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#### LESSON 3.PERIODIC CLASSIFICATION

- 1. Frequency of X-ray =  $\sqrt{v}$  = a(Z-b) where v is frequency, Z is atomic number and a, b are constants.
- 2. Atomic radius of homonuclear diatomic molecule =  $r_A$

$$r_A = \frac{d_{A-A}}{2}$$
 where  $d_{A-A}$  =Inter nuclear distance

3. Atomic radius of heteronuclear diatomic molecule.

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

$$\therefore r_{A} = d_{A-B} - r_{B}, \quad r_{B} = d_{A-B} - r_{A}$$

- 4.  $Metallic \ radius = \frac{Dis \ tan \ ce \ between two \ adjacent \ atom}{2}$
- 5. Effective nuclear charge =  $Z_{eff} = Z S$
- 6. Electronegativity = $X_A X_B = 0.182 \sqrt{E_{A-B}} (E_{AA} \times E_{BB})^{1/2}$

### Important points in periodic variation

	Periodic property	Unit	Across the period	Down the group
1.	Atomic radii	Å	decreases	Increases
2.	Ionic radii	Å	decreases	Increases
3.	Ionisation energy	kJ mol <sup>-1</sup>	increases	decreases
4.	Electron affinity	kJ mol <sup>-1</sup>	increases	decreases
5.	Electronegativity	No unit	increases	decreases
6.	Valency	No unit	increases	remains the same
7.	Chemical reactivity	No unit	increases	decreases
8.	Electropositive character	No unit	increases	decreases
9.	Metallic character	No unit	increases	decreases

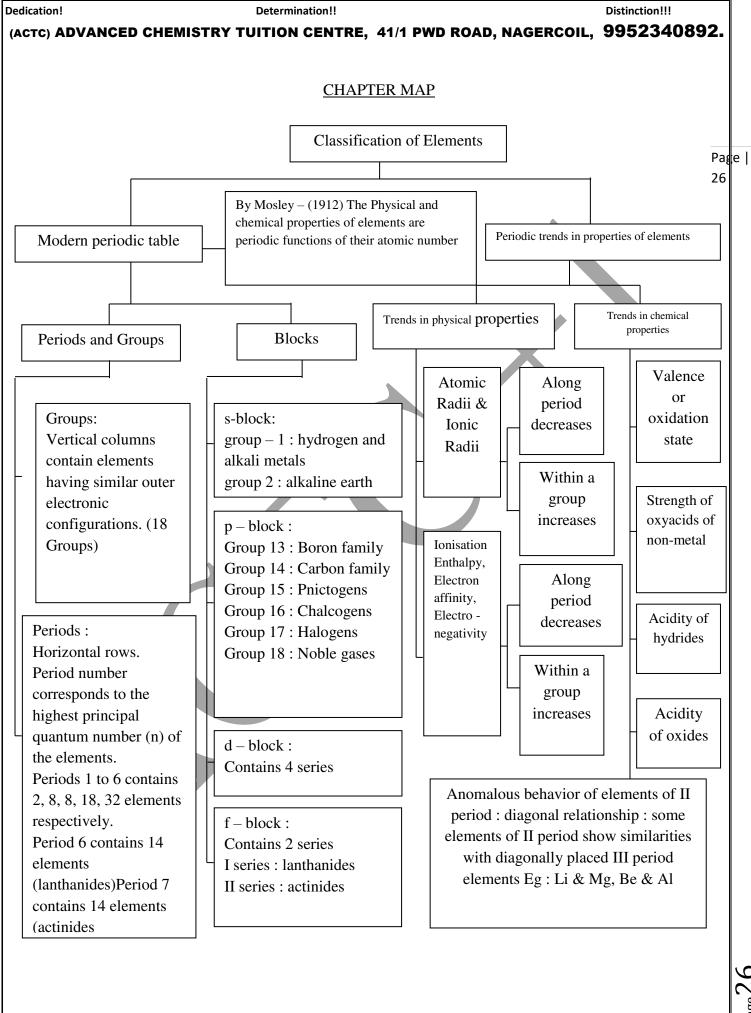
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Dedication! Distinction!!! Determination!! (ACTC) ADVANCED CHEMISTRY TUITION CENTRE, 41/1 PWD ROAD, NAGERCOIL, 9952340892. No unit Basic character increases Decreases

