HINTS & SOLUTIONS

EXERCISE - 1

Single Choice

3. The d-block has 10 columns, because a maximum of 10 electrons can occupy all the orbitals (5) in a d-subshell.

4. Eka silicon = Germanium and Eka aluminium = Gallium, according to Mendeleev periodic table.

6. Silver belongs to V^{th} period. So the atomic number of elements placed above and below will be $47 - 18 = 29$ and $47 + 32 = 79$ respectively.

7. As last electron enters in d-orbital, so it belongs to d-block. For this d-block element, group number $= 5 + 1 = 6$.

10. Yes, hydrogen can be placed in 1^{st} group on the basis of its valency +1 (H^+).

12. For isoelectronic species, as Z increases, Z_{eff} increases (and vice versa).

13. $r_{anion} > r_{atom} > r_{cation}$ (due to increasing Z_{eff}).

14. On moving left to right in a period, atomic radii decreases due to increase in Z_{eff} and addition of electrons to the same outermost shell.

16. Atomic radius increases on moving top to bottom in a group due to increasing number of shells. However, it decreasing on moving left to right in a period due to increasing Z_{eff} and addition of electrons to the same shell.

Nb (4d) $\approx$ Ta (5d) (due to poor shielding of nuclear charge by 4f electrons).

For isoelectronic species,

ionic radius $\propto \dfrac{1}{\text{nuclear charge}}$. So correct order is

$Y^{3+} < Sr^{2+} < Rb^{+}$.

19. Orbitals bearing lower value of n will be more closer to the nucleus and thus electrons will experience greater attraction from nucleus and so its removal will be difficult, not easier.

21. Removal of Ist electron is easier because of bigger size but 2nd electron is to be removed from $ns^2\ np^6$ configuration i.e. stable noble gas configuration. So $IE_2 >> IE_1$.

24. Across the period (i.e. 3^{rd} period) the size of atom decreases and nuclear charge increases. So generally the ionisation energy increases. However the ionisation energy of Mg is greater than Al because of more penetration power of 2s sub-shell electrons of Mg as compared to that of the 2p sub-shell electron of Al. Also, Mg has fully filled configuration.

26. O has exceptionally smaller value of electron affinity (minimum in family) due to smaller atomic size than sulphur (weaker electron-electron repulsion in larger 3p-subshell).

28. In chlorine, the addition of additional electron to larger 3p-subshell experiences less electron-electron repulsion than smaller 2p-subshell of fluorine. Phosphorus has very low electron affinity because there is high electron repulsion when the incoming electron enters an orbital that is already half filled.

32. Electronegativity of elements generally increases across the period (less increase) and decreases down the group (more decrease).

33. The addition of extra electron is difficult to the atom having stable configuration and so electron gain enthalpy will be positive. Similarly the removal of electron is quite difficult from stable configuration and so ionisation enthalpy is higher. However EN remains unaffected because it neither involves gain nor loss of electron.

37. $H_2S < H_2Se < H_2Te$ (on moving top to bottom, bond dissociation energy decreases, so acidic strength increases).

In case of oxyacids of same element, higher is the oxidation state of the central atom, greater is the acidity. Hence, H_2SO_4 is a stronger acid than H_2SO_3.

39. The element present in short period will be of 13th group (group no $= 10 + 3 = 13$) i.e. aluminium and its oxide will be Al_2O_3 which is amphoteric in nature; as react with acids as well as bases forming salt and water.

41. TlI_3 exists as Tl^+ and I_3^- while PbF_4 exists because of F^- being very weak reducing agent.

42. BiI_5 does not exists because of I^- being very strong reducing agent. So it reduces Bi^{5+} to Bi^{3+} and forms BiI_3.

65 On descending a group, the atoms and ions increase in size. On moving from left to right the size decreases. Thus on moving diagonally the size remains nearly the same. They also have nearly same IE & EN values.

