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BS-109 Engineering chemistry-I

General Properties of Elements

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PRESENT FORM OF THE PERIODIC TABLE: “long form” of the Periodic Table

- The horizontal rows are called periods and the vertical columns, groups.
- Elements having similar outer electronic configurations are arranged in vertical columns, referred to as groups. The groups are numbered from 1 to 18.
- There are altogether seven periods. The period number corresponds to the highest principal quantum number (n) of the elements in the period. The first period contains 2 elements. The subsequent periods consists of 8, 8, 18, 18 and 32 elements, respectively.
- 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

s-Block Elements:

- Group 1 (alkali metals) and Group 2 (alkaline earth metals) which have ns^1 and ns^2 outermost electronic configuration.
- They are all reactive metals with low ionization enthalpies. The metallic character and the reactivity increase as we go down the group.

p-Block Elements: (Group 13 to 18)

- together with the s -Block Elements are called Main Group Elements.
- The outermost electronic configuration varies from ns^2np^1 to ns^2np^6 in each period.
- Halogens (Group 17) and the chalcogens (Group 16) groups have highly negative electron gain enthalpies and readily add one or two electrons respectively to attain the stable noble gas configuration.
- The non-metallic character increases as we move from left to right across a period and metallic character increases as we go down the group.



Representative elements												Representative elements		Noble gases			
GROUP NUMBER												GROUP NUMBER		18			
1 2														0			
IA IIA												13 14 15 16 17		2			
1	2											III B	IV B	V B	VI B	VII B	He
3	4											5	6	7	8	9	10
Li	Be											B	C	N	O	F	Ne
2s ¹	2s ²											2s ² 2p ¹	2s ² 2p ²	2s ² 2p ³	2s ² 2p ⁴	2s ² 2p ⁵	2s ² 2p ⁶
11	12	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Na	Mg	III A	IV A	V A	VIA	VII A	VIII			IB	II B	Al	Si	P	S	Cl	Ar
3s ¹	3s ²											3s ² 3p ¹	3s ² 3p ²	3s ² 3p ³	3s ² 3p ⁴	3s ² 3p ⁵	3s ² 3p ⁶
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
4s ¹	4s ²	3d ¹ 4s ²	3d ² 4s ²	3d ³ 4s ²	3d ⁴ 4s ¹	3d ⁵ 4s ²	3d ⁶ 4s ²	3d ⁷ 4s ²	3d ⁸ 4s ²	3d ⁹ 4s ¹	3d ¹⁰ 4s ²	4s ² 4p ¹	4s ² 4p ²	4s ² 4p ³	4s ² 4p ⁴	4s ² 4p ⁵	4s ² 4p ⁶
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
5s ¹	5s ²	4d ¹ 5s ²	4d ² 5s ²	4d ³ 5s ¹	4d ⁴ 5s ²	4d ⁵ 5s ²	4d ⁶ 5s ²	4d ⁷ 5s ²	4d ⁸ 5s ¹	4d ⁹ 5s ¹	4d ¹⁰ 5s ²	5s ² 5p ¹	5s ² 5p ²	5s ² 5p ³	5s ² 5p ⁴	5s ² 5p ⁵	5s ² 5p 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	Po	At	Rn
6s ¹	6s ²	5d ¹ 6s ²	4f ¹⁴ 5d ² 6s ²	5d ³ 6s ²	5d ⁴ 6s ²	5d ⁵ 6s ²	5d ⁶ 6s ²	5d ⁷ 6s ²	5d ⁸ 6s ¹	5d ⁹ 6s ¹	5d ¹⁰ 6s ²	6s ² 6p ¹	6s ² 6p ²	6s ² 6p ³	6s ² 6p ⁴	6s ² 6p ⁵	6s ² 6p ⁶
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra	Ac**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
7s ¹	7s ²	6d ¹ 7s ²															