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- **❖ Elements known during 19<sup>th</sup> Century** − 118 Elements. Out of 118 known 92 elements are found in nature.
- ❖ Johann Dobereiner's classification Law of triads It was seen that invariable, the atomic weight of the other two members of the triad. He noted that elements with similar properties occur in groups of three which he called triads.
- ❖ Chancourtois classification In this system, elements that differed from each other in atomic weight by 16 or multiples of 16 fell very nearly on the same vertical line. Elements lying directly under each other showed a definite similarity. This was the First periodic law.
- ❖ Newland's classification Law of octaves This law states that, when elements are arranges in the order of increasing atomic weights, the properties of the eighth element are a repetition of the properties of the first element. This law was seemed to be applicable only for elements upto atomic number 20 (Calcium).
- ❖ Mendeleev's classification Mendeleev's periodic law This law states that the properties of the elements can be represented as periodic function of their atomic weights.
- ❖ Modern periodic law It was given by Henry Moseley in 1913. This law states that "The physical and chemical properties of the elements are periodic functions of their atomic numbers".
- ❖ Moseley's correlation between atomic number and the frequency of X-rays.  $\sqrt{\upsilon} = a(Z-b)$ , where  $\upsilon =$  frequency of the  $\dot{X}$ -rays emitted by the elements concerned. Z = atomic number; a and b = constants and have same values for all the elements.
- ❖ **Periodicity** The repetition of physical and chemical properties at regular intervals is called periodicity.
- ❖ Groups The vertical columns in the periodic table are called groups. There are 18 vertical columns which constitute 18 groups or families.
- ❖ Periods There are 7 horizontal rows in the periodic table known as periods.

First period 2 elements very short <sub>1</sub>H and <sub>2</sub>He

Second period 8 elements short <sub>3</sub>Li to <sub>10</sub>Ne

Third period 8 elements short <sub>11</sub>Na to <sub>18</sub>Ar

Fourth period 18 elements long 19K to 36Kr

Fifth period 18 elements long 37Rb to 54Xe

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Sixth period 32 elements very long <sub>55</sub>Cs to <sub>86</sub>Rn

Seventh period 32 elements very long 87Fr to 118Ogcontinued.

- ❖ Electronic configuration The distribution of electrons into orbitals, s, p, d and f, of an atom is called its electronic configuration.
- Lanthanides The first f-transition series consisting of 14 elements placed separately spanel at the bottom of the periodic table.
- ❖ Actinoids The second f transition series consisting of 14 elements placed separately as panel at the bottom of the periodic table.
- **❖ Group 17** Halogen family.
- **❖ Group 16** Chalcogen family (or) oxygen family.
- **❖ Division of elements based on electronic configuration** − The entire periodic table can be divided into s, p, d and f blocks.
- **❖** Group 18 Noble gases.
- **❖ Group 1** Alkali metals.
- ❖ Group 2 Alkaline earth metals.
- ❖ d-block elements The elements of the groups 3 to 12 are called p-block elements or transition elements with general valence shell electronic configuration ns<sup>1-2</sup>, (n-1)d<sup>1-10</sup>.
- p-block elements The elements of groups 13 to 18 are called p-block elements or representative elements and have a general electronic configuration ns<sup>2</sup>, np<sup>1-6</sup>.
- ❖ s-block elements The elements of group 1 and group 2 are called s-block elements, since the last valence electron enters the ns orbital. general electronic configuration ns<sup>1-2</sup>.
- ❖ f-block elements The lanthanides (4f<sup>1-14</sup>, 5d<sup>0-1</sup>, 6s<sup>2</sup>) and the actinides (5f<sup>0-14</sup>, 6d<sup>0-2</sup>, 7s<sup>2</sup>) are called f-block elements.
- **Types of elements -**

Basis of chemical behavior	Basis of physical properties		
Main group elements	Metals		
Noble gases	Non-metals		
Transition elements	Metalloids		
Inner transition elements	Metals		

- **Example for periodic properties** (i) Atomic radius (ii) Ionic radius (iii) Ionization enthalpy (iv) Electron gain enthalpy (v) Electrongativity.
- ❖ Atomic radius It is the distance between the centre of the nucleus of an atom and the outermost shell containing the valence electron.

