



NATIONAL TESTING AGENCY

Chemistry

Inorganic Chemistry - 1



NEET - UG

S.NO.	CONTENT	Page
		No.
	INORGANIC CHEMISTRY - 1	
1.	Classification of Elements and Periodicity Properties	1
2.	General Principles & Processes of Isolation of Elements	16
3.	The p-Block Elements (Nitrogen The p-Block Elements	40
	(Nitrogen	
4.	The p-Block Elements (Oxygen Family VIA-Group	69
	Elements)	
5.	The p-Block Elements (Halogen Family VIIA-Group	91
	Elements)	
6.	The p-Block Elements (Inert and Noble Gases)	114
7.	d & f-Block Elements	123
8.	Hydrogen and its Component	141

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Click on Scan QR

Choose the **QR from book**

chapter 1

Classification of Elements and Periodicity Properties

CHAPTER OUTLINE

- Mendeleev's Periodic law
- Types of Elements Metal, Non-metal and Metalloid
- Trends in Periodic Properties of Elements •

MENDELEEV'S PERIODIC LAW

- According to Mendeleev's periodic law, the physical and chemical properties of elements are periodic functions of their atomic weight.
- Mendeleev first created the short form periodic table by placing the elements in increasing atomic weight order.
- Mendeleev's periodic chart assisted in

 (a) Correcting the atomic weights of
 elements such as beryllium and indium.
 - (b) The discovery of elements such as Scandium, Gallium, Germanium, and so on.

Defects in Mendeleev's table

Defects in Mendeleev's table are as follows:

- (a) Elements with varying atomic weights, such as lanthanides (rare earths), are preserved in the same group.
- (b) Isotopes do not belong in the periodic table.
- (c) Abnormal pairs in which the element arrangement is inverted with respect to their rising order of atomic weights. Examples: Potassium and argon, tellurium and iodine, cobalt and nickel.

- Modern Periodic Law
- Nomenclature of Elements with Atomic Number > 100
- Nature of Oxides and Hydroxides
 - According to **Moseley's periodic law**, "The physical and chemical properties of elements are periodic functions of their atomic numbers".

MODERN PERIODIC LAW

According to the modern periodic law, "The physical and chemical properties of elements are the periodic function of their atomic numbers."

Modern Periodic Table

- A periodic table is a collection of elements with comparable properties.
- Elements have been ordered in ascending atomic number order.
- There are seven horizontal rows known as periods.
- There are sixteen vertical columns referred to as groups or families.
- Transition elements are positioned in the centre of extended periods.
- Because they have the same atomic number, isotopes of an element are placed to the same location.
- Dissimilar metals are grouped together. For example, noble metals and alkali metals are classified into groups I and II, respectively.



Periodic Table

					1	l		Atomic	number,	Z							
1					H	4		Elemen	t symbol								18
1 H 1.008	2				1.0	800	←	Relative	e atomic r	nass, A _r		13	14	15	16	17	2 He 4.00
3 Li 6.94	4 Be 9.01						,					5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.01	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.54	30 Zn 65.41	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.91	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	La–L u	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.23	77 lr 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 TI 204.37	82 Pb 207.19	83 Bi 208.98	84 Po 210	85 At 210	86 Rn 222
87 Fr 223	88 Ra 226.03	Ac–L r	104 Rf [261]	105 Db [262]	106 Sg [266]	107 Bh [264]	108 Hs [277]	109 Mt [268]	110 Ds [271]	111 Rg [272]	112 Uub [285]						

Lanthanoid s	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	138.91	140.12	140.91	144.24	146.92	150.36	151.96	157.25	158.92	162.50	164.93	167.26	168.93	173.04	174.97
Actinoid s	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
	227.03	232.04	231.04	238.03	237.05	239.05	241.06	244.07	249.08	252.08	252.09	257.10	258.10	259	262

Long Form of Periodic Table

- The long version of the periodic table is often referred to as the extended form of the periodic table or Moseley's periodic table.
- It was created by Range, Werner, and Burey on the basis of electronic element configuration.

Features of Long Form of Periodic Table

- On the basis of electronic configuration, table is separated into four blocks: s, p, d, and f.
- It is made up of seven horizontal rows known as **periods**.
- The **first period** is the shortest and has only two elements (H, He).