f- Inner transition elements

*Lanthanoids
4fⁿ5d⁰6s²

**Actinoids
5fⁿ6d⁰7s²

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
4f ¹ 5d ¹ 6s ²	4f ² 5d ¹ 6s ²	4f ³ 5d ⁰ 6s ²	4f ⁴ 5d ⁰ 6s ²	4f ⁵ 5d ⁰ 6s ²	4f ⁶ 5d ⁰ 6s ²	4f ⁷ 5d ⁰ 6s ²	4f ⁷ 5d ¹ 6s ²	4f ⁹ 5d ⁰ 6s ²	4f ¹⁰ 5d ⁰ 6s ²	4f ¹¹ 5d ⁰ 6s ²	4f ¹² 5d ⁰ 6s ²	4f ¹³ 5d ⁰ 6s ²	4f ¹⁴ 5d ⁰ 6s ²
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
5f ⁰ 6d ² 7s ²	5f ² 6d ¹ 7s ²	5f ³ 6d ¹ 7s ²	5f ⁴ 6d ¹ 7s ²	5f ⁵ 6d ⁰ 7s ²	5f ⁶ 6d ⁰ 7s ²	5f ⁷ 6d ⁰ 7s ²	5f ⁷ 6d ¹ 7s ²	5f ⁹ 6d ⁰ 7s ²	5f ¹⁰ 6d ⁰ 7s ²	5f ¹¹ 6d ⁰ 7s ²	5f ¹² 6d ⁰ 7s ²	5f ¹³ 6d ⁰ 7s ²	5f ¹⁴ 6d ⁰ 7s ²



***d*-Block Elements:** (Group 3 to 12)

- In the centre of the Periodic Table, characterised by the filling of inner *d* orbitals
- general outer electronic configuration $(n-1)d^{1-10}ns^{0-2}$.
- They are all metals. They mostly form coloured ions, exhibit variable valence (oxidation states), and paramagnetism.
- However, Zn, Cd and Hg which have the electronic configuration, $(n-1)d^{10}ns^2$ do not show most of the properties of transition elements. In a way, transition metals form a bridge between the chemically active metals of *s*-block elements and the less active elements of Groups 13 and 14 and thus take their familiar name “Transition Elements”.

f-Block Elements (Inner- Transition Elements):

- 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 ($Z = 103$)
- outer electronic configuration $(n-2)f^{1-14} (n-1)d^{0-1}ns^2$.
- They are all metals. Within each series, the properties of the elements are quite similar.
- chemistry of the early actinoids is more complicated than the corresponding lanthanoids, due to the large number of oxidation states possible for these actinoid elements. Actinoid elements are radioactive.



Trends in Physical Properties

a) Atomic Radius :

- Radius of the atom: distance from the nucleus to the outermost electron or up to point at which the probability of finding of electron is the maximum.
- Most of the time atoms are not in atomic state, so radius is measured as covalent radius, van der Waals radius and metallic radius.
- **Covalent radius**: one half of the internuclear distance in the homonuclear diatomic molecule. The bond distance in the chlorine molecule (Cl_2) is 198 pm and half this distance (99 pm), is taken as the atomic radius of chlorine.
- **Metallic radius**: half of the internuclear distance separating two adjacent metal atoms in a metallic lattice. Distance between two adjacent copper atoms in solid copper is 256 pm; hence the metallic radius of copper is assigned a value of 128 pm.
- **van der Waals radius**: shortest distance between two immediately adjacent atoms (either of same or different elements) in the structure of the solid compound in which they are not bonded to each other. The radii of the inert gas elements is generally expressed in terms of only van der Waals' radii because most of these gases (other than xenon and krypton) do not form chemical compounds.

1. Variation in a period:

- In s- and p- block elements, there is a general decrease of atomic radius in a period because the effective nuclear charge (Z_{eff}) increases across a row.
- For d-block elements, atomic radius initially decreases, then remains constant and finally increase again.



2. Variation in a group:

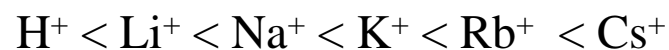
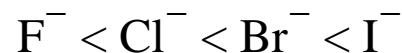
- (s- and p- block) elements, the atomic radii increases down the group, because extra shell is added.
- Some exceptions to this are:
- The radius of gallium is expected to be greater than that of aluminium but $r_{Al} \approx r_{Ga}$, because of the poor shielding effect of d-electrons.
- Similarly, the radius of thallium is expected to be greater than that of indium but $r_{Tl} \approx r_{In}$, because of the poor shielding of d and f electrons.
- For d-block elements, the trend in atomic radii is: $r_{3d \text{ series}} < r_{4d \text{ series}} < r_{5d \text{ series}}$. This is because the radius increases as the shell number increases.
- The radius of elements of 4d- series is about the same as elements of 5d series. This is due to the lanthanoid contraction that causes increase in Z_{eff} value due to poor shielding of f electrons.
- The exception to this behaviour is : $Sc < Y < La$. This is because there is no 4f electron in the electronic configuration of La.
- For f-block elements, in lanthanoids, the effective nuclear charge increases along the period so the atomic radius for the elements decreases. For actinoids, there is also a decrease in atomic radius from Th to Lr.