- ❖ Covalent radius It is one half of the internuclear distance between two identical atoms linked together by a single covalent bond.
- ❖ Metallic radius It is defined as one half of the distance between two adjacent metal atoms in the closely packed metallic crystal lattice.

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- ❖ **Ionic radius** It is defined as the distance from the centre of the nucleus of the ion up to which it exerts its influence on the electron cloud of the ion.
- **❖ Isoelectronic ions** The ions of different elements having the same number of electrons are called isoelectronic ions. e.g. Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, F<sup>-</sup>, O<sup>2-</sup>, N<sup>3-</sup>
- ❖ Ionization enthalpy The energy required to remove the most loosely bound electron from the valence shell of an isolated neutral gaseous atom is called as Ionization energy.
  The unit of lionization energy = KJ mole<sup>-1</sup>.
- **❖ Electron gain enthalpy (or) Electron affinity** The electron gain enthalpy of an element is the amount of energy released when an electron is added to a neutral gaseous atom. The unit of electron affinity = KJ mole⁻¹.
- ❖ Electronegativity The relative tendency of an element present in a covalently bonded molecule, to attract the shared pair of electrons towards itself.
- **❖** Valency It is defined as the combining capacity of an element.
- ❖ Valence electrons The total number of electrons in the valence shell or equal to eight minus the number of valence electrons.
- ❖ Diagonal relationship In a periodic table, a diagonal relationship exists among certain pairs of elements. Thus Li is similar to Mg, Be is similar to Al and B is similar to Si.

- I. Choose the best Answer:
- 1. What would be the IUPAC name for an element with atomic number 222?
- a) bibibiium
- b) bididium
- c) didibium
- d)bibibium
- 2. The electronic configuration of the elements A and B are 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>,3s<sup>2</sup> and 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>5</sup> respectively. The formula of the ionic compound that can be formed between these elements is
- a) AB
- b) AB<sub>2</sub>

- c) A<sub>2</sub>B
- d) none of the above.
- 3. The group of elements in which the differentiating electron enters the anti penultimate shell of atoms are called
- a) p-block elements b) d-block elements c)s-block elements
- d) f-block elements
- 4. In which of the following options the order of arrangement does not agree with the variation of property indicated against it? (NEET 2016 Phase 1)
- a) I < Br < Cl < F (increasing electron gain enthalpy)
- b) Li < Na < K < Rb (increasing metallic radius)
- c)  $Al^{3+} < Mg^{2+} < Na^{+} < F^{-}$  (increasing ionic size)
- d) B < C < O < N (increasing first ionisation enthalpy)
- 5. Which of the following elements will have the highest electronegativity?
- a) Chlorine
- b) Nitrogen
- c) Cesium
- d) Fluorine
- 6. Various successive ionisation enthalpies (in kJ mol<sup>-1</sup>) of an element are given below.

IE <sub>1</sub>	IE <sub>2</sub>	IE <sub>3</sub>	IE <sub>4</sub>	IE <sub>5</sub>
577.5	1,810	2,750	11,580	14,820

#### The element is

- a) phosphorus
- b) Sodium
- c) Aluminium
- d) Silicon
- 7. In the third period the first ionization potential is of the order.
- a) Na > Al > Mg > Si > P
- b) Na < Al < Mg < Si < P
- c) Mg > Na > Si > P > Al
- d) Na < Al < Mg < Si < P
- 8. Identify the wrong statement.
  - a) Amongst the isoelectronic species, smaller the positive charge on cation, smaller is the ionic radius
  - b) Amongst isoelectric species greater the negative charge on the anion, larger is the ionic radius
  - c) Atomic radius of the elements increases as one moves down the first group of the periodic table
  - d) Atomic radius of the elements decreases as one moves across from left to right in the 2nd period of the periodic table.
- 9. Which one of the following arrangements represent the correct order of least negative to most negative electron gain enthalpy
- a) Al < O < C < Ca < F
- b) Al < Ca < O < C < F
- c)  $C \leq F \leq O \leq Al \leq Ca$
- d) Ca < Al < C < O < F

