PERIODIC PROPERTIES

1 Mark

Easy

1. What is the shape of XeF_4 molecule?

Square planar

2. Give an example of compound having zero dipole moment.

CCl_4

3. Give an example of soft acid.

Hg^{2+}

Moderate

1. What is the shielding constant value for I s orbital electron?

0.30

2. What is the order of second ionisation potentials of carbon, nitrogen, oxygen and fluorine?

O > F > N > C

3. What is the hybridization of XeF_4?

Sp^3d^2.

Hard

1. What is the increasing order of electron affinity values of O, S and Se?

O < S > Se.

2. Write the increasing order of effective nuclear charge in Na, Al, Mg and Si?

Na < Mg < Al < Si.

5 Mark

Moderate

1. (a) State the reason for the presence of only one electron in the 4s subshell of chromium? 2

(b) Which of the following has larger size and why? (i) Mg^{2+} (ii) N^{3-}

The ground state electronic configuration of Chromium (24) is : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$. It has only one electron in 4s subshell as the second electron is shifted to 3d subshell to make it half filled to achieve additional stability.

(b) Mg^{2+} and N^{-3} ions have same number of valence electrons. Both are having total 10 electrons but Mg is a 3rd period element with one more orbital than N (2nd period) element. But in +2 state Mg is having only two orbitals, as N. As atomic number of Mg is 12 and that of N is 7, number of proton present in Mg is more than N and therefore exerting greater pull on outermost electrons resulting smaller size.

Hence we can conclude that N^{-3} has larger size than $Mg^{+2.}$

Hard

Arrange the halogens in ascending order as per their boiling point and mention the periodic trends of atomic radii. 5

In group 17, i.e., for halogens, the boiling points increase with increase in atomic number. Therefore, the ascending order of boiling point of halogens is --- F > Cl > Br > I

On moving from left to right in a period, the number of shells remain the same but due to increase in atomic number (no. of protons), the nuclear charge increases progressively and as a result atomic radii decreases. This trend continues upto group 17 (halogens) but for group 18 (inert gases), the size increases abruptly.

Easy

1. Differentiate between electronegativity and electron affinity of an element. Explain the acidity order of silicon halides as given by $SiF_4 > SiCl_4 > SiBr_4 > SiI_4$.

Electronegativity	Electron affinity
Electronegativity is the ability of an atom to attract electrons from outside.	Electron affinity is the amount of energy released when a neutral atom or molecule gains an electron from outside.
Qualitative property	Quantitative property
Measured from Pauling units	Measured from either eV or kj/mol
Applied for a single atom.	Can be applied for either an atom or a molecule.

Silicon halides can behave like Lewis acids although octet is fulfilled for Si atom in all silicon halides. This is due to the reason that the strongly electronegative halogens can pull electron density from silicon end (Si – X covalent bonds) towards themselves making silicon electron deficient. However, the acidic strength of silicon halides will depend on the electronegativity of halogens connected with Si atom.

Fluorine being most electronegative among halogens, SiF_4 has highest acidic character and reverse is true for SiI_4. Moreover, Br and I can donate their extra electron density to vacant 3d orbital of 'Si' via back bonding resulting lowering of electron deficiency of silicon.

Therefore, the acidic strength order is $SiF_4 > SiCl_4 > SiBr_4 > SiI_4$

15 Mark:

Easy:

1. (a) State Hund's rule of spin multiplicity and Pauli Exclusion principle. Write down the electronic configuration of Fe (Z = 26)

(b) Calculate the effective nuclear charge of 4s electrons of Fe (Z = 26) with the help of Slater's rule.

(c) Define Pauling Scale of electronegativity.

(d) Electron affinity of Cl is greater than F, explain the phenomenon.

(e) Between $BeCl_2$ and $BaCl_2$ which one has more melting point and why?

(f) Write short note on " Fajan's rule.

(a) Hund's rule of maximum multiplicity: Pairing of electrons in the degenerate molecular orbitals does not occur, until each of them has one electron.

Pauli's exclusion principle: Two electrons in the same orbital cannot have set of all the four quantum numbers identical. It means maximum number of electrons in a orbital is two and they must have opposite spins.

Electronic configuration of Fe (26) is ---- $1s^2, 2s^2, 2p^6\ 3s^2, 3p^6, 3d^6, 4s^2$.

(b)The ground state electronic configuration of Fe (26) is ---- $1s^2, 2s^2, 2p^6\ 3s^2, 3p^6, 3d^6, 4s^2$.