- The **second and third periods** are also shortest, with **eight** elements each.
- The **fourth and fifth periods** are both lengthy, with **eighteen** elements each.
- The **sixth period** is the longest and has the most elements (**32 in total**).
- The seventh period is unfinished and has twenty-six (26) elements.
- The largest group, Group III B (3rd vertical row), has thirty-two (32) elements, including lanthanides and actinides.
- Each period's first element is an alkali metal, while the last element is an inert gas.

								lop	Unleash	the topper	in you								
	Mai	n Grou	DS												Main (Groups			
		. 0.00	P ⁰															l	
	1																	18	
	1A																	8A	
1	1	2											13	14	15	16	17	2	
	H	2A											3A	4A	5A	6A	7A	He	
2	3	4		Transitional Groups									5	6	7	8	9	10	
	Li	Be										1	В	С	N	0	F	Ne	
3	11	12	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
	Na	Mg	3B	4B	5B	6B	7B		8B		1B	2B	AI	Si	Р	S	Cl	Ar	
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
•	K	Ca	Sc	Ti	v	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	56	
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
6	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
	Cs	Ba	La	Hf	Ta	w	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Ро	At	Rn	
7	87	88	89	104	105	106	107	108	109	110	111	112		114					
	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq					
		La	nthanio	des	58	59	60	61	62	63	64	65	66	67	68	69	70	71	
				-	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
		А	ctinide	es	90	91	92	93	94	95	96	97	98	99	100	101	102	103	
						Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Genesis of periodic Classification

- The Telluric Helix (1862), **Chancourtois** was the first to propose the concept of periodic arrangement of elements.
- The unitary hypothesis (1915) All elements, according to Prout's unitary theory, are built out of hydrogen atoms.
- The law of triads (1864), Dobereiner's law states that "elements can be grouped in groups of three, with the atomic weight of the second (middle) element equaling the arithmetic mean of the first and third elements". Atom constant is the difference in the atomic weights of successive elements. Examples-

• The octave law (1864) According to Newland's law, "if the elements are organised in increasing atomic weight order, the eighth element, starting from a given one, is a kind of repeat of the first."

- This is analogous to the octave in music, where the eighth note is equivalent to the first. For example, starting with lithium, the eighth element is sodium, hence the properties of lithium and sodium should be comparable according to this law.
- Lothar Meyer's (1869), he created a curve by plotting various physical attributes of atoms against their atomic weights. On that curve, he saw that comparable parts occupied similar places.

TYPE OF ELEMENTS

There are four types of known elements:

- The s-block and p-block elements -Representative elements
- The d-blocks elements Transition elements
- The f-blocks elements Inner transition elements

A. s-block elements

 S-block elements are those with ns¹ and ns² electrical configurations in their outermost shell.



- Elements having the ns¹ configuration are referred to as group 1 elements (alkali metals).
- Elements with ns² configuration are referred to as group 2 elements (alkaline earth metals).
- They are very reactive and can easily form **univalent or bivalent positive ions** by losing the valence electrons.
- Elements are soft, flexible, and good conductors of heat and electricity.
- They have low melting and boiling point.
- Elements have the largest atomic and ionic radiuses yet the lowest ionisation energies in their respective periods.
- They have constant valency and oxidation states.
- The loss of the outermost electron(s) occurs easily, resulting in the formation of M⁺ (in the case of alkali metals) or M⁺²) ions (in case of alkaline earth metals).

Exception case: Except for compounds of beryllium, all other compounds of the elements of this block are predominantly ionic.

- These metals and their salts give the flame a distinct colour.
 <u>Example</u>- Sodium salts gives the flame a golden yellow colour.
- Elements are huge in size, have a strong reducing character, are very electropositive, have very low electronegativity, ionisation energy, and electron affinity.

B. p-block elements

- p-block elements have atoms with incomplete p orbitals in their outermost shells or in which the final electron enters any p orbital.
- The general outer electrical configuration of these components ranges between ns² and np ⁽¹⁻⁶⁾.
- p-block elements include elements from groups 13 to group 18.

 Elements in Group 13 have one electron in their p orbital, whereas elements in Group 18 (inert gas) have six electrons in their outer p orbitals. In an inert gas, the outer p orbitals are completely filled with electrons.

Examples-

Boron	$1s^2 2s^2 2p^1$
Oxygen	$1 s^2 2 s^2 2 p^4$
Neon	$1s^2 2s^2 2p^6$

- They include both metals and non-metals, but there is a consistent gradient from metallic to nonmetallic character across the period.
- Elements **do not** give any **specific colour** to the flame.
- With the exception of fluorine and inert gases, all of the elements in this block have varying oxidation states.

Group	IIIA	IVA	VA	VIA	VIIA
0.S.	+3	+4	+5	+6	+7
		to	to	to	to
		-4	-3	-2	-1

- They have high ionisation energy, which increases as we move over the period from left to right.
- They mainly form **covalent compounds** such as oxides, halides, sulphides, and carbonates.
- Apart than metals, all of the elements in this block are **insulators**.
- Many elements in this block, including C, Si, Ge, S, and O, exhibit catenation and allotropy.
- There is a transition from reducing to oxidising properties as we proceed from left to right.

C. d-block elements

- The d-block is located between the s- and pblocks.
- These are the elements with partially filled d orbitals.
- Because their properties are intermediate between those of and p-block elements, dblock elements are referred to as transition elements.