Dedication!	Determination!!		Distinction!!!
	EMISTRY TUITION CENTRE,	•	•
	of electron gain enthalpy	with negative sig	n of F, Cl, Br and I navin
· ·	, 35 and 53 respectively is		
<i>'</i>	b) $F > Cl > Br > I$ c) C		,
11. Which one of the	following is the least electr	onegative elemen	
a) Bromine	b) Chlorine c)	Iodine	d) Hydrogen
12. The element with	positive electron gain enth	nalpy is	3
a) Hydrogen	b) Sodium c) A	Argon	d) Fluorine
13. The correct order	r of decreasing electronega	tivity values amo	ong the elements X, Y, Z
and A with atomic nur	mbers 4, 8, 7 and 12 respect	ively	
a) Y > Z > X > A	b) $Z > A > Y > X$ c) $X$	Z > Y > Z > A	d) $X > Y > A > Z$
14. Assertion: Heliu	m has the highest value of	f ionisation ener	gy among all the element
known			
Reason: Helium has	the highest value of electro	n affinity among	all the elements known
a) Both assertion a	and reason are true and reaso	n is correct explan	nation for the assertion
b) Both assertion	and reason are true but the	reason is not the	correct explanation for th
assertion			•
c) Assertion is tru	ie and the reason is false		
	and the reason are false	1	
<i>'</i>	onfiguration of the atom	having maximu	m difference in first an
second ionisation end	ergies is		
a) $1s^2$ , $2s^2$ , $2p^6$ , $3s^1$	b) 1s <sup>2</sup> , 2s <sup>2</sup> , 2p <sup>6</sup> , 3 2, 3p <sup>6</sup> , 4s <sup>1</sup> d) 1s <sup>2</sup> , 2s <sup>2</sup> , 2p <sup>6</sup> , 3	$3s^2$	
c) $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3s^2$	$^{2}$ 3n <sup>6</sup> 4s <sup>1</sup> d) 1s <sup>2</sup> 2s <sup>2</sup> 2n <sup>6</sup>	$3s^2 3p^1$	
	owing is second most electr		nt?
a) Chlorine	b) Fluorine	c) Oxygen	d) Sulphur
<i>'</i>	are 179 and 348 kcal mol		· •
reaction $Mg \rightarrow Mg^2$		respectively. 1	ne energy required for th
	b) - $169 \text{ kcal mol}^{-1} \text{ c}$ ) +	527 kasl mal <sup>-1</sup>	d) 507 kggl mgl <sup>-1</sup>
			u) - 327 Kcai iiioi
	ne order of screening effect		d) f > - > - > d
_	b) $s > p > f > d$ c) $f > g$	-	d) f > p > s > d
	owing orders of ionic radii	2	1\
a) $H^- > H^+ > H$	b) $Na^+ > F^- > O^{2-}$ c) $F > O^{2-}$		d) None of these
	ntion potential of Na, Mg		6, 737 and 786 kJ mol
	isation potential of Al will		1
a) 760 kJ mol <sup>-1</sup>	<b>b)</b> 575 <b>kJ mol</b> <sup>-1</sup> <b>c)</b> 80		· ·
	following is true about me	etallic character	when we move from left t
right in a period and	top to bottom in a group?		
a) Decreases in a per	iod and increases along the	e group	
b) Increases in a perio	d and decreases in a group		
c) Increases both in th	e period and the group		
d) Decreases both in the	ne period and in the group		

- 22. How does electron affinity change when we move from left to right in a period in the periodic table?
- a) Generally increases

b) Generally decreases

c) Remains unchanged

d)First increases and then decreases

### 23. Which of the following pairs of elements exhibit diagonal relationship?

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- a) Be and Mg
- b) Li and Mg
- c) Be and B
- d) Be and Al

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#### Write Brief Question with Answer

#### 24. Define modern periodic law.

The modern periodic law states that, "the physical and chemical properties of the elements are periodic functions of their atomic numbers."

### 25. What are isoelectronic ions? Give examples.

Ions of different elements having the same number of electrons are called iso electronic ions.

Ions of different elements	Na <sup>+</sup>	Mg <sup>+2</sup>	$Al^{+3}$	F	$O^{2-}$	$N^{3-}$
No. of electrons	10	10	10	10	10	10

#### 26. What is effective nuclear charge?

The net nuclear charge experienced by valence electrons in the outermost shell is called the effective nuclear charge.  $\mathbf{Z}_{\text{eff}} = \mathbf{Z} \cdot \mathbf{S}$ 

Where Z -atomic number 'S' - screening constant

# 27. Is the definition given below for ionisation enthalpy correct? "Ionisation enthalpy is defined as the energy required to remove the most loosely bound electron from the valence shell of an atom"

No the above definition is incorrect.