68 In zero group, He has 2 electrons in its outermost shell ; rest all elements have 8 electrons.

70 He^+, $1s^1$; Li^{2+}, $1s^1$; Be^{3+}, $1s^1$. All these ions have only one electron. So they do not have any inner orbital and thus do not experience any screening effect.

72 Mn is in +2 oxidation state in MnO while in other compounds, it is in higher oxidation state. As number of electrons per proton decreases, the size decreases.

73. For transition elements, the 3d-orbitals are filled with electrons after 4s-orbitals and before 4p-orbitals.

75 (1) Be has completely filled stable valence shell configuration i.e. $2s^2$ while in Be^+ because of positive charge, the removal of electron requires much higher energy. So, ionisation energy of Be^+ is greater than Be.
(3) Across the period, atomic size decreases and nuclear charge increases and thus valence shell electron(s) is/are tightly held by nucleus. So, ionisation energy of C is greater than Be.

78 The electronegativity difference between M_1 and O is 0.1, which indicates M_1 — O bond will be covalent. Since O—H bond have more ionic character thus bond will break and H^+ ions will release and thus acidic solution is formed. The difference between electronegativity of M_2 — O bond is 2.3, which will indicate that the M_2 — OH bond will break and thus, the solution will be basic in nature.

79. The tendency to attract bonded pair of electron in case of hybrid orbitals increases with increase in % s-character and so the order : $sp > sp^2 > sp^3$
The electron affinity values for 2p-series elements is less than that for 3p-series elements on account of small size and high inter electronic repulsions. Statements **(B)** and **(C)** are facts. Every cation releases more energy than neutral atom upon gain of an electrons.

94 As and Sb behave as metals as well as nonmetals because they form cations (M^{3+}) and anions (M^{3-}). Their oxides and hydroxides react with acid as well as base forming corresponding salts.

95. The first member of the lanthanide series is Cesium (Z= 58).

96 Z = 15 = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$; so element belongs to p-block. Thus its group number will be 10 + 2 + 3 = 15.
Z = 33 = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^3$; so element belongs to p-block. Thus its group number will be 10 + 2 + 3 = 15.
Z = 51 = $[Kr]^{36}\ 4d^{10}\ 5s^2\ 5p^3$; so element belongs to p-block. Thus its group number will be 10 + 2 + 3 = 15.
Hence, all these elements belongs to 15th group i.e. nitrogen family.

97 He described these elements as Eka-aluminium and Eka-silicon, but the elements were actually Ga and Ge.

98 This is a characteristic feature of transition metals.

99. The first four members of group 16th (p-block) are nonmetals and collectively they are called 'the chalcogens' (ore forming elements), because a large number of metal ores are oxides or sulphides. Their general electronic configuration is [inert gas] $ns^2\ np^4$.

100 (A) $_{21}Sc^{3+}$; $[Ar]^{18}\ 3d^0\ 4s^0$ and $_{21}Sc$; $[Ar]^{18}\ 3d^1\ 4s^2$
As last electron enters in d-subshell so it belongs to d-block and thus its group number = 2 + 1 = 3.
Element belong to 3rd group of Modern periodic table, not zero group.

101. The order of penetration effect of different orbitals depends upon the different energies of the various sub-shells for the same energy level, e.g., electrons in s-subshell will have lowest energy and thus will be closest to the nucleus and will have highest penetration power, while p-subshell electrons will penetrate the electron cloud to lesser extent and so on.

102. $r_{\text{Vander waal}} > r_{\text{Metallic}} > r_{\text{Covalent}}$. Noble gases have Vander waal's radius and experience largest inter-electronic repulsions because of its completely filled valence shell electron configuration, $ns^2\ np^6$.

103 For isoelectronic species,

$$\text{ionic radius} \propto \frac{1}{\text{Nuclear charge}}.$$

For As and Br, nuclear charges will be Z = 33 and 35 respectively.

104 Transition elements start from 4th period as they have valence shell configuration $(n-1)d^{1-10}ns^{1-2}$. So minimum possible value of n is 4.