- A transition element has an atom or at least one of its ions with an incomplete d orbital or the outermost electron in a d orbital.
- Their general outer electronic configuration is

$(n-1)d^{1-10} ns^{1-2}$

- These elements are found in three sets of ten elements each, ranging from group 2 to group 13. Because of the engagement of ns and (n-1) d electrons in the formation of their chemical bonds, they have varying valency and oxidation state.
- This is because the energies of these electrons are almost identical. These are metals having high melting and boiling points, densities, thermal stabilities, and hardness ratings.
- They are malleable and ductile.
- Because of the existence of mobile or free electrons, they are good conductors of heat and electricity.
- They combine to generate coloured ions and complexes.
- Because of the existence of unpaired electrons, these metals and their ions are often paramagnetic in nature.
- Due to their comparable sizes, these metals combine to form a variety of alloys.
- Catalysts are frequently made from these metals and their derivatives.

 These metals also form non-stoichiometric and interstitial compounds with small atoms such as H,C, N,O that may easily fit in the unoccupied spots of these metals' lattices. For instance, Fe_{0.93} O, ZrH₂.

D. f-block elements

- The elements in **two independent rows** at the bottom of the periodic table are referred to as **f-block elements**.
- In their electronic forms, they have **partially** filled f orbitals.
- Lanthanones, **lanthanoids**, and lanthamides are elements with incomplete 4f orbitals ranging from **cerium to lutetium**.
- Actinoids and actinides are elements with incomplete 5f orbitals ranging from thorium to lawrencium.
- They have 1 to 2 incomplete d orbitals in their penultimate shells, in addition to incompletely filled 5f orbitals.
- The general outer electronic configuration is $(n-2) f^{1-14}(n-1)d^{0-1}ns^2$.
- A large number of actinides are synthetic elements.
- **Transuranium** elements are elements that exist after uranium in the periodic table.
- These are metals with extremely high melting and boiling points.
- They have **varying oxidation states** (variable valency). Their most common and stable oxidation state, however, is +3.
- Actinides are **radioactive** in nature and generate **coloured ions** and **complexes**.

METALS, NON-METALS AND METALLOIDS

Metals	Non-metals	Metalloids
They are usually solids at room	They are usually solids or gases	The elements which lie on the
temperature (except Hg which	at room temperature with low	borderline between metals and
is a liquid at room temp.)	m.pts and b.pts.	non-metals show properties
		that are characteristic of both
		metals and non-metals.
They have high m.pts and b.pts,	They are poor conductors of	They are called semi-metals or
are good conductors of heat and	heat and electricity.	metalloids.
electricity and are malleable and	They are brittle and are neither	
ductile.	malleable nor ductile.	



NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBER > 100

The IUPAC proposed a system for naming element with $\mathbf{Z} > 100$ by using these following rules:

 The names come from the roots of the first three digits of the element's atomic number, plus the ending -ium. The roots are-

5

pent

6

hex

sept

8

oct

9

enn

0

nil

1

un bi tri

2 3

Δ

quad

- In some cases, the names are shortened. For example, bi ium and tri ium are shortened to bium and trium, and enn nil is shortened to ennil.
- 3. The first letters of the roots that generate up the name of the element are used to make the symbol for the element. The strange mix of Latin and Greek roots was chosen so that each symbol would be unique.

Atomic No.	Name	Symbol	Atomic No.	Name	Symbol
101	un-nil-unium	Unu	113	un-un-trium	Uut
102	un-nil-bium	Unb	114	un-un-quadium	Uuq
103	un-nil-trium	Unt	115	un-un-pentium	Uup
104	un-nil-quadium	Unq	116	un-un-hexium	Uuh
105	un-nil-pentium	Unp	117	un-un-septium	Uus
106	un-nil-hexium	Unh	118	un-un-octium	Uuo
107	un-nil-septium	Uns	119	un-un-ennium	Uue
108	un-nil-octium	Uno	120	un-bi-nilium	Ubn
109	un-nil-ennium	Une	130	un-tri-nilium	Utn
110	un-un-nilium	Uun	140	un-quad-nilium	Uqn
111	un-un-unium	Uuu	150	un-pent-nilium	Upn
112	un-un-bium	Uub			

TRENDS IN PERIODIC PROPERTIES OF ELEMENTS

When we move from left to right across the period or from top to bottom in any group, the properties of the elements change every time their atomic number does.

A. Atomic Size or Radius

- The atomic size is the distance between the centre of the atom's nucleus and the electron in the second-to-last shell from the outside.
- The exact size of an atom's radius can't be found because:
 - It's impossible to know where an electron is in an atom because orbitals don't have sharp edges.

- 2. Because an atom is so small, it is impossible to separate it so that its size can be measured.
- Bond lengths, which can be measured with X-ray diffraction, electron diffraction, infrared spectroscopy, and nuclear magnetic resonance spectroscopy, are used to figure out the sizes of atoms.
- Since the size of an atom can't be measured in absolute terms, it is described by terms like ionic radius, covalent radius, van der Waals radius, and metallic radius.
- (i) Covalent radius
 - It is half the distance between the nuclei of two atoms that are the same or similar in a covalent molecule. It is also known as the covalent radius of a single bond.





