DAY EIGHTEEN

Classification and Periodicity of Elements

Learning & Revision for the Day

- Earlier Attempts to Classify the Elements
- Periodic Law and Present form of Periodic Table
- Classification of Elements
- Periodic Trends in Properties of Elements

Earlier Attempts to Classify the Elements

Many attempts were made to classify the known elements from time to time. These are Prout's hypothesis, Dobereiner triads, Newland's law of octaves, Lothar Meyer's atomic volume curve, Mendeleef's periodic law (1869). The properties of elements are periodic functions of their atomic weight's and modern periodic law.

Modern Periodic Law and Present form of Periodic Table

- Henry Moseley showed that the atomic number is a more fundamental property of an element than its atomic mass and formulated modern periodic law.
- Modern periodic law can be stated as the physical and chemical properties of the elements. These are periodic functions of their atomic number.
- Modern periodic table is also called Bohr's periodic table and it is just graphical representation of Aufbau principle.
- In this table, elements are arranged in increasing order of atomic number (Z). The isotopes. These are all grouped together as they have the same atomic number.
- The table contains 7 periods (representing 7 orbits) and 18 groups (1-18). The concept of subgroup A and B is removed and groups are given number 1 to 18. The name of zero group is changed to group 18.

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	18			Argon	39.948 36 G Krypton	54 G Xenon	86 G Radon	118 X Ununoctium		71 S Lutetium 174.967	103 X Lr Lawrencium (262)
	- 17 MIN	VIB VIB	P Fluorine							Ytterbium 173.04	102 X Nobelium (259)
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	Group	Period	7	3	4	5	9	7			

Periodic Table

Classification of Elements

Depending upon the orbital in which last electron enters, the elements are classified as follows:

1. s-Block Elements

- Group I (alkali metals) and group II (alkaline earth metals) elements belong to this block, their last electron enters in *s*-orbital.
- General electronic configuration of *s*-block elements is ns^{1-2} .

2. p-Block Elements

- Groups 13th to 18th excluding He, belong to this block. Their last electron enters in *p*-block.
- General electronic configuration of *p*-block elements is ns^2 , np^{1-6} .
- *s* and *p*-block elements are known as representative elements or main group elements.

Diagonal Relationship

The first member of each group of *s* and *p*-block elements shows different characteristics from the rest of the members of the same group.

However, the first three elements of second period (Li, Be, B) shows diagonal similarity with elements (Mg, Al, Si) of third period placed on the right hand side. This is called diagonal relationship.

3. d-Block or Transition Elements

- Elements of group 3rd to 12th in periodic table belong to *d*-block. Their last electron enters in *d*-block.
- Two outermost shells of *d*-block elements are incomplete.
- General electronic configuration of *d*-block elements is $(n-1)d^{1-10} ns^{0-2}$

4. f-Block or Inner-Transition Elements

- General configuration $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$.
- Last electron enters in *f*-orbital.
- Two series 4f (lanthanoids) and 5f (actinoids).
- Also known as rare earth elements.

IUPAC Nomenclature of Elements with Atomic Number >100

The names are derived by using roots for the three digits in the atomic number of the elements followed by adding '-ium' at the end. The roots for the numbers are as:

S.No.	Digit	Name	Abbreviation
1.	0	nil	n
2.	1	un	u
3.	2	bi	b
4.	3	tri	t
5.	4	quad	q
6.	5	pent	р
7.	6	hex	h
8.	7	sept	S
9.	8	oct	0
10.	9	enn	е
e.g.			
Atomic number 101	un-nilur		

Periodic Trends in Properties of Elements

The elements in the periodic table are arranged in order of increasing atomic number. All of these elements display several other trends and we can use the periodic law and table formation to predict their chemical, physical and atomic properties. Some of the physical and chemical properties of the elements are discussed below :

1. Atomic Radius

Atomic radius is defined as the distance from the centre of the nucleus to the outermost shell containing electrons. It is referred to both covalent or metallic radius depending on whether the element is a non-metal or a metal. On moving left to right in a period atomic radii decreases; on moving down the group atomic radii increases. Atomic radii are of three types

(i) Covalent radius

(a) In homodiatomic molecule, (A - A)

$$r = \frac{n - n}{2}$$

- d_{A-A} = bond length or distance between two covalently bonded atoms.
- (b) In heterodiatomic molecule (A B): When $(\chi_A - \chi_B)$ is very small : Bond length $= d_{A-B} = r_A + r_B$

 r_A and r_B = covalent radii of A and B respectively

 χ_A and χ_B = electronegativities of A and B

When
$$(\chi_A - \chi_B)$$
 is considerable.

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

- (ii) Metallic radius, $r' = \frac{d}{2}$, where r' >actual size of atom
 - where, d = distance between the adjacent metal ions in the metallic lattice
- (iii) van der Waals' radius, $r_1 = \frac{d}{2}$

where, d = distance between the nuclei of identical two non-bonded isolated atoms.

 $r_1 >>>$ actual size of atom

Covalent radius < Metallic radius

< van der Waals' radius

At the end of the period, atomic radii of inert gases are exceptionally large because they do not form molecule and their radii are simply van der Waals' radii.

2. Ionic Radius

- Distance of the outermost shell of an ion from its nucleus is called ionic radius.
- Cationic radii is always smaller than its neutral atom while an ionic radii is always greater than its neutral atom.
- Greater the negative charge on ion, larger is its radii, e.g. $O^{2-} > O^- > O$.
- For isoelectronic species [possess same number of electrons] ionic radii $\sim \frac{1}{\text{magnitude of nuclear charge}}$

3. Ionisation Enthalpy

It is the energy required when an electron is removed from the outermost orbit from an isolated gaseous atom, so as to convert it into gaseous cation.