The correct definition is, Ionisation energy is defined as the <u>minimum amount of</u> energy required to remove the most loosely bound electron from the valence shell of the <u>isolated</u> <u>neutral gaseous atom in its ground state.</u>

# 28. Magnesium loses electrons successively to form Mg<sup>+</sup>, Mg<sup>2+</sup> and Mg<sup>3+</sup> ions. Which step will have the highest ionisation energy and why?

$$Mg + I.E_1 \rightarrow Mg^+ + 1e^-$$
 ----- (i)

$$Mg + I.E_2 \rightarrow Mg^{2+} + 1e^{-}$$
 ----- (ii)  
 $Mg^{2+} I.E_3 \rightarrow Mg^{3+} + 1e^{-}$  ----- (iii)

As Mg<sup>2+</sup> ion having the stable [Ne] inert gas configuration, it requires more energy to loose one electrons and forming Mg<sup>3+</sup> ions. So **third step** will have the highest ionisation energy.

$$I.E_1 > I.E_2 > I.E_3$$

(Or)

•  $Mg^{2+}$  consist of 10 electrons (2, 8) attaining the stable noble gas configuration of Neon (Z = 10)

• Since the valence orbital is completely filled, more energy will be required to remove electrons.

#### 29. Define electronegativity

It is defined as the relative tendency of an element present in a covalently bonded molecule, to attract the shared pair of electrons towards itself.  $\overline{Pa}$ 

# 30. How would you explain the fact that the second ionisation potential is always higher than the ionisation potential?

The total number of electrons are less in the cation than the neutral atom while the nuclear charge remains the same. Therefore the effective nuclear charge of the cation is higher than the corresponding neutral atom. Thus the successive ionisation energies, always increase in the following order  $\mathbf{IE}_1 < \mathbf{IE}_2 < \mathbf{IE}_3 < \dots$ 

# 31. Energy of an electron in the ground state of the hydrogen atom is $-2.18 \times 10^{-18}$ J. Calculate the ionisation enthalpy of atomic hydrogen in terms of kJ mol<sup>-1</sup>

Ionisation energy is the amount of energy required to remove the electron from the ground state ( $E_1$ ) to excited state ( $E_{\infty}$ ).  $E_1 = -2.18 \times 10^{-18} \text{ J}$ ;  $E_{\infty} = 0$ 

$$\Delta \mathbf{E} = \mathbf{E}_{\infty} - \mathbf{E}_{1}$$
 = 0 - (-2.18 × 10<sup>-18</sup> J) = 2.18 × 10<sup>-18</sup> J

I.E per hydrogen atom =  $2.18 \times 10^{-18}$  J

I.E per mole of H-atom =  $2.18 \times 10^{-18} \text{ J} \times 6.023 \times 10^{23}$ 

$$= 13.13 \times 10^5 \,\mathrm{J \, mol^{-1}} = +1313 \,\mathrm{KJ mol^{-1}}$$

# 32. Give the general electronic configuration of atom is one of the important factor which affects the value of ionisation potential and electron gain enthalpy. Explain

- i. Electronic configuration of an atom affects the value of ionization potential and electron gain enthalpy.
- ii. Half-filled valence shell electronic configuration and completely filled valence shell electronic configuration are more stable than partially filled electronic configuration.
- iii. For example: Be (Z=4)  $1s^22s^2$  (Completely filled electronic configuration) N (Z=7)  $1s^22s^22p^3$  (half filled electronic configuration)
- iv. Beryllium, Nitrogen the addition of extra electron will disturb their stable electronic configuration and they have almost zero electron affinity.
- v. Ionisation energy and electron affinity is the amount of energy released or required in pulling out or adding an electron to a neutral atom. So both depend electronic configuration of the element

# 33. In what period and group will an element with Z = 118 will be present?

**Ans:** 7<sup>th</sup> period, 18<sup>th</sup> group.

# **Explanation:**

$$(Z = 118; [_{86}Rn] 5f^{14} 6d^{10} 7s^2 7p^6$$

In the periodic table the element with Z = 118 is located in p – block. Period no. = 7 (as n = 7 for valence shell)

Group no. = 18 (group no = 10 + ns electrons + np electrons) (n – outer most shell))

 $P_{age}33$ 

Dedication! Determination!! Distinction!!!