Figure: Covalent Radius

• If the bond length in between the two atoms say A - A is ' *a* ', then Covalent radius $(r_{cov}) = 1/2$ [internuclear distance between two covalently bonded similar atoms] = 1/2a.

(ii) Van der waals radius

 It is half the distance between the nuclei of two unbonded, isolated atoms that are next to each other and are part of two molecules of the same element that are next to each other in the solid state.



Figure: Van der Waals Radius

(iii) Metallic radius

 In a tightly packed crystal lattice, it is half the distance between any two nuclei of two metal atoms next to each other.



Figure: Metallic Radius

(iv) Ionic radius

 It is the distance from the centre of an ion's nucleus to the point where the ion has an effect on the electron cloud.



Figure: Ionic Radius

Facts to Remember

 Van der Waals radius > Metallic radius > Anionic radius > Covalent radius > Cationic radius

Factors affecting size

Effective nuclear charge and screening effect:

- The force of repulsion exerted by inner shell electrons on these valence electrons reduces the force of attraction between the nucleus and the valence electrons.
- It is called screening or shielding effect and the net force is called effective nuclear charge.
- It is denoted to Z_{eff}

$$Z_{eff} = Z - \sigma$$

 $\sigma \propto$ Number of inner shell electrons Here, Z is atomic number and σ is screening constant.

- Size $\propto \frac{1}{\text{Effective nuclear charge}}$
- Size ∝ Number of orbits
- Size \propto Number of inner shell electrons (σ)
- Size ∝ Electronic repulsion
- Size $\propto \frac{1}{\text{Bond order or multiplicity}}$

Variation in the value of radii Period

- In a period, moving from left to right, atomic size reduces as the number of atomic orbitals remains constant but the number of electrons increases, resulting in an increase in effective nuclear charge.
- The order of atomic radius for various groups is given as

 $IA > IIA > IIIA > IVA > VA \approx VI > VII < zero group$

Example:

 $Li > Be > B > C > N \approx 0 > F$

Na > Mg > Al > Si > P > S > Cl

 Van der Waals radius is always greater than covalent radius and is considered in case of zero group.



Group

 In a group, atomic radius increases from top to bottom as the number of shells or orbitals increase and screening effect increases so Z_{eff} decreases.

For example:

$$\label{eq:starsessense} \begin{split} Li < Na < K < Rb < Cs \\ F < Cl < Br < I \end{split}$$

Size of Cation

- Size of a cation is always smaller than its atom.
- During cation formation, the outermost orbital is broken down and number of valence electron decreases so Z_{eff}, increases and size decreases.
- Size of cation $\propto 1/Z_{eff}$ or magnitude of positive charge
- $M^{+3} < M^{+2} < M^+ < M$ For example: $Fe^{+3} < Fe^{+2} < Fe$

Size of Anion

- Size of an anion is always greater than the size of its atom.
- As during anion formation electrons are taken up so Z_{eff} decreases and size increases.
- Size of anion ∝ magnitude of negative charge

 $M^{-4} > M^{-3} > M^{-2} > M^{-} > M$ For example: $0^{-2} > 0^{-} > 0$

In general, anion > atom > cation
 For example: X⁻ > X > X⁺

Isoelectronic Species

In general, for isoelectronic species, ionic size decreases as follows:

 $M^{-4} > M^{-3} > M^{-2} > M^{-} > M^{+} > M^{+2}$ > $M^{+3} > M^{+4}$

For example:

 $\begin{array}{l} C^{-4} > N^{-3} > 0^{-2} > F^{-} > Na^{+} > Mg^{+2} > Al^{+3} > Si^{+4} \\ P^{-3} > S^{-2} > Cl^{-} > K^{+} > Ca^{+2} > Sc^{+3} > Ti^{+4} > V^{+5} \end{array}$

General Format

Period/Group	Ι	II	III	IV	v	VI	VII	
1	Н 0.32							ľ
2	Li 1.23	Be 0.89	В 0.80	C 0.77	N 0.75	O 0.73	F 0.72	S
3	Na 1.54	Mg 1.36	Al 1.20	Si 1.17	Р 1.10	S 1.04	Cl 0.99	crease
4	K 2.03	Ca 1.74	Ga 1.26	Ge 1.22	As 1.20	Se 1.16	Br 1.14	E
5	Rb 2.16	Sr 1.91	In 1.44	Sn 1.41	Sb 1.40	Te 1.36	I 1.33	
6	Cs 2.35	Ba 1.98	Tl 1.48	Рb 1.47	Bi 1.46	Po 1.46	,	Ļ
	<u>.</u>		्य					

Decreases

Values of Atomic radius in p.m.

Facts to Remember

If the covalent bonds between atoms have differing electronegativities, the atomic radius is calculated using the Shoemaker and Stevenson formula.

 $D_{(A-B)} = r_A + r_B - 0.09(X_A - X_B)$

Here \boldsymbol{X}_A and \boldsymbol{X}_B are electronegativities of A and B respectively.

