nuclear charge increases from $M_{(g)}$ to $M^{n+}_{(g)}$, *i.e.*, force of attraction of the outermost electron towards nucleus increases.

Factors affecting the value of ionisation potential

	Properties	Affect
1.	Atomic Size	Larger the atomic size, smaller is the value of ionisation potential.
2.	Screening Effect	Higher the screening effect, the lesser is the value of ionisation potential.
3.	Nuclear charge	Ionisation potential increases with the increase in nuclear charge.
4.	Penetration effect or Shape of orbtial	Values of ionisation potential for *s, p, d* and *f* electrons are as : $s > p > d > f$.

If an atom has fully filled or half-filled orbitals, its IE is higher than expected normally from its position in the periodic table.

e.g.	Li	Be	B	C	N	O	F	Ne
	$2s^1$	$2s^2$	$2s^22p^1$	$2s^22p^2$	$2s^22p^3$	$2s^22p^4$	$2s^22p^5$	$2s^22p^6$
eV	5.4	9.3	8.3	11.2	14.5	13.6	17.4	21.6

Be (fully filled 2*s* orbital) and N (half filled 2*p* orbital) have higher values than expected due to stable configurations.

- **Variation of (IE) in a group**

Force of attraction between electrons and nucleus decreases and tendency to remove the valence electron increases. Hence (IE) decreases on moving down the group.

- **Variation of (IE) in a period**

On moving across a period, the atomic size decreases and nuclear charge increases and therefore the force of attraction exerted by the nucleus on the electron in outermost shell increases. Hence **(IE) increases along a period** from left to right.

- The energies required to remove subsequent electrons from the atom in the gaseous state, are known as **successive ionisation energies.** The term first, second, third ..... ionisation energy refers to the removal of first, second, third ..... electron respectively.

Successive ionisation energies are higher : The second ionisation energies are higher than the first ionisation energies. This is mainly due to the fact that after the removal of the first electron, the atom changes into monovalent positive ion. In the ion, the number of electrons decreases but the nuclear charge remains the same. As a result of this, the remaining electrons are held more tightly by the nucleus and it becomes difficult to remove the second electron. Hence, the value of second ionisation energy, IE_2, is greater than that of the first (IE_1).

Electron affinity

- The amount of energy released when an electron is added to an isolated gaseous atom to produce a monovalent anion is called electron affinity or first electron affinity.

$$A + e \longrightarrow A^{-} + \text{energy}$$

- Most elements have a negative electron affinity. This means they do not require energy to gain an electron; instead, they release energy. Atoms more attracted to extra electrons have a more negative electron affinity. Chlorine most strongly attracts extra electrons; radon most weakly attracts an extra electron.

Although electron affinities vary in a chaotic manner across the table, some patterns emerge. Generally, nonmetals have more negative electron affinities than metals. However, the noble gases are an exception: they have positive electron affinities.

Factors affecting the value of electron affinity

	Properties	Affect
1.	Nucelar charge	Electron affinity increases with the increase in nuclear charge.
2.	Atomic size	With the increase in atomic size, electron affinity decreases.
3.	Electronic configuration	Electron affinities are low or almost zero in cases of stable configurations i.e. half filled or full-filled valence shell.

	Li	Be	B	C	N	O	F	Ne
	$2s^1$	$2s^2$	$2s^22p^1$	$2s^22p^2$	$2s^22p^3$	$2s^22p^4$	$2s^22p^5$	$2s^22p^6$
eV	–0.61	0.0	– 0.30	–1.25	– 0.20	–1.48	–3.6	0.0

Be, N and Ne have low values due to stable configurations.

- The electron affinities increase across a row (since the radius slightly decreases, because of the increased attraction from the nucleus, and the number of electrons in the top shell increases, helping the atom reach maximum stability) in the periodic table and decrease going down a family (because of a large increase in radius and number of electron that decrease the stability of the atom, repulsing each other).
- Electron affinities are not limited to the elements but also apply to molecules. For instance the electron affinity for benzene is positive, that of naphthalene near zero and that of anthracene positive.

- **Successive electron affinities**

Like ionisation energies, the second and higher electron affinities are also possible. However, second electron is added to a negatively charged ion and the addition is opposed by coulombic repulsions. The energy has to be supplied to force the second electron into the anion.