The shielding constant contribution calculation -----

For 4s electrons:

No. of electrons in the same group (4s) = 0

14 electron in (n – 1) groups, (3s, 3p) and 3d: 0.85 each : 0.85 x 14 = 11.90

10 electrons in groups further left, i.e., ≤ (n – 2): 1.0 each : 1.0 x 10 =10.0

Total (σ) = (11.90 + 10.0) = 21.90

Thus $Z_{eff} = 26 – 21.90 = 4.10$.

(c) Pauling scale: Let us consider a chemical reaction: $A_2 + B_2 \rightarrow 2\ A – B$

The reaction can also be represented as --- $A - A + B - B \rightarrow 2(A - B)$

According to Pauling, the bond dissociation energy of the A – B bond is $E_A - E_B$ which will be equal to the bond dissociation energies E_{A-A} and E_{B-B} for A – A and B – B molecules respectively.

Thus, $E_{A-B} = \sqrt{} E_{A-A} . E_{B-B}$

If we consider the electronegativity of atom 'A' and 'B' as χ_A and χ_B respectively, then according to Pauling, the difference in electronegativity between these two atoms will be ---

$\chi_A - \chi_B = \sqrt{} \Delta/23.06 + \alpha = 0.208 \sqrt{} \Delta + \alpha$

Where α is a constant.

Therefore, if electronegativity value of any one of these two (χ_A or χ_B) is known, the other can be calculated.

(d) Down the group we expect the electron affinity to decrease, but in this case the lesser electron affinity of fluorine with respect to chlorine is due smaller size of fluorine. The smaller size results very strong repulsion between the incoming electron and the relatively compact 2p sub shell of fluorine. As a result the electron affinity decreases. On the contrary, the relatively large 3p subshell of chlorine can accommodate the incoming electrons more easily resulting greater electron affinity than fluorine.

(e) According to Fajan's rule, polarization power of cations increases with decrease in size, i.e., smaller the size of the cation greater is the polarization power.

Therefore, polarization power of $Be^{2+} > Ba^{2+}$

Therefore, $BeCl_2$ is more covalent than $BaCl_2$. Hence , $BaCl_2$ will be less covalent and has higher melting point.

(f) Fajan's Rule: The electrovalent compounds are never 100% ionic in nature. There is always some percentage of covalent character in it. The concept of development of partial covalent character in the ionic compounds was first introduced by Fajon.

When a cation approaches an anion, the positively charged cation attracts the electron cloud of the anion.

The ability of a cation to deform the electron cloud around the anion is said to be polarization power of the cation and the tendency of an ion to get polarized or deformed is called polarizability.

The extent of polarizability of an anion and polarizing power of a cation is governed by a number of rules, commonly known as Fajon's rule. As per these rules, the polarization in ionic compounds is favoured by

(i) High positive charge on cation

(ii) Small size of cation

(iii) High negative charge on anion

(iv) Large size of anion.

(i) The polarization power of the cation increases with increasing the charge, i.e., higher the charge on the cation greater is the polarization power. Hence, the polarization power varies, $B^{+3} > Be^{+2} > Li^{+}$

(ii) The polarization power of cations increases with the decrease in size, i.e., smaller the size of the cation greater is its polarization power. Hence, the polarization power in this series is as follows, $Li^{+} > Na^{+} > K^{+}$.

(iii) Greater the negative charge of an anion, higher is its polarizability because it is difficult for a highly charged anion to control its outer orbital electrons and hence it can be deformed very easily. For example, the polarizability of halides follows the order, $I^{-} > Br^{-} > Cl^{-} > F^{-}$.

(iv) Larger the size of an anion greater is its polarizability. This is because, with increasing size, the distance between the electrons of the outermost orbit and the nuclei increases and hence the nuclei cannot control the electrons of the outer most shell.

Thus the order of polarizability in the halide series is as follows: $I^{-} > Br^{-} > Cl^{-} > F^{-}$.

Therefore, the Fajan's rule can be the summarized as smaller cations with low positive charge and smaller anions carrying low negative charge will favour the formation of ionic compounds whereas smaller cations carrying high positive charge will lead to the formation of covalent compounds.