B. Ionization Enthalpy

- Ionization enthalpy can also be referred to as ionisation energy or ionisation potential.
- It is defined as the amount of energy necessary to remove the most loosely attached electron from a gaseous isolated atom, resulting in the production of a positive ion.

 $\begin{array}{rl} M-1e^- & \longrightarrow M^+-I_1 \\ M^+-1e^- & \longrightarrow M^{+2}-I_2 \\ M^{+2}-1e^- & \longrightarrow M^{+3}-I_3 \end{array}$

Here I_1 , I_2 and I_3 are the first, second and third ionization enthalpies respectively.

$$I_1 < I_2 < I_3 < I_4$$

- The value increases as removal of the electron becomes more and more difficult.
- Ionisation energy is always positive because energy is always required to remove the electron from an atom.
- Its units are eV/atom or kcal/mole or kJ/mole.



Factors Affecting Ionization Energy

- Ionization energy \propto Nuclear charge (Z_{eff})
- Ionization energy $\propto \frac{1}{\text{Atomic size}}$
- Ionization energy ∝

1 Penetration effect of the electrons

This indicates that the higher the magnitude of ionisation energy, the closer an orbital is to the nucleus, due to the larger force of attraction between electrons and the nucleus. The amplitude of ionzation energy increases in the following orders for orbitals: s > p > d > f

• Ionization energy ∝

Screening effect of the inner electrons Due to greater screening effect Z_{eff} decreases and removal of valence electron becomer easier.

• Ionization energy ∞ Stable electronic configuration.

Electronic configurations of fully or partially filled orbitals are stable. Because electron removal is difficult in such configurations, a larger value of ionisation energy is observed.

$$N > 0$$

$$2p^{3}2p^{4}$$

$$Be > B$$

$$2 s^{2}2p^{1}$$

Variation in value of ionization energy Period

 In a period, moving from left to right in a period increases the ionisation energy as Z_{eff} increases and size decreases, making electron removal more difficult.

 $s^{1} \quad s^{2} \quad p^{1} \quad p^{2} \quad p^{3} \quad p^{4} \quad p^{5} \quad p^{6} \\ IA < IIA > IIIA < IVA < VA > VIA < VIIA < VIIIA \\ (maximum)$

 The value of initial ionisation energy in group IIA is greater than that in group IIIA because in group IIA, ns² (completely filled state) is present, but in group IIIA, the configuration is np¹ (incomplete), which is less stable.

- The value of initial ionisation energy in group VA is greater than that in group VIA because group VA contains the ns² np³ configuration (half-filled more stable state), whereas group VIA has the ns² np⁴ configuration (incomplete, less stable state).
- Because of its stable octet state, an inert gas has the highest value of initial ionisation energy at any given time.
- In the case of alkali metals, the highest gap between IE₁ and IE₂ is observed as ns¹ configurations transition into inert gas configurations (ns² np⁶).

Examples:

- $\begin{array}{ll} \mathrm{IE_1:} & \mathrm{Li} < \mathrm{Be} > \mathrm{B} < \mathrm{C} < \mathrm{N} > \mathrm{O} < \mathrm{F} < \mathrm{Ne} \\ & \mathrm{Na} < \mathrm{Mg} > \mathrm{Al} < \mathrm{Si} < \mathrm{P} > \mathrm{S} < \mathrm{CI} < \mathrm{Ar} \end{array}$
- $$\begin{split} \text{IE}_2: \quad \text{Li} > \text{Ne} > \text{O} > \text{F} > \text{N} > \text{B} > \text{C} > \text{Be} \\ \text{Na} > \text{Ar} > \text{CI} > \text{S} > \text{P} > \text{Al} > \text{Si} > \text{Mg} \end{split}$$

Group

- In a group Ionization energy decreases as Z_{eff} decreases from top to bottom in a group.
- Also, as the size increases, the removal of electrons gets easier and easier.

Examples:



Figure: Variation of First Ionization Enthalpies with Atomic Number for Elements with Z = 1 to 60

Facts to Remember

In the periodic table, **helium** has the **maximum value** of first ionization energy (1500eV) while **cesium** has the **lowest** value for the same.



The largest gap between IE_2 and IE_3 is observed in alkaline earth metals as configuration changes from ns^1 to inert gas configuration (ns^2np^6) . Be $\longrightarrow Be^+ \longrightarrow Be^{2+} \longrightarrow Be^{3+}$

 $1s^2 2s^2 IE_1 2s^1 IE_2 1s^2 IE_3$

 $\leftrightarrow \text{for} \quad \text{IA} \rightarrow \text{I}_1 <<< \text{I}_2 \text{ IIIA} \rightarrow \text{I}_3 <<< \text{I}_4$

Importance of ionization energy

- Low ionisation energies elements are reducing agents, basic in nature, create cations, form ionic compounds, and have the greatest photoelectric effect.
- <u>Examples</u>- K and Cs have the maximum photoelectric effect and are hence utilised in photoelectric cells.
- C. Electron Gain Enthalpy or Electron Affinity (EA)
- The amount of energy released when a neutral isolated gaseous atom receives an electron to form a gaseous anion is referred to as **electron gain enthalpy.**

 $M + Ie^- \rightarrow M^- + E_1$

 $M^- + Ie^- \rightarrow M^{-2} + E_2$

 $M^{-2} + Ie^- \rightarrow M^{-3} + E_3$

where E_1, E_2 and E_3 stand for the first, second and third electron gain enthalpies respectively.