Generally left to right in period IE increases; down the group it decreases but half-filled orbitals and fully-filled orbitals are highly stable and thus, have high IE.

Various factors with which ionisation energy varies are:

- (i) Atomic size : varies inversely
- (ii) Screening effect : varies inversely
- (iii) Nuclear charge : varies directly
- Helium has the highest IE₁ while Cs has the lowest.
- IE values of inert gases are exceptionally higher due to stable configuration and smaller size while alkali metals have lowest IE values due to their large size.
- IE₁ of group 2 elements is greater than corresponding elements of group 13 due to their fully-filled *s*-orbitals.
- The effective nuclear charge experienced by valence electron in an atom will be less than the actual charge on the nucleus because of "shielding" or "screening" electrons

of the valence electron from the nucleus by intervening electrons.

• Shielding (or **screening effect**) is the repulsion of valence electrons by the electrons in penultimate shell to reduce effective nuclear charge.

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

where, *Z* = atomic number, σ = shielding constant σ = [0.35 × number of electrons in *n*th shell excluding last (valence) electron] + [0.85 × number of electrons in $(n - 1)^{\text{th}}$ shell] + [1.0 × number of electrons in inner shell]

4. Electron Gain Enthalpy

- It is the energy released when an electron is added to an isolated gaseous atom to form gaseous anion.
- Electron gain enthalpy increases [or becomes more negative] across the period while it decreases down the group.
- Chlorine has the highest electron affinity but oxidising power of fluorine is larger than chlorine.
- Various factors affecting electron gain enthalpy are:
 (i) Atomic size : varies inversely
 - (ii) Nuclear charge : varies directly
 - (iii) Configuration : Half-filled orbitals and fully-filled orbitals are highly stable, therefore electron gain enthalpy will be low.
- F and O-atoms have small size and high charge density, therefore have lower electron gain enthalpy.
- Electron gain enthalpies of elements of group 2 and 15 is low because of their stable half-filled configuration but for group 18 it is positive because of complete shell.

5. Electronegativity

- It is the tendency of an atom to attract the shared pair of electrons towards itself in a covalent bond. F is the most electronegative element while Cs is the least.
- Decreasing order of electronegativity

$$F > O > Cl \approx N > Br > S \approx C > I > H$$

In periods : left to right electronegativity increases.

In groups : down the group electronegativity decreases.

Measurement of Electronegativity

Some important scales to measure electronegativity of elements are

(i) Pauling Scale

Difference in the electronegativities of two atoms (*A* and *B*), $\chi_A - \chi_B = 0.102 \sqrt{\Delta}$

where, Δ = actual bond energy – energy for 100% covalent bond.

$$\therefore \qquad \Delta = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$$

Here, E_{A-B} = dissociation enthalpy of A - B (kcal mol⁻¹)

$$E_{A-A}$$
 = dissociation enthalpy of $A - A$ (kcal mol⁻¹)

 E_{B-B} = dissociation enthalpy of B - B (kcal mol⁻¹)

(ii) Mulliken's Scale

• Representation of Mulliken's scale is

$$\chi_M = \frac{\text{IE} + \text{EA}}{2}$$

• Mulliken values are ≈ 2.8 times greater than Pauling values

$$\chi_p = \frac{1E + EA}{5.6}$$
 or $\chi_p = 0.336 [\chi_M - 0.615]$

- Unit of electronegativity = eV
- For noble gases, its value is taken as zero.

NOTE *sp* hybridised carbon is more electronegative than a sp^2 hybridised carbon, which in turn is more electronegative than sp^3 hybridised carbon.

6. Valency

- The valency of an element is related to the electronic configuration of its atom and usually determined by electrons present in valence shell (outer shell).
- In a period, valency of the elements with respect to hydrogen increases from 1 to 4 upto 14th group and then decreases to 1. e.g. NaH, CaH_2 , AlH_3 , SiH_4 , PH_3 , H_2S , HCl.

But valency of the elements with respect to oxygen increases from one to seven along a period. e.g. Na₂O, CaO, Al_2O_3 , SiO_2 , P_4O_{10} , SO_3 , Cl_2O_7

- All elements in a group have same valency as they have same number of electrons in their outer shell.
- *p*-block elements show variable valency on account of inert pair effect.

- Term oxidation state is also being used for covalence, which indicates the actual charge on atom in that particular molecule. It follows the same trend along period or group as valence.
- NOTE Tin has maximum number of isotopes (10 in number) and Os has the highest oxidation state or valence (+8).
- Transition metals and inner-transition metals show variable valence of 1, 2 or 3 as they use electrons from outer as well as penultimate or inner-penultimate shell.

7. Chemical Reactivity

- Reactivity of metals increases with decrease in ionisation energy, electronegativity and increase with atomic radii and electropositive character. Reactivity of non-metals increases with increase in electronegativity and electron gain enthalpy and decreases with increase in atomic radii.
- On moving down the group, reactivity of metals increases while for non-metals it decreases.
- Reactivity of metals decreases while reactivity of non-metals increases across the period.
- The reducing character of the elements increases down the group. The oxidising character of the element decreases down the group. Alkali metals are most reactive, strongest reducing agent and have lowest ionisation enthalpy. Halogen are most reactive strongest oxidising agent and have higher ionisation enthalpy.
- Metals form basic oxides while non-metals form acidic oxides. Basic strength of the oxides or hydroxides increases down the group. Acidic nature of oxides increases along a period. Almost all metallic oxides are basic but ZnO and Al_2O_3 are amphoteric. Similarly non-metallic oxides are acidic but CO, N_2O and NO are neutral. Cl_2O_7 is the most acidic oxide.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

- **1** The period number in the long form of the periodic table is equal to
 - (a) magnetic quantum number of any element of the period
 - (b) atomic number of any element of the period
 - (c) maximum principal quantum number of any element of the period
 - (d) maximum azimuthal quantum number of any element of the period
- **2** Which pair of atomic number of elements has same chemical properties?