105 It has only one orbital and single electron. So, shielding effect is not possible.

106 Phosphorus has stable half filled valence shell electronic configuration, $3s^2\ 3p^3$. Even Mg has fully filled configuration $3s^2$, but P has greater nuclear charge also.

107 As elements are ionized, the proton to electron ratio increases, so the attraction between valence shell electron and nucleus increases and as a result the size decreases. Therefore, the removal of electron from smaller cation requires higher energy. Hence the second ionisation enthalpy is greater than its first ionisation enthalpy.

108. **(C)** For possible $ns^2\ np^1$ configuration, the removal of fourth electron will be possibly from an inert gas electron configuration. So there will be high jump in the fourth ionisation enthalpy than the third ionisation enthalpy which will take place from ns^1 electron configuration.

109 All are isoelectronic species but as number of protons i.e. atomic number increases, the attraction between electron (to be removed) and nucleus increases and thus ionisation enthalpies increase.
Order of Z : Te^{2-} (52) < I^- (53) < Cs^+ (55) < Ba^{2+} (56). So same will be the order of IE.

110. Be and N has $1s^2\ 2s^2$ and $1s^2\ 2s^2\ 2p^3$ stable configurations respectively. So addition of extra electron is difficult in their valence shell. The atomic size of C is smaller than B and also C has higher nuclear charge ; so addition of electron will be easier in C than B.

111 Order of $\Delta_{eg}H$ for halogens : Cl > F > Br > I & Order of $\Delta_{eg}H$ for chalcogens : S > Se > Te > Po > O.
Cl and F have the highest and II^nd highest values in Modern periodic table.

112 Due to 4f-orbital electrons (poor shielding effect), there is increase in effective nuclear charge which leads to the contraction of the size of atoms. This is called lanthanide contraction.

113 **(A)** Successive addition of d-electrons screen the outermost electrons (4s) from the inward pull of the nucleus. As a result of this, the size of the atom does not change much from Cr to Cu.
(B) This is due to lanthanide contraction.

114 **(A)** Larger the value of ionisation enthalpy, more difficult will be the removal of electron to form cation.

(B) Electron gain enthalpy is the measure of the ease with which an atom receives the additional electron in its valence shell in gaseous phase. So, larger is the value of electron gain enthalpy, easier is the formation of anion.

(C) Electronegativity (Mulliken)

$$= \frac{\text{Ionisation energy} + \text{Electron affinity}}{2}.$$

(D) As Z_{eff} increases, the valence shell as well as inner shells electrons are more strongly attracted by the nucleus. This causes the contraction in atomic size.

115. Tl^{3+} gets reduced to Tl^+ because of I^- and then it forms the compound TlI.

116. As ΔEN (difference in electronegativities between element and oxygen) decreases, the acidic character increases.

Acidic character of oxides increases on moving left to right and decreases on moving top to bottom.

So, order : $SiO_2 < CO_2 < N_2O_5 < SO_3$.

117 Both Sn and Zn react with acid as well as base forming salts.

$$SnO + H_2SO_4 \longrightarrow SnSO_4 + H_2O \quad ;$$

$$SnO + 2NaOH \longrightarrow Na_2SnO_2 + H_2O.$$

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O \quad ;$$

$$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O.$$

Ca forms basic oxide, N forms acidic as well as neutral oxides while B forms acidic oxide.

118 **(A)** The elements having large negative values of electron gain enthalpy generally act as strong oxidising agents. E.g. Halogens.

(B) The elements having low values of ionisation enthalpies act as strong reducing agents.E.g. Alkali metals.

(C) The formation of S^{2-}(g) from S(g) is an endothermic process. ($\Delta_{eg}H_1$ = small negative value, $\Delta_{eg}H_2$ = large positive value).

EXERCISE - 2

Part # I : Multiple Choice

1. Al is solid, metallic and a very good conductor of electricity.

2. **(B)** Isoelectronic series of ions; all have the xenon electron configuration.