Facts to Remember

 $E_1 > E_2 > E_3$

The value of **electron affinity decreases** as the addition of electron becomes more and more difficult and possible only by absorbing some part of energy, that is, E_2 becomes endothermic in comparison to E_1 . (E_2 is exoergonic and E_2 is endoergonic). For example,

$$0 + e^{-} \xrightarrow{E_{1}} 0^{-} \xrightarrow{E_{2}} 0^{2}$$
$$E_{2} << E_{1}$$

- Its units are eV/ atom or Kcal/mole or kJ/mole.
- Electron affinity's value can be obtained indirectly from **Born-Haber cycle**.

Factors affecting electron affinity

- Electron affinity $\propto \frac{1}{\text{Atomic size}}$
- Electron affinity ∝ Effective nuclear charge
- Electron affinity $\propto \frac{1}{\text{Screening effect}}$
- Electron affinity $\propto \frac{1}{\text{Stable electronic configuration}}$
- The electron affinity of inert gases is 0 due to the presence of the ns² np⁶ configuration in the valence shell, which eliminates the possibility of adding an additional electron.
- Because of the increased stability of totally filled s orbitals in Mg and Be, their electron affinity is nearly nil.
- The electron affinity of an atom with halffilled orbitals is quite low (in case of fifth group).

<u>Variation in value of electron affinity</u> Period

- In a period, moving from left to right in a period, electron affinity increases as Z_{eff} increases and size decreases.
- In general, electron affinity follows the following series:

Halogens > Oxygen family > Carbon family > Nitrogen family > Metals of group I and XIII > Metals of group II > Zero group.

• The sequence of electron affinity in **second period** is as follows:

Be < N < Li < B < C < 0 < F

The sequence of electron affinity in third period is as follows:

Mg < Na < Al < P < Si < S < Cl.

Group

 In a group, moving down the group, the electron affinity decreases, as Z_{eff} decreases and size increases.



• Exceptional cases:

 $\begin{array}{rcl} E_a \mbox{ of } F &< & E_a \mbox{ of } Cl \\ E_a \mbox{ of } C &< & E_a \mbox{ of } Si \\ E_a \mbox{ of } N &< & E_a \mbox{ of } P \end{array}$

- $E_a^{"}$ of $0 < E_a^{"}$ of S
- Electron affinity is lower in group II elements due to their small size and higher electrical repulsion, making electron addition difficult.



Figure: Electron Affinity Vs Atomic number

Facts to Remember

- The sequence of electron affinity of group VII is as follows: I < Br < F < Cl
- Oxidizing power of an element ∝ Electron affinity
- Reactivity of non-metals ∝ Electron affinity

D. Electronegativity

- According to Pauling (1931), the ability or tendency of an atom in a molecule to attract the shared pair of electrons towards itself is referred to as electonegativity.
- His observation was: 1/2(A - A) + 1/2(B - B)A - B
- The bond dissociation energy of (A-B) is greater than the mean of (A-A) and (B-B) bond dissociation energies (B-B).
- Their difference Δ is proportional to the difference in electronegativities of A and B.

 $\Delta = E(A - B) - 1/2 [(E(A - A) + E(B - B)]^{1/2}$ = 23(X_A - X_B)² $\Delta = 23(X_A - X_B)^2$ 0.208 $\sqrt{\Delta} = (X_A - X_B)$ Here E(A - B), E(A - A) and E(B - B)represent bond dissociation energies of A - B, A - A and B - B respectively. X_A and X_B are electronegativities of A and Brespectively.

 Pauling took geometrical mean instead of arithmetic mean of E(A – A) and E(B – B) and introduced the empirical relation:

$$\begin{split} & \mathrm{E}(\mathrm{A}-\mathrm{B}) - (\mathrm{E}(\mathrm{A}-\mathrm{A})\times\mathrm{E}(\mathrm{B}-\mathrm{B}))^{1/2} = \Delta \\ & = 30(X_{\mathrm{A}}-X_{\mathrm{N}}) \\ & 0.182\sqrt{\Delta} = X_{\mathrm{A}} - X_{\mathrm{B}} \end{split}$$

 Allred and rochow's method: This method defines electronegativity as the electrostatic force of attraction exerted by an atom's nucleus on valence electrons. The following empirical relationship is utilised to calculate the electronegativity value in this approach.

$$X = -0.359 \frac{Z_{\rm eff}}{r^2} + 0.744$$

Here, X is the electronegativity and 'r' is covalent radius of the atom.