(a) 13, 22	(b) 3, 11	(c) 4, 24	(d) 2, 4
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- Both lithium and magnesium display several similar properties due to the diagonal relationship: however, the one which is incorrect is → JEE Main 2018
 - (a) both form basic carbonates
 - (b) both form soluble bicarbonates
 - (c) both form nitrides
 - (d) nitrates of both Li and Mg yield NO_2 and O_2 on heating
- **4** Atomic radii of fluorine and neon (in Å) are respectively given by
 - (a) 0.72, 1.60 (c) 0.72, 0.72
- (b) 1.60, 1.60 (d) None of these

5 Which one of the following ions has the highest value of ionic radius?

(a) Li^+ (b) B^{3+} (c) F^- (d)	d) O ²⁻
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6 Which of the following series of elements have nearly the same atomic radii?

(a) F, Cl, Br, I	(b) Na, K, Rb, Cs
(c) Li, Be, B, C	(d) Fe, Co, Ni, Cu

7 Chloride ion and potassium ion are isoelectronic, then

(a) their sizes are same

- (b) Cl⁻ ion is bigger than K⁺ ion
- (c) K⁺ ion is relatively bigger
- (d) their sizes depend on other cation and anion
- ${\pmb 8}$ The ions $O^{2-}, F^-, Na^+, Mg^{2+}$ and Al^{3+} are isoelectronic. Their ionic radii show
 - (a) an increase from O^{2-} to F $^-$ and then decrease from Na^+ to AI^{3+}
 - (b) a decrease from O^{2-} to F^- and then increase from Na^+ to Al^{3+}
 - (c) a significant increase from O^{2-} to AI^{3+}
 - (d) a significant decrease from O^{2-} to AI^{3+}
- 9 The ionic radii (in Å) of N³⁻,O²⁻ and F⁻ respectively are → JEE Main 2015
 - (a) 1.36,1.40 and 1.71 (b) 1.36,1.71 and 1.40 (b) 1.71,1.40 and 1.36 (d) 1.71,1.36 and 1.40
- 10 The increasing order of the ionic radii of the given isoelectronic species is → AIEEE 2012
 (a) Cl⁻ Ca²⁺ K⁺ S²⁻
 (b) S²⁻ Cl⁻ Ca²⁺ K⁺

(a) CL, Ca ⁻⁺ , K ⁺ , S ⁻	(b) S ⁻ , CL, Ca ⁻⁺ , K ⁺
(c) Ca ²⁺ , K ⁺ , Cl ⁻ , S ²⁻	(d) K ⁺ , S ²⁻ , Ca ²⁺ , Cl ⁻

- 11 The correct sequence which shows decreasing order of the ionic radii of the elements is → AIEEE 2010
- **12** Which of the following properties shows a clear periodic variation along a group?
 - (a) First ionisation energy
 - (b) Molar mass of the element
 - (c) Number of isotopes of the atom
 - (d) All of the above
- 13 Which of the following atoms has the highest first ionisation energy? → JEE Main 2016
 (a) Na
 (b) K
 (c) Sc
 (d) Rb
- **14** Generally the first ionisation energy increases along a period. But there are some exceptions. One which is not an exception is
 - (a) N and O $\,$ (b) Na and Mg $\,$ (c) Mg and Al (d) Be and B $\,$
- **15** A sudden jump between the values of second and third ionisation energy will be associated with the electronic configuration

(a)
$$1s^2$$
, $2s^2 2p^6$, $3s^1$ (b) $1s^2$, $2s^2 2p^6$, $3s^2 3p^1$
(c) $1s^2$, $2s^2 2p^6$, $3s^2 3p^6$ (d) $1s^2$, $2s^2 2p^6$, $3s^2$

- **16** The first ionisation potential of Na, Mg and Si are respectively 496,737 and 786 kJ mol⁻¹. The ionisation potential of Al will be closer to

 (a) 760 kJ mol⁻¹
 (b) 575 kJ mol⁻¹
 (c) 801 kJ mol⁻¹
 (d) 419 kJ mol⁻¹
- 17 Which of the following represents the correct order of increasing first ionisation enthalpy for Ca, Ba, S, Se and Ar? → JEE Main 2013
 (a) S < Se < Ca < Ba < Ar
 (b) Ba < Ca < Se < S < Ar
 (c) Ca < Ba < S < Se < Ar
 (d) Ca < S < Ba < Se < Ar
- 18 The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na⁺ will be → JEE Main 2013 (a) 5.1 eV (b) 10.2 eV (c) + 2.55 eV (d) 2.55 eV
- **19** The correct order of first ionisation potential of carbon, nitrogen, oxygen and fluorine is
 (a) C > N > O > F
 (b) O > N > F > C
 (c) O > F > N > C
 (d) F > N > O > C
- **20** The electronic configuration of four elements are given
below. Arrange these elements in the correct order of
magnitude (without sign) of their electron affinity.
I. $2s^2 2p^5$ II. $3s^2 3p^5$ III. $2s^2 2p^4$ IV. $3s^2 3p^4$