Electronegativity

- Electronegativity is a measure of the tendency of an element to attract electrons to itself.

$$X_{(g)} + e^- \rightarrow X^-_{(g)}$$

In a molecule, tendency of the atom to attract bonding pair towards itself is its electronegativity. B is said to be more electronegative than A if it pulls bonding pair towards itself.

$$(A) \overset{\bullet}{\times} (B) \longrightarrow \overset{\delta+}{(A)} - \overset{\delta-}{(B)}$$

- An arbitrary value of 4.0 has been assigned to fluorine (most electronegative element) and the electronegativities of other elements have been calculated against this standard by application of following formula:

$$X_A - X_B = 0.208\,[E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2}]^{1/2}$$

where X_A and X_B are the electronegativities of two atoms A and B and E_{A-B}, $E_{(A-A)}$ and E_{B-B} are bond energies of molecules $A - B$, A_2 and B_2, respectively.

- Mulliken regarded electronegativity as the average value ionisation potential and electron affinity of an atom.

$$\text{Electronegativity} = \frac{\text{IP} + \text{EA}}{2}$$

- On Pauling scale, $\text{electronegativity of an atom} = \dfrac{\text{IP} + \text{EA}}{5.6}$

Values of IP and EA are taken in eV

$$\text{Electronegativity of an atom} = \frac{\text{IP} + \text{EA}}{2 \times 62.5}$$

values of IP and EA are taken in kilo calories per mole

- The **Allred-Rochow scale** in chemistry is a measure of electronegativity. The electrostatic force of attraction between an electron and the nucleus is given by: e^2Z/r^2

where r is the distance between the electron and the nucleus (covalent radius) and e is the charge on an electron. eZ is the charge effective at the electron due to the nucleus and its surrounding electrons.

The quantity Z/r^2 correlates well with Pauling electronegativities and the two scales can be made to coincide by expressing the Allred-Rochow electronegativity as:

$AR = 0.744 + 0.359Z/r^2$

- **Electronegativity trends**

Each element has a characteristic electronegativity ranging from 0 to 4 on the Pauling scale. The most strongly electronegative element, fluorine, has an electronegativity of 3.98 while weakly electronegative elements, such as lithium, have values close to 1. The least electronegative element is francium at 0.7. In general, the degree of electronegativity decreases down each group and increases across the periods. Across a period, non-metals tend to gain electrons and metals tend to lose them due to the atom striving to achieve a stable octet. Down a group, the nuclear charge has less effect on the outermost shells. Therefore, the most electronegative atoms can be found in the upper, right hand side of the periodic table, and the least electronegative elements can be found at the bottom left. Consequently, in general, atomic radius decreases across the periodic table, but ionization energy increases.

- **Importance of electronegativity :**

(i) Nature of the bond between two atoms can be predicted from the electronegativity difference of the two atoms.

(a) The difference $X_A - X_B = 0$, *i.e.,* $X_A = X_B$, the bond is purely covalent.
(b) The difference $X_A - X_B$ is small, *i.e..* $X_A > X_B$, the bond is polar covalent.
(c) The difference $X_A - X_B$ is 1 .7, the bond is 50% covalent and 50% ionic.
(d) The difference $X_A - X_B$ is very high, the bond is more ionic and less covalent.

Percentage ionic character may be calculated as:

Percentage of ionic character = $16 \mid X_A - X_B \mid + 3.5 (X_A - X_B)^2$

where X_A and X_B represents electronegativity of bonded atoms A and B.

(ii) Greater the value of difference $(X_A - X_B)$ more stable will be the bond.

	H — F	H — Cl	H — Br	H — I
$(X_A - X_B)$	1.9	0.9	0.7	0.4

Stability decreases $\longrightarrow$

Stability of compounds in which $X_A - X_B$ is very small are unstable in nature, NCl_3 (0.0), PH_3 (0), AsH_3 (0.1) are unstable.

In short, periodic properties can be studied as follows:

Properties	along the period	down the group
Ionisation potential	increases	decreases
Electron affinity	increases	decreases
Electronegativity	increases	decreases
Atomic radii	decreases	increases
Ionic radii	iso-electronic ions decrease their radii with increase in atomic number	increases
Atomic volume	decreases upto metals and then increases	increases

Properties	along the period	down the group
Melting point/ boiling point	increases along the period for metals	decreases
Density	increases for metals	increases
Oxidant-reductant nature	reducing nature decreases	reducing nature of metals increases oxidising nature of non metals decreases
Metallic character	decreases	increases
Electropositive character	decreases	increases
Oxide nature	basic character decreases	basic character increases
Hydride nature	basic character decreases or acidic character increases	basic character increases
Valency	with respect to oxygen increases from 1-7 along the period, with respect to hydrogen increases from 1 to 4 and then decreases to 1.	remains the same

End