Illustration 1

Which of the following species will have the largest and the smallest size?

Mg, Mg^{2+}, Al, Al^{3+}

Soln.: Atomic radii decrease across a period. Cations are smaller than their parent atoms. Among isoelectronic species, the one with the larger positive nuclear charge will have a smaller radius.

Hence the largest species is Mg; the smallest one is Al^{3+}.

Ionisation Enthalpy

- The amount of energy required to remove the most loosely bound valence shell electron from an isolated atom is called ionization energy (*IE*).

  $M_{(g)}$ + ionisation energy $\rightarrow M^+_{(g)} + e^-_{(g)}$

  Thus, the ionization energy gives the ease with which the electron can be removed from an atom. The smaller the value of the ionization energy, easier it is to remove the electron from the atom.
- **Factors affecting ionisation enthalpy**
  - ***Size of the atom :*** Size increases, ionisation enthalpy decreases.
  - ***Nuclear charge :*** Nuclear charge increases, ionisation enthalpy increases.
  - ***Screening effect :*** Effective nuclear charge (Z_{eff}) $= Z - S$

    Z = nuclear charge, S = screening effect

    So, S increases, Z_{eff} decreases, ionisation enthalpy decreases.
  - ***Penetration power :*** $s > p > d > f$

    Penetration power increases, ionisation enthalpy increases.
- **Variation along a period :** The ionization energy increases from left to right with increasing atomic number in a period. This is because of increase in nuclear charge and decrease of atomic size across a period from left to right.

  For transition elements it remains almost same.

  However some irregularities have been noticed due to the extra stability of the half filled and completely filled configurations.
- **Variation in a group :** The ionization energy decreases gradually on moving from top to bottom in a group due to,
  - an increase in the atomic size,
  - increase in the shielding effect on the valence electron,
  - the effect of increase in atomic size and the shielding effect is much more pronounced than the effect of increased nuclear charge.

Li	Be	B	C	N	O	F	Ne	
520	899	801	1086	1402	1314	1681	2080	kJ mol⁻
Na	Mg	Al	Si	P	S	Cl	Ar	
496	737.6	577	786	1011	999	1255	1520	kJ mol⁻

Illustration 2

How much energy in joules must be needed to convert all the atoms of sodium to sodium ions present in 2.3 mg of sodium vapours? Ionisation enthalpy of sodium is 495 kJ mol^{-1}. (At. mass of Na = 23).

Soln.: According to the definition of ionisation enthalpy,

$Na_{(g)} + IE \rightarrow Na^+_{(g)} + e^-_{(g)}$

$I.E. = 495$ kJ mol^{-1}

The amount of energy needed to ionise 1 mole of sodium vapours = 495 kJ mol^{-1}

Moles of sodium vapours present in given sample

$$= \frac{2.3 \times 10^{-3}}{23} = 1 \times 10^{-4} \text{ mol}$$

$\therefore$ Amount of energy needed to ionise 1×10^{-4} mole of sodium vapours

$= 495 \times 1 \times 10^{-4}$

$= 0.0495$ kJ or 49.5 J

Electron Affinity

- Electron affinity is the amount of energy released when an electron is added to an isolated gaseous atom to form gaseous anion.

  $X_{(g)} + e^- \longrightarrow X^-_{(g)}$ + Electron affinity
- Electron affinity is the ability of an atom to hold an additional electron. If the atom has more tendency to accept an electron then energy released will be large and consequently the electron affinity will be high.
- **Factors affecting electron affinity**
  - ***Nuclear charge :*** Charge increases, electron affinity increases.
  - ***Atomic size :*** Size decreases, electron affinity increases.
  - ***Electronic configuration :*** Elements with stable configuration (half-filled or completely filled) have less tendency to accept electrons, so lower electron affinity.
- **Variation along a period :** Electron affinity increases in a period from left to right. Since size of an atom decreases and the nuclear charge increases on moving across a period which results in greater attraction for the incoming electron.
- **Variation in a group :** Electron affinity decreases from top to bottom in a group since atomic size increases.
- Electron affinity for some third period elements (*e.g.*, P, S, Cl) is greater than corresponding second period elements (*e.g.*, N, O, F) because of the smaller atomic size of second period elements, which produces larger electronic repulsions for the additional electron, so that the additional electron is not accepted easily.

Illustration 3

The amount of energy released when 1×10^{10} atoms of chlorine in vapour state are converted to Cl^- ions according to the equation, $Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$ is 57.86×10^{-10} J.

Calculate the electron gain enthalpy of chlorine atom in terms of kJ mol^{-1} and eV per atom.

Soln.: The amount of energy released when 1×10^{10} atoms of chlorine in vapour state are converted to Cl^- ions, according to the equation,

$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$ is 57.86×10^{-10} J.

$\therefore$ The electron gain enthalpy of chlorine, *i.e.*, the amount of energy released when 1 mole (6.023×10^{23}) atoms of chlorine are converted into Cl^- ions according to the above equation will be

$$= -\frac{57.86 \times 10^{-10}}{1 \times 10^{10}} \times 6.023 \times 10^{23}$$

$= -348.49 \times 10^3$ J/mol $= -348.49$ kJ/mol

Now 1 eV/atom = 96.49 kJ mol^{-1}

$\therefore$ Electron gain enthalpy of chlorine

$$= -\frac{348.49}{96.49} = -3.61 \text{ eV/atom}$$

Electronegativity

- The relative tendency of an atom in a molecule to attract a shared pair of electrons towards itself is termed as electronegativity. Electronegativity is measured on a number of scales but most commonly used are of Pauling or Mulliken.
- **Factors affecting electronegativity**
  - ***Atomic size :*** Size increases, electronegativity decreases.
  - ***Ionisation enthalpy and electron affinity :*** Ionisation energy and electron affinity increase, electronegativity also increases.
  - ***s-Character :*** *s*-Character increases electronegativity increases.

    Order of electronegativity : $sp > sp^2 > sp^3$
  - ***Charge on the ion :*** Electronegativity order : cation > parent ion > anion.
- **Variation along a period :** Electronegativity increases in a period from left to right since atomic size decreases and nuclear charge increases from going left to right in a period. Electronegativity of a series of transition metals is almost similar.
- **Variation in the group :** Electronegativity decreases down the group because the atomic size increases.

Group →	1 IA	2 IIA	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA
I Period	H 2.1						
II Period	Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
III Period	Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
IV Period	K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
V Period	Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.01	I 2.5
VI Period	Cs 0.7	Ba 0.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 1.76	At 2.2

Increases

Decreases

Valency

- The electrons present in the outermost shell are called valence electrons. The valency of an element is defined as its 'combining capacity'. Number of valence electrons determine the valency of an atom.
- **Variation along a period :** The number of valence electrons increases from left to right in a period. So, the valency of the elements first increase from 1 to 4 and then decrease to zero. Noble gases have zero valency.

Group	1	2	13	14	15	16	17	18
Number of valence electrons	1	2	3	4	5	6	7	8
Valence on hydrogen scale	1	2	3	4	3	2	1	0

- **Variation in a group :** On moving down the group the number of valence electrons remains same and therefore all the elements in the group exhibit the same valency. For example, the elements of group-1 show monovalency while the elements of group-2 show divalency.

	In a period	In a group
Atomic radii	Decreases	Increases
Ionic radii	Decreases	Increases
Ionisation enthalpy	Increases	Decreases
Electron affinity	Increases	Decreases
Electronegativity	Increases	Decreases