 $Select the correct answer using the codes given below : \\ (a) \ I < II < IV < III \\ (b) \ II < I < IV < III \\ (c) \ I < III < IV < II \\ (d) \ III < IV < I < II \\ \end{cases}$

- **21** Which is the correct order of second ionisation potential of C, N, O and F in the following? \rightarrow JEE Main (Online) 2013 (a) O > N > F > C (b) O > F > N > C(c) F > O > N > C (d) C > N > O > F
- **22** The successive ionisation energy values for an element are given below:
 - I. 1st ionisation energy = 410 kJ mol^{-1}
 - II. 2nd ionisation energy = 820 kJ mol⁻¹
 - III. 3rd ionisation energy = 1100 kJ mol^{-1}
 - IV. 4th ionisation energy = 1500 kJ mol^{-1}
 - V. 5th ionisation energy = 3200 kJ mol^{-1}

Find out the number of valence electron for the atom *x*. (a) 4 (b) 3 (c) 5 (d) 2

- 23 The incorrect statements among the following is(a) the first ionisation potential of Al is less than the first ionisation potential of Mg
 - (b) the second ionisation potential of Mg is greater than the second ionisation potential of Na
 - (c) the first ionisation potential of Na is less than the first ionisation potential of Mg
 - (d) the third ionisation potential of Mg is greater than the third ionisation potential of Al
- **24** Two elements whose electronegativities are 1.2 and 3.0, the bond formed between them would be

(a) ionic	(b) covalent
(c) coordinate	(d) metallic

25 AB is predominantly ionic as A⁺B⁻ if (IE stands for ionisation energy, EA for electron affinity and EN for electronegativity). Then,

(a)
$$(IP)_A < (IP)_B$$
 (b) $(EA)_A < (EA)_B$
(c) $(EN)_A < (EN)_B$ (d) $(IP)_B < (IP)_A$

26 What will be the electronegativity of carbon at Pauling scale?

Given that $E_{\rm H-H} = 104.2 \text{ kcal mol}^{-1}$,

$$E_{\rm C-C} = 83.1 \,\rm kcal \,\rm mol^{-1}$$

 $E_{\rm C}$ —H = 98.8 kcal mol⁻¹

Electronegativity of	hydrogen = 2.1
(a) 0.498	(b) 0.598
(c) 2.134	(d) 2.598

- **27** The statement that is not correct for the periodic classification of elements, is
 - (a) the properties of the elements are the periodic function of their atomic number
 - (b) non-metallic elements are lesser in number than metallic elements
 - (c) the first ionisation energies of elements along a period do not vary in a regular manner with increase in atomic number
 - (d) for transition elements the *d*-subshells are filled with electrons monotonically with increase in atomic numbers
- **28** Match the element (in Column I) with its unique properties (in Column II).

Column I		Column II
F	1.	Maximum ionisation energy
CI	2.	Maximum electronegativity
Fe	З.	Maximum electron affinity
He	4.	Recently named by IUPAC
Ds	5.	Variable valence
	Fe	CI 2. Fe 3. He 4.

Codes

А	В	С	D	Е	
(a) 5	4	1	2	3	
(b) 3	4	2	1	5	
(c) 2	3	5	1	4	
(d) 3	1	4	2	5	

29 Valence electrons in the element *A* are 3 and that in element *B* are 6. Most probable compound formed from *A* and *B* is

(a) <i>A</i> ₂ <i>B</i>	(b) <i>AB</i> ₂
(c) <i>A</i> ₆ <i>B</i> ₃	(d) <i>A</i> ₂ <i>B</i> ₃

30 The oxide of an element whose electronic configuration is $1s^22s^22p^63s^1$ is

(a) neutral	(b) amphoteric
(c) basic	(d) acidic

31 Which among the following factors is the most important in making fluorine the strongest oxidising agent ?

(a) Electron affinity	(b) Ionisation enthalpy
(c) Hydration enthalpy	(d) Bond dissociation energy

- **32** The element with which of the following outer electron configuration may exhibit the largest number of oxidation states in its compounds \rightarrow JEE Main (Online) 2013 (a) $3d^54s^2$ (b) $3d^84s^2$ (c) $3d^74s^2$ (d) $3d^64s^2$
- Which one of the following orders present the correct sequence of the increasing basic nature of the given oxides? → AIEEE 2011

 (a) Al₂O₃ < MgO < Na₂O < K₂O
 (b) MgO < K O < ALO → Na O

(b) MgO< K₂O< Al₂O₃ < Na₂O (c) Na₂O< K₂O< MgO< Al₂O₃ (d) K₂O< Na₂O< Al₂O₃ < MgO

34 Considering the elements F, Cl, O and N, the correct order of their chemical reactivity in terms of oxidising property is

(a) F> CI> O> N	(b) F> O> CI> N
(c) CI> F> O> N	(d) O> F> N> Cl

Direction (Q. Nos. 35-39) In the following questions, Assertion (A) followed by a Reason (R) is given. Choose the correct answer out of the following choices.

- (a) Assertion and Reason both are correct statements and Reason is the correct explanation of the Assertion
- (b) Assertion and Reason both are correct statements but Reason is not the correct explanation of the Assertion
- (c) Assertion is correct incorrect and Reason is incorrect
- (d) Both Assertion and Reason are incorrect
- **35** Assertion (A) Boron has a smaller first ionisation enthalpy than beryllium.

Reason (R) The penetration of 2s electron to the nucleus is more than the 2p electron hence 2p electron is more shielded by the inner core of electrons than the 2s electrons.