• Mulliken's method IE + EA

$$X = \frac{12}{2}$$

where, IE = Ionization energy in eV EA = Electron affinity in eVWhen these are expressed in kJ/mol replace

2 by 540.

Factors affecting electronegativity

• Electronegativity $\propto Z_{eff}$

$$\propto \frac{1}{\text{Size}}$$

- Electronegativity ∝ Ionization energy
 ∝ Electron affinity
- Charge on an atom
 - A cation is more electronegative than its parent atom, who is more electronegative than its anion. The larger an atom's positive charge (oxidation state), the greater its electronegativity.
 - $\circ~$ For example: Electronegativity of Fe^{+3} is greater than that of Fe^{+2}



• Effect of substitution

- The electronegativity of an atom is determined by the type of substituent connected to it.
- For example: Carbon atom in CF₃I acquires greater positive charge than CH₃I. Therefore, C-atom in CF₃I is more electronegative than in CH₃I.
- The difference in electronegativity of an atom caused by substituents, results in different chemical behaviour of that atom.
- Electronegativity ∝ s percentage. Therefore, the electronegativity follows the order sp > sp² > sp³.

Consequently, the value of electronegativity follows the order

 $C \equiv C > C = C > C - C$

Electronegative

Variation in electronegativity value

Period

- In a period, moving left to right, the electronegativity increases as Z_{eff} increases and size decreases.
- Order for first electronegativity in any period follows the order.

 $\mathsf{IA} < \mathsf{IIA} > \mathsf{IIIA} < \mathsf{IVA} < \mathsf{VA} > \mathsf{VIA} < \mathsf{VIA}$

Minimum Maximum

For Example:

Li < Be < B < C < N < O < F

Na < Mg < Al < Si < P < S < Cl

- Halogens have the highest electronegativity in any given period, whereas alkali metals have the lowest.
- The electronegativity of zero group elements is zero because they have no tendancy to attract electrons due to their stable octet state.

Group

 In a group, moving from top to bottom, electronegativity decreases as Z_{eff} decreases and size increases.





Facts to Remember

- Decreasing order of electronegativity
 F > O > N > Cl > C > B
 - 4 3.5 3 2.97 2.5 2
- Metalloids have nearly 2 times the value of electronegativity as compared to the above elements.

Applications of electronegativity

- Calculation of partial ionic character in a covalent bond. It depends upon two factors:
 - 1. The difference in electronegativity between the two bonded atoms
- 2. Dipole moment
- In a covalent bond, ionic character percentage is calculated through Hannay and Smyth equation:

 $= 16(X_A - X_B) + 3.5(X_A - X_B)^2$ Ionic character percentage

$$= 1 - e^{-1/4} (X_A - X_B)^2$$

- When electronegativity difference is greater than 1.7 the compound will be ionic in nature.
- CsF is most ionic due to a very large electronegativity difference of 3.3 between its constituent atoms, (the highest amongst any other combination of elements.)

Percent Ionic Character of a Bond Per cent ionic character

 $= \frac{\text{Actual dipole moment of the bond}}{\text{Dipole moment of a pure ionic bond}} \times 100$



SUMMARY OF THE TRENDS IN THE PERIODIC PROPERTIES OF ELEMENTS



- Non-metallic nature, electronegative nature, oxidising nature, electronegativity, ionisation energy, electron affinity, lattice energy, and hydration energy are examples of properties whose values increases from left to right in a period and decreases from top to bottom in a group.
- Metallic nature, electropositive nature, reducing nature, basic nature, radius or size, and ionic mobility are examples of properties whose values decreases from left to right and increases from top to bottom in a group.

NATURE OF OXIDES AND HYDROXIDES

PERIOD: Moving left to right, **basic nature decreases** while **acidic nature increases**.

For example,

 $\label{eq:starsest} \begin{array}{ll} Na_2 0, Mg0, Al_2 0_3, SiO_2, P_2 O_5, SO_2, Cl_2 O_7 \\ Most & Most \\ basic & acidic \\ NaOH > Mg(OH)_2 > Al(OH)_3 > Si(OH)_4 \\ Most basic & Most acidic \\ \textbf{GROUP: On moving downwards, basic nature} \end{array}$

increases.

<u>For example</u>: In group IA, Cs_2O and CsOH will be most basic.

Nature of Oxy-acids

• When we move from left to right in a period, the strength of the oxy-acids formed by nonmetals increases. Examples:

Period II

$$H_3BO_3$$
 H_2CO_3 HNO_3

Period III

 $\xrightarrow{H_2SiO_3 H_2PO_4 H_2SO_4 HClO_4}$ Strength increases

 On moving down the group, the strength of the oxyacids of non-metals decreases.
 Examples:

Group V

$$\xrightarrow{\text{HNO}_3 \text{H}_3\text{PO}_4 \text{H}_3\text{AsO}_4}_{\text{Strength decreases}}$$

Group VII

$$\xrightarrow{HNO_3 H_3PO_4 H_3AsO_4}$$

Nature of Hydrides

• While moving from left to right in a period, the nature of the hydrides changes from basic to acidic.