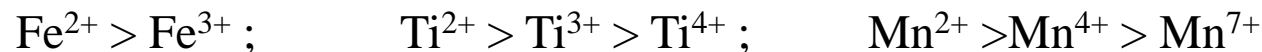
b) Ionic radius :

- When a positive ion is formed, effective nuclear charge is increased which results in and outer electrons are being attracted more strongly by the nucleus. Thus a positive ion is always smaller than the corresponding atom and more the electrons removed smaller is the ion.
- When a negative ion is formed, one or more electrons are added to an atom which results in reduced effective nuclear charge. As, electron cloud expands and the size of anion is more than that of the atom.
- Ionic radius depends upon following factors:

1. Down the group, the shell number increases so the ionic radius increases. Eg.



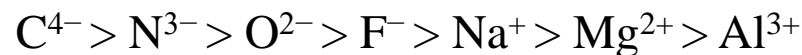
2. (a) If the charge of cation increases, the ionic radius decreases. For example,



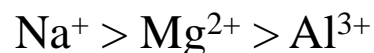
- (b) If the charge of anion increases, the ionic radius increases. For example,



3. For isoelectronic species, as the number of protons increases the radius of ion decreases.



4. The ionic radii decreases moving from left to right across any period, and this is partly due to the increased number of charges on the nucleus and also to the increasing charge on ion.





c) Ionization energy:

- Ionization energy (IE) is the energy required to remove an electron from an isolated gaseous atom in its ground state.



- It is measured in eV atom^{-1} or kJ mol^{-1} .
- 1. The ionization energy for an atom is always positive and for an ion may be negative.
- 2. Successive ionization energy always increases for any species because the e/p ratio gradually decreases.
- 3. Observing the sudden jump of successive IE values, number of valence shell electrons of the corresponding atom can be predicted. For example,

Element	IE ₁	IE ₂	IE ₃	IE ₄	IE ₅	No. of valence electrons
Na	5.139	47.28	71.68	98.91		1
Ge	11.26	26.38	47.44	77.41	392.07	4
Al	5.98	18.22	28.44	119.4		3

*Ionization energy is expressed in eV/atom^{-1} .

- Ionization energy depends upon the following factors:
- 1. It decreases when shell number or the radius increases.
- 2. It increases when Z_{eff} increases.
- 3. It decreases when σ (shielding constant) increases.
- 4. It is more for half-filled and fully-filled electronic configurations.
- 5. It also depends upon the orbitals from which the electron is removed. If the principal quantum number is the same, then the energy required for removal of electrons from different orbitals shows the following order: $s > p > d > f$.



Periodic variations in ionization energy (IE)

(s and p block)

Along period: the Z_{eff} increases in a period, hence IE increases.

Irregular trend

$$\begin{cases} \text{Li} < \text{B} < \text{Be} < \text{C} < \text{O} < \text{N} < \text{F} < \text{Ne} \\ \text{Na} < \text{Al} < \text{Mg} < \text{Si} < \text{S} < \text{P} < \text{Cl} < \text{Ar} \\ \text{K} < \text{Ga} < \text{Ca} < \text{Ge} < \text{Se} < \text{As} < \text{Br} < \text{Kr} \end{cases}$$

Regular trend

$$\begin{cases} \text{Rb} < \text{Sn} < \text{In} < \text{Sn} < \text{Sb} < \text{Te} < \text{I} < \text{Xe} \\ \text{Cs} < \text{Ba} < \text{Tl} < \text{Pb} < \text{Bi} < \text{Po} < \text{At} < \text{Rn} \end{cases}$$

Exceptions to trends are

(i) $\text{Be} > \text{B}$ $\text{Mg} > \text{Al}$ $\text{Ca} > \text{Ga}$

Be, Mg and Ca have fully filled ns^2 , but B, Al & Ga attain fully filled ns^2 after losing one electron.

(ii) $\text{N} > \text{O}$ $\text{P} > \text{S}$ $\text{As} > \text{Se}$

N, P, As have half filled np^3 , while O, S, Se obtain half filled np^3 on losing $1e^-$.

(iii) (a) IE_2 of group 1A $>$ IE_2 of group 2A elements.

(b) IE_3 of group 5A $>$ IE_3 of group 6A elements.



In a group: IE generally decreases down the group. Some exceptions are:

(i) $\text{Al} (577 \text{ kJ/mol}) \approx \text{Ga} (579 \text{ kJ/mol})$ [because poor shielding effect of $10 d e^-$ in Ga]

(ii) $\text{In} (558 \text{ kJ/mol}) < \text{Tl} (589 \text{ kJ/mol})$ [due to lanthanoid contraction]

So, for Group 13, order is $\text{B} > \text{Tl} > \text{Ga} \geq \text{Al} > \text{In}$.