36 Assertion (A) Electron gain enthalpy becomes less negative as we go down a group.

Reason (R) Size of the atom increases on going down the group and the added electron would be farther from the nucleus.

- 37 Assertion (A) Cesium and fluorine both reacts violently.Reason (R) Cesium is most electropositive and fluorine is most electronegative.
- **38** Assertion (A) The atomic radii of the elements of the oxygen family are smaller than the atomic radii of the corresponding elements of the nitrogen family.
 Reason (R) The members of the oxygen family are more electronegative and thus, have lower values of nuclear charge than those of the nitrogen family.
- **39** Assertion (A) Fluorine has a less negative electron affinity than chlorine.

Reason (R) There is relatively greater effectiveness of 2p electrons in the small fluorine atom to repel the additional electron entering the atom than to 3p electrons in the larger Cl atom.

(Day practice session 2)

PROGRESSIVE QUESTIONS EXERCISE

1 The formation of the oxide ion, O²⁻ (*g*) from oxygen atom requires first an exothermic and then an endothermic step as shown below:

 $O(g) + e^- \rightarrow O^-(g); \Delta H^{\ominus} = -141 \text{ kJ mol}^{-1}$ $O^-(g) + e^- \rightarrow O^{2-}(g); \Delta H^{\ominus} = +780 \text{ kJ mol}^{-1}$

Thus, process of formation of O^{2-} in gas phase is unfavourable even though O^{2-} is isoelectronic with neon. It is due to the fact that,

- (a) oxygen is more electronegative
- (b) addition of electron in oxygen results in larger size of the ion
- (c) electron repulsion outweights the stability gained by achieving noble gas configuration
- (d) $\ensuremath{\mathsf{O}^-}$ ion has comparatively smaller size than oxygen atom
- **2** The increasing order of the first ionisation enthalpies of the elements B, P, S, and F is

(a) F < S < P < B	(b) P < S < B < F
(c) B < P < S < F	(d) B < S < P < F

3 *A*, *B*, *C* are elements in the third short period. Oxide of *A* is ionic, that of *B* is amphoteric and of *C* a giant molecule. *A*, *B* and *C* will have atomic number in the order

(a) <i>A</i> < <i>B</i> < <i>C</i>	(b) <i>C</i> < <i>B</i> < <i>A</i>
(c) <i>A</i> < <i>C</i> < <i>B</i>	(d) <i>B</i> < <i>A</i> < <i>C</i>

- **5** Mixture containing aqueous Li⁺ , Na⁺, K⁺ ions are electrolysed. Cations are discharged at cathode in the order

	$M^{+}(aq) + e^{-}$	$\longrightarrow M$
(a) Li ⁺ , Na ⁺ , K ⁺		(b) K ⁺ , Na ⁺ , Li ⁺
(c) Li ⁺ , K ⁺ , Na ⁺		(d) Na ⁺ , K ⁺ , Li ⁺

6 The electronic configuration of an element is $1s^22s^22p^6$, $3s^23p^3$. The atomic number and the group number of the element '*X*' which is just below the above element in the periodic table are respectively

(a) 23 and 5 (b) 23 and 15 (c) 33 and 15 (d) 33 and 5

- **7** The atomic number of elements *A*, *B*, *C* and *D* are Z 1, Z, Z + 1 and Z + 2 respectively. If *B* is a noble gas, choose the correct option from the following options.
 - I. A has highest electron affinity
 - II. C exists in +2 oxidation state
 - III. *D* is an alkaline earth metal
 - (a) I and II (b) II and III (c) I and III (d) I,II and III

- **8** Ionisation potential and electron affinity of fluorine are 17.42 and 3.45 eV respectively. What will be the ratio of electronegativity of fluorine on Mulliken scale and Pauling scale ?
 - (a) 2.80 : 1 (b) 1.80 : 1 (c) 2.40 : 1 (d) 4.20 : 1
- **9** An extra electron is added at the periphery of nitrogen atom in the formation of anion. What will be the ratio of effective nuclear charge of nitrogen atom and nitrogen anion ?

(a) 2.09 : 1 (b) 0.09 : 1 (c) 3.09 : 1 (d) 1.09 : 1

- **10** The atomic numbers of vanadium (V), chromium (Cr), manganese (Mn) and iron (Fe) are respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionisation enthalpy ?
 - (a) V (b) Cr (c) Mn (d) Fe
- **11** The IE values of $AI(g) \longrightarrow AI^+ + e^-$ is 577.5 kJ mol⁻¹ and ΔH for $AI(g) \longrightarrow AI^{3+}(g) + 3e^-$ is 5140 kJ mol⁻¹. If the ratio of second and third IE is 2 : 3, the values of IE₂
 - and IE_3 are respectively
 - (a) 1825 and 2737.5 kJ mol⁻¹
 - (b) 182.5 and 273.75 kJ mol⁻¹
 - (c) 1825 and 2700 J mol⁻¹
 - (d) 2737.5 and 1825 kJ mol⁻¹
- 12 Following transition elements (IE)₁ drops abruptly (Ga, In and TI). This is due to
 - (a) decrease in effective nuclear charge
 - (b) increase in atomic radius
 - (c) removal of an electron from the singly occupied *np*-orbitals of higher energy than the *ns*-orbitals of Zn, Cd and Hg
 - (d) None of the above is correct
- **13** Following statements regarding the periodic trends of chemical reactivity to the alkali metals and the halogens are given. Which of these statements give the correct picture?
 - (a) The reactivity decreases in the alkali metals but increases in the halogens with increase in atomic number down the group
 - (b) In both the alkali metals and the halogens the chemical reactivity decreases with increase in atomic number down the group
 - (c) Chemical reactivity increases with increase in atomic number down the group in both the alkali metals and halogens
 - (d) In alkali metals the reactivity increases but in the halogens it decreases with increase in atomic number down the group