Example-

NH ₃	H ₂ O	HE	
Weak base	Neutral	Weak acid	
PH ₃	H ₂ S	HCI	0
Very weak base	Weak acid	Strong acid	

Boiling Point, Melting Point and Density

As we progress through a period, the **boiling temperature, melting point,** and density **climb to a maximum and then fall**. Their values increase as they move along the group.

Hydration Energy $\left(\Delta H_{y} ight)$ and Lattice Energy

 $\Delta H_{Y} \text{ or } U \propto \text{Charge on ion}$ $\propto \frac{1}{\text{Size of ion}}$

- This increases from left to right in a period and decreases down the group.
- For example: $Li^+ < Be^{2+} < B^{3+}$ $Li^+ > Na^+ > K^+$



Ionic Mobility

Ionic mobility

 \propto Charge on ion \propto Size of Hydrated Ion.

- It decreases from left to right in a period and increases down the group.
- For example:

 $Li^+ > Be^{2+} > B^{3+}$ $Li^{+} < Na^{+} < K^{+} < Rb^{+} < Cs^{+}$

Points to Remember

Diagonal relationship

- Several period II components are comparable to period III ones that are diagonal to them. This is referred to as a diagonal relationship.
- It happens because of comparable ionic sizes, electronegativities, and polarising power.



Si

Mg AI Diagonal relationship is not observed after group IV.

Example: Li_2CO_3 and $MgCO_3$ both exhibit diagonal relationship where, on heating they form their oxides and CO_2 .

 $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$

Na

 $MgCO_3 \longrightarrow MgO + CO_2$

BeO and Al_2O_3 are amphoteric oxides.

Carbides of Be and Al, on hydrolysis, give • methane gas.

 $Al_4C_3 + 12H_2O \rightarrow 4A1(OH)_3 + 3CH_4$ $Be_2C + 2H_2O \rightarrow 2BeO + CH_4$

- A covalent bond is formed when the difference between ionization energy and electron affinity is high.
- These elements form amphoteric oxides = H, Be, Al, Ga, In, Tl, Sn, Pb, Sb, Bi

Fe, CO and Ni have nearly same Z_{eff} value, so they have almost same size and ionization energy.

NEET AND AIIMS ESSENTIALS

In the following questions, two statements Assertion (A) and Reason (R) are given. Mark

- (a) If A and R both are correct and R is the correct explanation of A;
- (b) If A and R both are correct but R is not the correct explanation of A;
- (c) A is true but R is false;
- (d) A is false but R is true
 - 1. (A) : Bond dissociation energy of F_2 is less than Cl₂.
 - (R): Due to smaller size of fluorine there is greater electron repulsion between the F atoms than Cl atoms.
 - 2. (A) : Ions K^+ , S^{2-} , Sc^{3+} are isoelectronic.
 - (R) : In each ion the total number of electrons are 18.
 - 3. (A) : Ionisation energy of Magnesium is more than that of Aluminium.
 - (R) : In Aluminium 3p-orbital is full filled whereas in Magnesium it is not full filled.
 - 4. (A) : Fluorine is more electronegative than chlorine.
 - (R) : Fluorine is smaller in size than chlorine.
 - 5. (A) : Ionisation energy for s-electrons is more than the p-electrons for the same shell.
 - (R) : s-electrons are closer to the nucleus than p-electrons hence more tightly attached.
 - 6. (A) : Li and Mg diagonal show relationship.
 - (R) : Li and Mg have same atomic radius.



- 7. (A) : He and Be both have the same outer electronic configuration like ns^2 type.
 - (R) : Both are chemically inert.
- 8. (A) : The first ionization energy of N is more stable than that of O.
 - (R) : Oxygen after losing one electron gets a stable electronic configuration.
- (A) : For noble gases in the solid state the crystal radii are actually Van der Waal's radii.
 - (R) : In crystals of noble gas no chemical forces operate between the atom.
- (A) : Electron gain enthalpy of oxygen is less than that of fluorine but greater than that of nitrogen.

- (R) : Ionization enthalpy is as follows $N>0>F. \label{eq:nonlinear}$
- (A) : Second ionization enthalpy will be higher than the first ionization enthalpy.
 - (R) : Ionization enthalpy is a quantitative measure of the tendency of an element to lose electron.
- 12. (A) : Noble gases have large positive electron gain enthalpy.
 - (R) : Electron has to enter the next higher principle quantum level.

ANSWER KEY

9. 1. (a) 2. (a) 3. (c) 4. (b) 5. (a) 6. (c) 7. (c) 8. (b) (b) 10. (c)

11. (b) 12. (a)

Unleash the topper in you