(ACTC) ADVANCED CHEMISTRY TUITION CENTRE, 41/1 PWD ROAD, NAGERCOIL, 9952340892. 34. Justify that the fifth period of the periodic table should have 18 elements on the basis of quantum numbers.

- i. According to Aufbau's principle 5<sup>th</sup> period has nine orbital (one 5s, five 4d and three 6p) to be filled.
- ii. Nine orbitals can accommodate a maximum of 18 electrons. Hence fifth period of the periodic table should has 18 elements from rubidium (2 = 37) to Xenon (Z = 54).

#### 35. Elements a, b, c and d have the following electronic configuration:

$$a: 1s^2, 2s^2, 2p^6$$

$$b: 1s^2, 2s^2, 2p^6, 3s^2, 3p^1$$

$$c: 1s^2, 2s^2, 2p^6, 3s^2, 3p^6$$

$$d:1s^2,2s^2,2p^1$$

# Which group of element among will belongs to the same group of the periodic table

Elements of a and c belongs to group 18; Elements of b and d belongs to group 13

### 36. Give the general electronic configuration of lanthanides and actinides

Lanthanides :  $[_{54}Xe] 4f^{1-14} 5d^{0-1} 6s^2$ Actinides :  $[_{86}Rn] 5f^{0-14} 6d^{0-2}7s^2$ 

#### 37. Why halogens acts as a oxidizing agents

- i. (i) Due to low bond dissociation enthalpy, high electronegativity and large negative electron gain enthalpy halogens have a strong tendency to accept electron and thus get reduced  $X_2 + 2e^- \rightarrow 2X^-$
- ii. (ii) The ready acceptance of the electron is due to the strong oxidising nature of the the halogens.
- iii. F<sub>2</sub> is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. In general, a halogen oxidises halide ions of higher atomic number
- iv. Hence, the oxidising ability of halogens decreases from fluorine to iodine as:

$$F_2 > Cl_2 > Br_2 > I_2$$

# 38. Mention any two anomalous properties of second period elements.

- i. Lithium and Beryllium form more covalent compounds, unlike the alkali and alkali earth metals which predominantly form ionic compounds.
- ii. The elements of the second period have only four orbitals (2s & 2p) in the valence shell and have a maximum co-valence of 4, whereas the other members of the subsequent periods have more orbitals in their valence shell and shows higher valences.

For example, boron forms BF<sub>4</sub> and aluminium forms AlF<sub>6</sub><sup>3</sup>-

# 39. Explain the pauling method for the determination of ionic radius.

#### **Ionic radius:**

**Definition:** The distance from the centre of the nucleus of the ion upto which it exerts its influence on the electron cloud of the ion.

Ionic radius of uni-univalent crystal can be calculated using Pauling's method from the interionic distance between the nuclei of the cation and anion. Ex: NaF, KCl, RbBr, CsI

i. Pauling assumed that ions present in a crystal lattice are perfect spheres, and they are in contact with each other therefore,

$$d = r_C^+ + r_A^-$$
 ----- (1)

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**Where** d - the distance between the centre of the nucleus of cation  $C^+$  and anion  $A^-$ .

 $r_{\text{C+}},\,r_{\text{A}}^{-}\,\,$  - the radius of the cation and anion respectively .

Pauling also assumed that the radius of the ion having noble gas electronic configuration is inversely proportional to the effective nuclear charge.

$$r_{C}^{+} \alpha \frac{1}{(z_{eff})_{C^{+}}}$$
 ----- (2)  
 $r_{A}^{-} \alpha \frac{1}{(z_{eff})_{A^{-}}}$  ----- (3)

Where  $Z_{eff}$  is the effective nuclear charge and  $Z_{eff} = Z - S$ 

Dividing the equation 2 by 3

$$\frac{r_{C^{+}}}{r_{A^{-}}} = \frac{(Z_{eff})_{A^{-}}}{(Z_{eff})_{C^{+}}} \qquad ------ (4)$$

On solving equation and (1) and (4) the values of  $r_C^+$  and  $r_{A^-}$  can be obtained.

# 40. Explain the periodic trend of ionisation potential.

The energy required to remove the most loosely held electron from an isolated gaseous atom is called as ionisation potential.