- **14** In which of the following arrangements the order is not according to the property indicated against it ?
 - (a) Li < Na < K < Rb : increasing metallic radius
 - (b) I < Br < F < CI : increasing electron gain enthalpy (with negative sign)
 - (c) B < C < N < O: increasing first ionisation enthalpy
 - (d) $Al^{3+}\ <\ Mg^{2+}\ <Na^+\ <F^-:$ increasing ionic size
- **15** Consider the following statements.
 - I. Cs⁺ is highly hydrated than the other alkali metal ions.
- II. Among the alkali metals Li, Na, K and Rb, lithium has the highest melting point.
- III. Among the alkali metals only lithium forms a stable nitride by direct combination.

Of these statements

- (a) I, II and III are correct
- (b) I and II are correct
- (c) I and III are correct
- (d) II and III are correct

ANSWERS

(SESSION 1)	1 (c)	2 (b)	3 (a)	4 (a)	5 (d)	6 (d)	7 (b)	8 (d)	9 (b)	10 (c)
	11 (d)	12 (a)	13 (c)	14 (b)	15 (d)	16 (b)	17 (b)	18 (a)	19 (d)	20 (d)
	21 (b)	22 (a)	23 (b)	24 (a)	25 (a)	26 (d)	27 (d)	28 (c)	29 (d)	30 (c)
	31 (c)	32 (a)	33 (a)	34 (a)	35 (a)	36 (a)	37 (a)	38 (c)	39 (a)	
(SESSION 2)	1 (c)	2 (d)	3 (a)	4 (b)	5 (b)	6 (c)	7 (c)	8 (a)	9 (d)	10 (b)
	11 (a)	12 (c)	13 (d)	14 (c)	15 (d)					

Hints and Explanations

SESSION 1

1 Since, each period starts with the filling of electrons in a new principal quantum number, therefore, the period number in the long form of the periodic table refers to the maximum principal quantum number of any element in the period.

Period number = maximum n of any element

[where, n = principal quantum number]

2 The pair which belongs to same group, i.e. in which both the elements have same outer electronic configuration has same chemical properties.

$$3 \Rightarrow 1s^2, 2s^1$$
$$11 \Rightarrow 1s^2, 2s^2 2p^6, 3s^1$$

3 Mg can form basic carbonate, while Li cannot.

$$\begin{array}{l} 5 \text{Mg} + \ 6 \text{CO}_3^{2-} + \ 7 \text{H}_2 \text{O} \longrightarrow \\ \\ 4 \text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5 \text{H}_2 \text{O} + \ 2 \text{HCO}_3^- \end{array}$$

- **4** Atomic radii of neon (1.60) being van der Waals' radius is higher than that of fluorine (0.72) which is infact covalent radius. Also Ne is an inert gas all the orbital are completely filled and hence the interelectronic repulsion is maximum.
- **5** The ionic radii of cation is smaller than its parent atom while the size of anion is larger than its parent atom. Greater the negative charge on the ion, larger is its radii. Hence, O²⁻ has the highest value of ionic radius.
- 6 The atomic and ionic radii of transition elements in a given series show a decreasing trend for first five elements and then becomes almost constant for next five elements. i.e. Fe, Co, Ni, Cu
- 7 In isoelectronic species, anion is larger in size than the cation. As the magnitude of nuclear charge increases, force of attraction by the nucleus on the electrons increases and hence, ionic radius decreases. Therefore, Cl⁻ ion is bigger than K⁺ ion.

- **8** Ionic radii $\propto \frac{1}{7}$ for isoelectronic ion.
 - Thus, $O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$ (Z) 8 9 11 12 13
- **9** N³⁻,O²⁻ and F⁻ are isoelectronic species with 10 electrons. For isoelectronic species,

Ionic radii $\propto \frac{1}{\text{nuclear charge}}$

Thus, the correct order of their radii would be

$$F^{-}_{(1.36)} < O^{2-}_{(1.40)} < N^{3-}_{(1.71)}$$

10 For isoelectronic species, $r_n \propto \frac{1}{7}$

Species	Ζ	Electrons
CI-	17	18
Ca ²⁺	20	18
K+	19	18
S ²⁻	16	18

Thus, ionic size is in order

 $Ca^{2+} < K^+ < Cl^- < S^{2-}$.

- **11** O²⁻, F⁻, Na⁺, Mg²⁺ and Al³⁺ are isoelectronic species and higher the nuclear charge, smaller the radii of isoelectronic species.
- **12** First ionisation energy shows a clear periodic variation along a group. It decreases down the group.
- 13 As, all the given elements belong to IA group except Sc, their ionisation energy decreases down the group. Order of first ionisation energy is Sc > Na > K > Rb.
 Due to poor shielding effect, removal of one electron form 4s orbital is difficult

as compared to 3s orbital.14 Na and Mg belongs to 2nd period, IA and IIA group. On moving from left to right, first IE increases, therefore IE of Mg is greater than that of Na.