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

Atomic number : Te = 52; I = 53; Cs = 55; Ba = 56.

(D) Due to poor shielding of nuclear charge by 4f electrons.

7. Elements of Group 1 & 2 have low IE values. So they impart colour to flame. E.g . Li, Na, K, Ca, Ba etc.

8. Order of IE_1 in 13th group : B > Al > Ga > In < Tl
(irregularity due to poor shielding of nuclear charge by 3d & 4f electrons).

9. According to Mulliken, electronegativity

$$= \frac{\text{Ionisation energy} + \text{Electron affinity}}{2}$$

Greater the EN, greater is the attraction of electron cloud.

12. Consider the factors on which these properties depend

(A) Cation is smaller while anion is bigger than its parent atom.

(B) Correct order is Cl > F > Br > I.

(C) Cation is smaller as it is formed by the loss of electron(s). The anion is formed by the gain of electron(s). The size of anion increases with increase in charge on anion i.e. as the Z/e ratio decreases the size increases.

(D) Across the period the size decreases and nuclear size increases. So, ionisation energy increases. However, the first ionisation energy of Mg is greater than Al because of high penetration power of $2s^2$ electrons of Mg as compared to that of $2p^1$ electron of Al.

20. **(A)** $S^-(g) \longrightarrow S^{2-}(g)$;
$\Delta H_{eg} = (+)$ ve because of electrostatic repulsion.
(B) $Ne\,(g) + e^-\,(g) \longrightarrow Ne^-(g)$; $\Delta H_{eg} = (+)$ ve because of stable completely filled electron configuration.
(C) $N(g) \longrightarrow N^-\,(g)$; $\Delta H_{eg} = (+)$ ve because of stable half filled electron configuration.
(D) $Al^{2+}(g) \longrightarrow Al^{3+}(g)$; $\Delta H_{IE} = (+)$ ve because of the removal of electron from cation.

21. **(A)** IE (I) of N is more than O due to stable half filled electronic configuration of valence shell in N.
(B) Electron gain enthalpy of O (-141 kJmol^{-1}) is less than sulphur and selenium due to its exceptionally small atomic size.
(C) Electronegativity on Mulliken scale is 2.8 larger than electronegativity on Pauling scale.
(D) The ionic radius decreases as more electrons are ionized off. $Cr^{6+} = 44$ pm, $Cr^{3+} = 61.5$ pm.

22. **(A)** Correct order is F > Cl > Br > I. As fluorine has highest reduction potential and therefore, it is strongest oxidising agent.
(D) Correct order is Li < Na < K < Rb < Cs. The chemical reactivity increases down the group with decreasing ionisation energy. Although Li has highest negative reduction potential but its reactivity with water is lowest on account of its highest ionisation energy.

Part # II : Assertion & Reason

1. **S-1 :** It is true. Across the period for addition of each successive element, the nuclear charge increases by one unit as electrons are added in the same shell. Hence the size of atom decreases along the period from left to right.
S-2 : The higher electronegativity of O than N is due to more nuclear charge in O than N.

6. **S-1 :** NO is a neutral oxide while CrO_3 is an acidic oxide.

7. **S-1 :** It is correct statement. Across the period the nonmetallic character increases, therefore, the acidic character of oxides increases. On the other hand down the group the metallic character increases, therefore, the acidic character of oxides decreases. Hence the correct order of acidic character is $SO_3 > N_2O_5 > CO_2 > SiO_2$.
S-2 : It is incorrect statement. Acidic character of oxides decreases on moving top to bottom in a group and increases on moving left to right in a period in Modern periodic table.

8. **S-1 :** It is correct statement and this can be understood by taking the following example.
Negative electron gain enthalpy of O and F is less than S or Cl respectively.
S-2 : It is incorrect statement. This is due to the fact that when an electron is added to O or F, the added electron goes to the smaller n = 2 energy level and experiences significant repulsion from the other electrons present in this level. In S or Cl, the electron goes to the larger n = 3 energy level and consequently occupies a larger region of space leading to much less electron-electron repulsion.