#### Variation along a period:

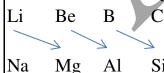
- Ionisation energy usually *increases along a period*.
- This is due to *increase of nuclear charge* and *decrease in size* as we move from left to right in a period.

#### Periodic variation in group:

- Ionisation energy decreases down a group.
- A gradual increase in atomic size.
- As we move down a group, the valence electron occupies new shells, the distance between the nucleus and the valence electron increases.
- So, nuclear forces of attraction on valence electron decreases and hence ionisation energy also decreases down a group.

### 41. Explain the diagonal relationship.

- On moving diagonally across the periodic table the second and third period elements show certain similarities.
- Even though the similarity is not same as we see in a group, it is quite pronounced in the following pair of elements.



• The similarity in properties existing between the diagonally placed elements is called diagonal relationship.

# 42. Why the first ionisation enthalpy of sodium is lower than that of magnesium while its second ionisation enthalpy is higher than that of magnesium?

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The electronic configuration of sodium (Z = 11)  $1s^2 2s^2 2p^6 3s^1$ 

Magnesium (Z = 12) 
$$1s^2 2s^2 2p^6 3s^2$$

Magnesium atom has a *smaller radius* and *higher nuclear charge* than a sodium atom, thus more energy will be required to remove the electron from the same orbital (3s), making.

The first ionisation energy of magnesium higher than that of sodium.

However, the second ionization enthalpy of sodium is higher than that of magnesium This is because after losing 1 electron, sodium attains the stable noble gas configuration of neon  $(1s^2 2s^2 2p^6)$ . On the other hand, magnesium, after losing 1 electron still has one electron in the 3s- orbital $(1s^2 2s^2 2p^6 3s^1)$ . In order to attain the stable noble gas configuration, Thus, the energy required to remove the second electron in case of sodium is much higher than that required in case of magnesium. Hence, the second ionization enthalpy of sodium is higher than that of magnesium.

43. By using paulings method calculate the ionic radii of  $K^+$  and  $C\Gamma$  ions in the potassium chloride crystal. Given that  $d_{K+-Cl-}=3.14$  Å

$$r(K^{+}) + r(C\Gamma) = d(K^{+} - C\Gamma) = 3.14 \text{ Å}$$
 ----- (1)

The effective nuclear charge for K+ and Cl- can be calculated as follows.

$$K^+ = (1s^2)$$
  $(2s^2 2p^6)$   $(3s^2 3p^6)$   
Innershell  $(n-1)^{th}$  shell  $n^{th}$  shell

$$Z^*(K-) = Z - S$$
= 19 - [ (0.35 \times 7) + (0.85 \times 8) + (1 \times 2)]
= 19 - 11.25 = 7.75

$$Z^*(Cl^-) = 17 - [(0.35 \times 7) + (0.85 \times 8) + (1 \times 2)]$$

$$= 17 - 11.25 = 5.75$$

$$\frac{r(K^+)}{r(Cl^-)} = \frac{Z^*(Cl^-)}{T^*(K^+)} = \frac{5.75}{7.75} = 0.74$$

$$\mathbf{r}(\mathbf{C}\mathbf{l}^{-}) = \mathbf{z}^{*}(\mathbf{K}^{+}) = 7.75 = 0.74$$
  
 $\mathbf{r}(\mathbf{K}^{+}) = \mathbf{0.74} \ \mathbf{r}(\mathbf{C}\mathbf{l}^{-}) = \mathbf{0.74} \mathbf{r}(\mathbf{C}\mathbf{l}^{-})$ 

Substitute (2) in (1)

$$0.74 \text{ r(Cl}) + \text{r(Cl}) = 3.14 \text{ Å}$$

$$0.74 \text{ r(Cl}) = 3.14 \text{ Å};$$

$$\text{r(Cl}) = \frac{3.14A}{1.74} = 1.81\text{ Å}$$

- 44. Explain the following, give appropriate reasons.
  - (i) Ionisation potential of N is greater than that of O.
- (ii) First ionisation potential of C-atom is greater than that of B atom, where as the reverse is true is for second ionisation potential.
- (iii) The electron affinity values of Be, Mg and noble gases are zero and those of N  $(0.02\,$  eV) and P  $(0.80\,$  eV) are very low
- (iv) The formation of  $F^{\text{-}}_{(g)}$  from  $F_{(g)}$  is exothermic while that of  $O^{2\text{-}}_{(g)}$  from  $O_{(g)}$  is endothermic.
  - i. Electron configuration of nitrogen (Z = 7)  $1s^2 2s^2 2p^3$ Electron configuration of oxygen (Z = 8)  $1s^2 2s^2 2p^4$

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Dedication! Determination!! Distinction!!!