- **15** As the sudden jump in ionisation is observed between IE_2 and IE_3 thus it has 2 valence electrons, so its electronic configuration must be $1s^2 2s^2 2p^6 3s^2$.
- **16** Ionisation potential (I.P) increases from left to right while in case of elements possessing fully filled or half-filled orbitals, their ionisation potential is more as compared to the element having unstable configuration. Since, Na, Mg, Al and Si all belongs to the same period thus, the order of their IP values would be Na<Mg<Al<Si. But Mg possesses fully filled 3s² orbitals, thus, its ionisation potential value would be larger than that of Al. Thus, the correct order would be : Na<Al<Mg<Si. Hence, ionisation potential value of Al would lie between Na and Mg, i.e. 496 and 737. Thus, ionisation potential of Al should be 575 kJ mol⁻¹.
- 17 Ionisation energy increases along a period from left to right and decreases down a group. Therefore, increasing order of first ionisation enthalpy is, Ba < Ca < Se < S < Ar.
- **18** Na $\frac{\Delta H = + 5.1 \text{ eV}}{\Delta H = -5.1 \text{ eV}}$ Na⁺ + e⁻, here the

backward reaction releases same amount of energy as that of forward reaction and known as electron gain enthalpy.

19 As the first ionisation potential increases down the group, the observed order for increasing IP should be C < N < O < F, but the correct order is C < O < N < F.</p> C <O <N <F. This is because of the half-filled stable configuration of nitrogen ($1s^22s^22p^3$), which has more IP than that of oxygen.

- **20** In general electron affinity increases down the group. Electron affinity for the elements of third period are higher than those of second period due to their small size and high electron density and thus added electron, experience large inter electronic repulsion resulting in release of lower amount of energy. The increasing order of electron affinity is $2s^{2}2p^{4} < 3s^{2}3p^{4} < 2s^{2}2p^{5} < 3s^{2}3p^{5}.$
- **21** Second ionisation potential represents the amount of energy required to remove an electron from a unipositive ion. The electronic configuration of unipositive ions of given atoms is

 $C^{+}(6-1=5) = 1s^{2}, 2s^{2}, 2p^{1}$ $N^{+}(7-1=6) = 1s^{2}, 2s^{2}, 2p^{2}$ $O^{+}(8-1=7) = 1s^{2}, 2s^{2}, 2p^{3}$ $F^{+}(9-1=8) = 1s^{2}, 2s^{2}, 2p^{4}$

From the electronic configuration, it is clear that the second ionisation potential of O is highest because here the electron which is to be removed belongs to half-filled (so more stable) *p*-orbital. Moreover, along a period, as the number of electrons increases, size decreases, effective nuclear charge increases and hence, ionisation potential increases. Thus, the correct order of second ionisation potential is O> F> N> C.

- **22** In the given values, there is a biggest jump between IE_4 and IE_5 . Hence, there are 4 valence electrons for the atom X.
- 23 IE₂ of Mg is lower than that of Na because in case of Mg²⁺, 3s electron has to be removed while in case of Na⁺, an electron from the stable inert gas configuration (neon) has to be removed.
- **24** When the electronegativity difference is more than 1.7, the bond formed will be ionic in nature.

25
$$A \longrightarrow A^+ + e^-$$
, if $(IE)_A < (IE)_B$
 $B + e^- \longrightarrow B^-$, if $(EA)_B > (EA)_A$
 $(EN) = \frac{(IE) + (EA)}{2}$
 A^+B^- is formed if $(EN)_A < (EN)_B$

26 $\chi_C - \chi_H = 0.208 \sqrt{\Delta}$

where,
$$\Delta = E_{C - H} - \sqrt{E_{C - C} \times E_{H - H}}$$

 $\Delta = 98.8 - \sqrt{83.1 \times 104.2}$
 $\therefore \Delta = 5.75$
 $\chi_{C} - 2.1 = 0.208 \sqrt{5.75}$
 $\chi_{C} - 2.1 = 0.497$
 $\chi_{C} = 2.598$

- **27** For transition elements, *d*-subshells are not filled with electrons monotonically (one at a time) because of extra stability of d^5 and d^{10} configuration. Besides these, there are many other exceptions, e.g. Nb, Mo, Ru, Rh, Pb etc.
- **28** $A \rightarrow 2$: $B \rightarrow 3$: $C \rightarrow 5$: $D \rightarrow 1$: $E \rightarrow 4$
- **29** Valence electrons in A = 3Valence electrons in B = 6Thus, A is electropositive and B is electronegative; A can lose three electrons and B can gain two electrons to attain stable configuration. Thus, A exists as A^{3+} and B as B^{2-} Thus, compound is A_2B_3 .
- **30** Na (11) \rightarrow 1s²2s²2p⁶3s¹. It is an alkali metal whose oxide are basic in nature.
- **31** Due to small size of fluorine, it has high hydration energy which makes it strongest oxidising agent.
- **32** Due to the presence of maximum number of unpaired electrons, element having 3d⁵, 4s², configuration may exhibit the largest number of oxidation states in its compounds.
- **33** Oxides when dissolved in water form hydroxides.

 $\begin{array}{l} Na_2O + H_2O \longrightarrow 2 \text{ NaOH} \\ MgO + H_2O \longrightarrow Mg(OH)_2 \\ Al_2O_3 + 3H_2O \longrightarrow 2Al(OH)_3 \end{array}$

Smaller the size of cation and larger the charge, greater the polarising power of cation, hence greater the covalent character and lesser the basic nature.