→ $\text{Sn} (707 \text{ kJ/mol}) < \text{Pb} (715 \text{ kJ/mol})$ [due to lanthanoid contraction in Pb]

So, for Group 14, order is $\text{C} > \text{Si} > \text{Ge} > \text{Pb} > \text{Sn}$

(d-block) Period: IE slightly increases due to increase in Z_{eff} . (But not prominent)

B'coz $\text{Cu} \rightarrow \text{Zn}$, $\text{Ag} \rightarrow \text{Cd}$ and $\text{Au} \rightarrow \text{Hg}$ there is sudden jump due to fully filled configuration.

Group:

IE_1 of 3d series $\approx \text{IE}_1$ of 4d series $< \text{IE}_1$ of 5d series
should decrease but more due to lanthanide contraction.

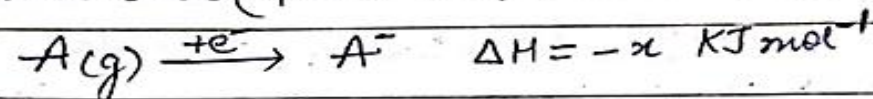
exception: $\text{Sc} (6.54 \text{ eV}) > \text{Y} (6.38 \text{ eV}) > \text{La} (5.57 \text{ eV})$

regular trend as La element has no lanthanide contraction.



ELECTRON AFFINITY : (EA)

→ Energy released when 1 mole electron is added to 1 mole of an element in its isolated gaseous state (Ground state).



→ also known as electron gain enthalpy (ΔH_{eg})

- (1) electron affinity for 1st electron is greater than that of 2nd electron [$EA_1 > EA_2$]
- (2) Successive electron affinity always decreases.
- (3) ΔH_{eg2} for all elements is +ve.

* Periodic trends *

- (1) In a group, there is a decrease of electron affinity down the group.
- (2) In a period, electron affinity increases from left to right as Z_{eff} increases.
except for inert gases.

- (3) P-block element of
Second period and third period.

EA of second period < EA of 3rd period

b'coz 3rd period have empty d-orbital.

2 nd		3 rd
B	<	Al
C	<	Si
N	<	P
O	<	S
F	<	Cl



(4) EA of alkali metals $>$ EA of alkaline earth metals.

b'coz alkali metals will attain fully filled state & it will disturb for alkaline earth metals.

(5) EA of Group 14 $>$ EA of group 15 $\left[\begin{array}{l} \text{b'coz adding } e^- \text{ to G-14 will lead to} \\ \text{half filled configuration.} \end{array} \right]$
(C) (N)

So, EA depends upon:

- (i) decreases when radius increases.
- (ii) increases when Z_{eff} increases.
- (iii) EA of half filled and fully filled configuration is less.
- (iv) EA order for addition of e^- in different orbitals having same principal quantum number is $s > p > d > f$.
- (v) decreases when shield constant increases.



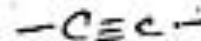
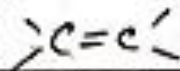
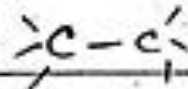
ELECTRO NEGATIVITY:

→ In 1931, Pauling defined electronegativity of atom as tendency of atom to attract e^- (bond pair) towards itself when combined in a compound.

Electronegativity depends upon following factors:

- (i) it decreases when radius increases.
- (ii) it increases when Z_{eff} increases.
- (iii) decreases when shielding constant increases.
- (iv) increases when oxidation state of element increases.
- (v) larger is the s -character, larger is electronegativity.

eg → $sp^3 \rightarrow 2.5$ $sp^2 \rightarrow 2.75$ $sp \rightarrow 3.25$



If two atoms have similar electronegativity values, the bond between them is largely covalent. But when electronegativity difference is large, bond has high degree of polar character.



Periodic Variation

1. In a period, electronegativity increases from left to right as Z_{eff} increases.
2. In a group, electronegativity decreases.

Some important points :

1. Fluorine has the highest electronegativity in the periodic table. (i.e. 4)
2. Caesium is having lowest electronegativity in periodic table (excluding radioactive element).
i.e. (0.7)
3. Alkali metals have the lowest electronegativity in respective periods.
4. Halogens have the highest electronegativity in respective period.
5. Electronegativity of inert gases is zero.



Table 2.1: Electronegativity values (L. Pauling Scale)

<i>Group → Period ↓</i>	<i>I (1)</i>	<i>II (2)</i>	<i>III (13)</i>	<i>IV (14)</i>	<i>V (15)</i>	<i>VI (16)</i>	<i>VII (17)</i>
1	H 2.1						
2	Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
3	Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
4	K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
5	Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
6	Cs 0.7	Ba 0.9	Tl 1.8	Pb 1.9	Bi 2.0	Po 2.0	At 2.2
7	Fr 0.7	Ra 0.9					