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Nitrogen has a half filled electronic configuration and its more stable. Due to stability, ionisation energy of nitrogen is high.

Hence nitrogen would require more ionization energy to remove an electron from it's outer shell than oxygen.

Electron configuration of Carbon (Z = 6)  $1s^2 2s^2 2p^2$ Electron configuration of Boron (Z = 5)  $1s^2 2s^2 2p^1$ 

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- The size of a carbon atom is smaller than boron. So the valence electron of carbon has greater nuclear charge than that of boron.
- Hence the first I.E of carbon is greater than that of boron.
- However, the second ionization enthalpy of boron is higher than that of carbon.
- This is because after losing 1 electron, Boron has a fully filled orbital (2s<sup>2</sup>) than carbon (2p1). Fully filled orbitals have more stability than partially filled orbitals so greater amount of energy will be needed to remove an electron from boron. So in this case, the second I.E of boron is higher than that of carbon.
- The electron affinities of Be, Mg and noble gases are almost zero.

Be  $(Z=4: 1s^2 2s^2)$  and

Mg (Z = 12;  $1s^2 2s^2 2p^6 3s^2$ ) are having s fully filled in their valence shell.

- Fully filled orbitals are most stable due to symmetry.
- Therefore, these elements would be having least tendency to accept electron.

Hence, Be and Mg would be having zero electron affinity.

• N (Z = 7;  $1s^2 2s^2 2px^1 2py^1 2pz^1$ ) and

 $P(Z = 15) 1s^2 2s^2 2p^6 3s^2 3p^3$  is having half-filled 2p- subshell.

- Half-filled sub shells are *most stable due to symmetry* (Hund's rule).
- Thus, nitrogen and phosphorous are having least tendency to accept electron.

Hence, have low electron affinity.

iv. 
$$F(Z = 9) 1s^2 2s^2 2p^5$$

Fluorine is *highly electro negative* in nature therefore as it gains the one electron to attain the nearest inert gas configuration, become stable and releases the energy so exothermic.

$$O(Z = 8) 1s^2 2s^2 2p^4$$

While in oxygen the addition of first electron is exothermic in nature but addition of second electron experiences high repulsive force. So needs extra external energy to enter outer shell, hence endothermic in nature.

# 45. What is screening effect?

**Screening effect:** The repulsive force between the inner shell electrons and the valence electrons leads to a decrease in the electrostatic attractive forces acting on the valence electrons by the nucleus. Thus, the inner shell electrons act as a shield between the nucleus and the valence electrons. This effect is called shielding effect (or) Screening effect.

46. Briefly give the basis for pauling's scale of electronegativity.

**Pauling's scale:** Pauling, he assigned arbitrary value of electro negativities for hydrogen and fluorine as 2.2 and 4.0 respectively. Based on this the electronegativity values for other elements can be calculated using the following expression.

$$(X_A - X_B) = 0.182 \sqrt{E_{AB}} - (E_{AA} * E_{BB})^{\frac{1}{2}}$$

Where  $E_{AB}$ ,  $E_{AA}$  and  $E_{BB}$  are the bond dissociation energies of AB,  $A_2$  and  $B_2$  molecules respectively.

The electronegativity of any given element is not a constant and its value depends on the element to which it is covalently bound.

The electronegativity values play an important role in predicting the nature of the bond.

Pauling assigned arbitrary value of electro negativities for hydrogen and fluorine as 2.1 and 4.0 respectively.

# 47. State the trends in the variation of electronegativity in group and periods.

#### (i) Variation of Electronegativity in a period:

- The electronegativity generally *increases across a period from left to righ*t.
- The atomic radius decreases in a period, as the attraction between the valence electron and the nucleus increases.
- Hence the tendency to attract shared pair of electrons increases.
- Therefore, electronegativity also increases in a period.

#### (ii) Variation of Electronegativity in a group:

- The electronegativity generally *decreases down a group*.
- As we move down a group the atomic radius increases and the nuclear attractive force on the valence electron decreases.
- Hence, the electronegativity decreases.