2. (a) What is screening constant? Calculate the effective nuclear charge (Z_{eff}) of one 4s electron of the following: Cu (Z = 29) and K (Z = 19) 5

(b) p – block elements form acidic, basic and amphoteric oxides. Explain each property by giving two examples and also write the reactions of these oxides with water. 6

(c) What is the merits and demerits of long periodic table? 4

(a) Screening constant: In multi – electron atoms, the nuclear charge realized by the outer orbital electrons become less due to the shielding or screening of the inner orbital electrons. This is called shielding or screening effect. The actual amount of nuclear charge felt by an electron is termed as effective nuclear charge. The effective nuclear charge (Z_{eff} or Z^*) is --- $Z^* = Z - \sigma$

Where Z is the actual nuclear charge and σ is the screening or shielding constant.

The magnitude of screening depends on the number of inner orbital electrons. Greater the number of inner electrons, higher would be the screening effectand consequently the effective nuclear charge felt by the outer orbital electrons will decrease. Hence, we can conclude that with decreasing effective nuclear charge, ionization energy decreases.

Cu (29) has ground state electronic configuration: $1s^2$, $2s^2$, $2p^6$ $3s^2$, $3p^6$, $3d^{10}$, $4s^1$.

Effective nuclear charge for one (4s) electron is calculated as follows----

No other electron in the same group (4s) = 0

18 electrons in (n – 1) groups, (3s, 3p) and 3d : 0.85 each : 0.85 x 18 = 15.3

10 electrons in groups further left, i.e., ≤ (n – 2) : 1.0 each : 1.0 x 10 = 10.00

Total (σ) = 25.30

Thus Z_{eff} = 29.00 -25.30 = 03.70

K (19) has ground state electronic configuration $1s^2$, $2s^2$, $2p^6$ $3s^2$, $3p^6$, $4s^1$.

No of electron in the same group (4s) = 0

8 electrons in (n – 1) groups, (3s, 3p): 0.85 each : 0.85 x 8 = 6.80

10 electrons in groups further left, i.e., ≤ (n – 2) : 1.0 each : 1.0 x 10 = 10.00

Total (σ) = 16.80

Thus, Z_{eff} = 19.00 – 16.80 = 02.00

(b) In p – block elements last electron (valence electron) enters the p-orbitals. In p – block elements some are metals, some are non – metals and some are metalloids.

Metals --- Al, Ga, Tl, Bi

Nonmetals --- B, C, N, S

Metalloids: As, Sb, Si, Ge

Types of oxides of p-block elements are described below and two examples each of different types are also given.

<u>Basic oxides</u> --- Bi_2O_3, Tl_2O_3

The basic oxides react with acids to form salts

$Bi_2O_3 + 6\ HCl \rightarrow 2BiCl_3 + 3H_2O$

$Ti_2O_3 + 3H_2SO_4 \rightarrow Ti_2(SO_4)_3 + 3H_2O$

Acidic oxides----- CO_2, SO_2

These oxides are said to be acidic oxides because they react with water to form acid

$CO_2 + H_2O \rightarrow H_2CO_3$ (Carbonic acid)

$SO_2 + H_2O \rightarrow H_2SO_3$ (sulphurous acid)

Amphoteric Oxides --- Al_2O_3, PbO

These oxides have both basic and acidic properties. These oxides react with both strong acids and strong bases.

$Al_2O_3 + 6HCl \rightarrow 2Al^{3+} + 6Cl^- + 3H_2O$

$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na^+ + 2[Al(OH)_4]^-$

$PbO + 2HNO_3 \rightarrow Pb^{2+} + 2NO_3^- + H_2O$

$PbO + NaOH \rightarrow Na^+ + [PbO.OH]^-$

(c)Merits of long periodic table:

1. It is based on atomic number, which is an even better fundamental property compared to atomic mass

2. Position of an element in the tables related to its electronic configuration

3. It shows regular changes in properties of elements on moving across a period or down a group.

Defects of long periodic table:

1. Position of hydrogen is still not satisfactory, as the properties relate to both Group I and Group 17.
2. It fails to accommodate the inner transition elements, i.e., the lanthanides and the actinides, into the main body of the periodic table.

Moderate

1. (a) What is the difference between ionization energy and electron affinity? The first ionization energy of carbon is greater than that of boron whereas the reverse is true for the second ionization energy. 5

(b) Why does Mn (II) is $3d^5$? Would you classify Zn as a transition element? Give reasons for your answer. 5

(c) Explain that ionisation energy of neon is more than any other element of the second period? Why do the transition elements form complexes readily? 5

(a) Ionization energy is the amount of energy required to remove the most loosely bound electron from an isolated atom in the gaseous state while electron affinity is the amount of energy released when an electron is added to an isolated atom in the gaseous state.