Oxides Basic Decreases in a period

Charge $AI^{3+} > Mg^{2+} > Na^+ = K^+$ Size $AI^{3+} < Mg^{2+} < Na^+ < K^+$ Polarising power $Al^{3+} > Mg^{2+} > Na^+ > K^+$

Basic nature of oxides

 $AI_2O_3 < MgO < Na_2O < K_2O$

- 34 Oxidising property depends on the easiness with which the element is reduced, i.e. it gain electrons which in turn is its electronegativities.
 Electronegativity F > Cl > O > N. Thus, correct option is (a).
- **35** Boron has a smaller first ionisation enthalpy than beryllium because the penetration of 2s electron to the nucleus is more than the 2p electron. Hence, 2p electron is more shielded by the inner core of electron than the 2s electron.
- **36** Electron gain enthalpy becomes less negative as the size of an atom increases down the group. This is because within a group screening effect increases on going down in a group and the added electron would be farther away from the nucleus.
- **37** Cesium and fluorine both reacts violently because cesium is most electropositive and fluorine is most electronegative.
- **38** The atomic radii of the elements of oxygen family are smaller than atomic radii of the corresponding elements of the nitrogen family because of increase in effective nuclear charge the results in the increased attraction of electrons to the nucleus.
- **39** Fluorine has a less negative electron affinity than chlorine. There is relatively greater effectiveness of 2 *p* electrons in the small fluorine atom to repel the additional electron entering the atom than to 3*p* electrons in the larger Cl atom.

SESSION 2

- **1** The process of formation of O²⁻ in gas phase is unfavourable even though O²⁻ is isoelectronic with neon because electron repulsion outweights the stability gained by achieving noble gas configuration.
- 2 Examine the positions in periodic table? B C N O F

The ionisation enthalpy increases across the period but decreases down the group.

Phosphorus has stable half-filled configuration. Hence, order is $B < S < P < F. \label{eq:B}$

3 The correct order for atomic number is A < B < C

4 For isoelectronic,

lonic radii $\sim \frac{1}{\text{Magnitude of nuclear charge}}$ The correct order for radii is

 $Mg^{2+} < Na^+ < F^- < O^{2-}$.

5 Greater the hydration, smaller the ionic mobility of cation to move towards cathode, Li, is heavily hydrated, thus has least ionic mobility and hence, discharged at the end.

K⁺ is least hydrated, due to its large size, has maximum ionic mobility and is discharged first.

- 6 Atomic number of the given element = 15 Group number = 10 + 5 (valence electron) = 15 Period = 3 Atomic number of the element just below = 33
- 7 Atomic number of element B = Z[*B* is noble gas, so it belongs to zero group] Atomic number of element, A = Z - 1[i.e. halogens] Atomic number of element, C = Z + 1[i.e. group IA]

Atomic number of element D = Z + 2[i.e. group IIA]

Thus, element *A* must be a halogen i.e. it has highest electron affinity and element *C* must be an alkali metal and exist in +1 state and element *D* must be an alkaline earth metal with + 2 state.

$$8 (\chi_{\rm F})_{M} = \frac{|{\rm P} + {\rm EA}|}{2}$$

$$(\chi_{\rm F})_{M} = \frac{17.42 + 3.45}{2} = 10.435$$

$$(\chi_{\rm F})_{P} = \frac{10.435}{2.8} = 3.726$$

$$(\chi_{\rm F})_{M} : (\chi_{\rm F})_{P} = 2.80 : 1$$

9
$$Z_{\text{eff}} = Z - \sigma$$
; $\sigma = [0.35 \times \text{electrons in} n \text{ th shell excluding last electron}] + [0.85 \times \text{electrons in } (n - 1) \text{ shell}]$

(i) For N atom = $1s^2$, $2s^22p^3$ \therefore $\sigma = [4 \times 0.35] + [2 \times 0.85] = 3.10$ $\therefore Z_{\text{eff}} = 7 - 3.10 = 3.90$ (ii) For N⁻ ion $1s^2$, $2s^2$, $2p^4$ $\sigma = [5 \times 0.35] + [2 \times 0.85] = 3.45$ $\therefore Z_{\rm eff} = 7 - 3.45$ = 3.55 Z_{eff} (N atom) : Z_{eff} (N⁻ anion) 1.09 $Fe^+(25) = [Ar] 3d^6, 4s^1$ 10 $Mn^+(24) = [Ar] 3d^5, 4s^1$ $V^+(22) = [Ar] 3d^3, 4s^1$ $Cr^{+}(23) = [Ar] 3d^{5} 4s^{0}$ By first ionisation potential, the electronic configuration of Cr⁺ is most

electronic configuration of Cr⁺ is most stable, hence formation of Cr²⁺ by second ionisation potential requires maximum enthalpy.

11 Given,
$$IE_1$$
 of $AI = 577.5 \text{ kJ mol}^{-1}$...(i)
 $[IE_1 + IE_2 + IE_3]$ of $AI = 5140 \text{ kJ mol}^{-1}$

...(ii)

Given, $IE_2 = (2 / 3) IE_3$...(iii) Solving (i), (ii) and (iii), we get $IE_2 = 1825 \text{ kJmol}^{-1}$ $IE_3 = 2737.5 \text{ kJmol}^{-1}$

- **12** It is due to the removal of an electron from the singly occupied *np*-orbitals of higher energy than *ns*-orbitals of Zn, Cd and Hg.
- **13** In alkali metals reactivity increases down the group as electropositivity increases but for halogens reactivity decreases down the group as molecular stability of elements increases.
- 14 Metallic radii increase in a group from top to bottom.
 Thus, Li < Na < K < Rb is true.
 - Electron gain enthalpy of Cl > F and decreases along a group. Thus, I < Br < F < Cl is true.
 - Ionisation enthalpy increases along a period from left to right but due to presence of stable half-filled orbitals in N, ionisation enthalpy of N > O. Thus, B < C < N < O is incorrect.
- **15** Correct Statement I Cs⁺ because of its large size is least hydrated.