The first ionization energy of carbon is greater than boron as nuclear charge on carbon (Z = 6) is greater than the nuclear charge on boron (Z = 5).

The second ionization energy of boron is greater than carbon as the second electron has to be removed from 2s orbital of B^+ in ($1s^2\ 2s^2$) which requires more energy than the removal of electron from 2p orbital of C^+ ion ($1s^2\ 2s^2\ 2p^1$).

(b) The electronic configuration of Mn is $3d^5\ 4s^2$ and that of Mn (II) is $3d^5$. All the 5 electrons in d orbital are unpaired. It is this maximum possible number of unpaired electrons the d- orbitals which makes it most paramagnetic amongst bivalent ions of the first transition series. Also it is half field state, which is very stable configuration.

Zinc (Z = 30) has electronic configuration [Ar] $3d^{10}4s^2$. It has fully filled d – subshell in its elemental from as well as its common oxidation state i.e., Zn^{2+} in having $3d^{10}$ configuration. According to definition of transition element, it cannot be included in the transition elements. It does not show the characteristic properties of transition element, excepting its tendency to form complexes. But it is classified with transition elements because the last electron enters in the d – orbitals of its penultimate shell.

(c) Noble gases have the highest ionization energy in their respective periods. For example, ionization energy of Ne is more than any other element of the second period. So is the case with Ar. This is due to the fact that $ns^2\ np^6$

arrangement which occurs in noble gases is highly stable and hence larger amount of energy is needed to remove an electron from this stable arrangement.

The transition elements form complexes due to

(i) Their small cation size

(ii) High effective nuclear charge

(iii) Availability of vacant (n – 1)d orbitals of appropriate energy for accepting lone pairs of electrons donated by ligand.

Hard

1. (a) "The complexes of first transition series are mainly high-spin while those of second and third transition series are of low – spin type" ---- Explain. First ionisation energies of 5d elements are higher than 3d and 4d elements. Give reason. 5

(b) Explain why the second ionization energies for copper and chromium are enormously high? Iron is a transition element but sodium is not. Explain. 5

(c) First ionisation energies of copper is higher than those of alkali metals while second and third energies are lower. Explain. Why are lanthanides and actinides placed in separate rows at the bottom of the periodic table? 5

(a) The element of the first transition series, i.e., from Sc to Zn involve filling of 3d – orbitals. As compared to 4d and 5d orbitals, the 3d orbitals are relatively smaller in volume. Therefore, Inter electronic repulsion, which may come into play due to occupation by two electrons in an orbital (low spin) would be very large. Therefore, crystal field splitting for 3d block of elements is small. First raw transition metals prefer to form high spin complexes.

On the other hand, in the second and third transition series, 4d and 5d orbitals have bigger sizes than 3d orbitals. Therefore, in the second and third transition series, inter electronic repulsion are quite small. Hence, crystal field splitting energy is quite high which result in low spin complexes.

First ionisation energies of 5d elements are higher than 3d and 4d elements. This is due to the fact that outer valance electrons of 5d elements experience greater effective nuclear charge than 3d and 4d elements due to poor shielding of the nucleus by 4f electrons.

(b) Cu =[Ar] $3d^{10}$ $4s^1$; and Cr = [Ar] $3d^5$ $4s^1$ Their first ionization energies are low because removal of one electron gives a stable $3d^{10}$ or $3d^5$ configuration. The second ionization energies are expected to be high because of removal of an electron from stable completely filled orbital $3d^{10}$ for Cu^+ and half filled orbital $3d^5$ for Cr^+.

Iron has electronic configuration =[Ar] $3d^6$ $4s^2$ while sodium has electronic configuration [Ne}$3s^1$.Thus in iron last electron enters a d- orbital, so it is a transition element while in sodium last electron enter s – block element.

(c) Cu has =[Ar] $3d^{10}$ $4s^{1\text{configuration.}}$ As filled 3d sub shell is much less effective in shielding the outer s- electron than a noble gas shell present in alkali metal, so the 4s electron of copper is more tightly bound than in alkali metal. However, 2nd and 3rd ionization energy values of copper are lower as compared to those of alkali metals due to the loss of electron from diffused d- orbital, while 2nd ionization energy in alkali metal would be very high as this electron is being removed from a noble gas core.

This arrangement has been made due to the following reasons:

(i) to keep the elements having similar properties in a single row.

(ii) to avoid sidewise expansion of the periodic table.