10. **S-1 :** Electron gain enthalpy does not always becomes less negative as we go down a group in Modern periodic table. Ex. $\Delta_{eg}H$ (2p series) < $\Delta_{eg}H$ (3p series).

EXERCISE - 3

Part # I : Matrix Match Type

1. **(A)** This configuration belongs to He which has highest first ionisation enthalpy amongst all the elements of the periodic table. This is attributed to stable configuration and its small size.
(B) and **(C)** Group 17th has $ns^2\,np^5$ valence shell electron configuration. They have highest EN values and very high negative electron gain enthalpy because they can attain stable noble gas electronic configuration by picking up an electron. **(B)** configuration belongs to fluorine and F has highest electronegativity on Pauling scale. **(C)** configuration belongs to Cl, which has the maximum negative electron gain enthalpy (even greater than F ; due to its larger size and lesser interelectronic repulsion).
(D) This configuration belongs to C and it shows -4 oxidation state because it attains inert gas configuration of neon by gaining four electrons.

Part # II : Comprehension

Comprehension # 3 :

4. Element just above $Z = 43$ will be $Z = 43 - 18 = 25$ and will have electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$.

5. All these elements have outermost configuration $ns^2 np^5$. So they belong to Group $(12 + 5 = 17)$ means halogen family.

Comprehension # 4 :

3. Both N^{3-} and Al^{3+} are isoelectronic species, but Al^{3+} has greater nuclear charge. So, it will have smaller size. Zr(4d) ≈ Hf(5d), because of Lanthanide contraction.
Zn > Cu, their occur greater interelectronic repulsions in completely filled electronic configuration of 12th group elements.

Comprehension # 5 :

2. The non-metallic character of the elements is highest at the extreme right and then decreases from right to left across the period. Also it decreases more on moving top to bottom.

3. **(A)** Ionisation enthalpies of elements generally decrease along a group and increase along a period in Modern periodic table.
(B) In the 3rd period of Modern periodic table, the two most reactive elements are sodium and chlorine.
(C) Iodine has the least negative electron gain enthalpy among all halogens.
(D) Ionisation enthalpy of Pb is greater than that of Sn, because of poor shielding of nuclear charge by 4f-electrons.

EXERCISE - 4

Subjective Type

7. $5.92 = \sqrt{n(n+2)}$; n = 5 i.e. ion with +3 oxidation state has five unpaired electrons. As the element belongs to 3d-series it must be Iron (Z = 26) with electron configuration $[Ar]^{18} 3d^5 4s^0$ in +3 oxidation state. So electron configuration of ${}_{26}Fe$ is $[Ar]^{18} 3d^6 4s^2$. Last electron enters in d-orbital, so it belongs to d-block. Thus, the group number is 6 + 2 = 8. Principal quantum number of valence shell is 4, so it is fourth period element.

9. 1g ≡ 1/24 mole

$$\begin{tikzcd} & Mg \arrow[dl] \arrow[dr] & \\ Mg^{2+} & & Mg^{+} \\ \frac{1}{24} - x & & x \end{tikzcd}$$

$$x \times 720 + \left(\frac{1}{24} - x\right)(720 + 1440) = 50$$

$$720\,x + \frac{2160}{24} - 2160\,x = 50$$

$$\Rightarrow \quad 1440\,x = 90 - 50 = 40$$

$$\Rightarrow \quad x = \frac{40}{1440} = \frac{1}{36}$$

$$\therefore \quad \%\text{ of } Mg^+ = \frac{x}{1/24} \times 100 = \frac{24}{36} \times 100 \approx \mathbf{66.67\ \%}$$

12. $K(g) + F(g) \rightarrow F^-(g) + K^+(g)$ $\quad \Delta H = 18.4\ \text{kCal} = 0.8\ \text{eV}$
$K(g) \rightarrow K^+(g) + e^-$ $\quad IE = 4.3\ \text{eV}$
$F(g) + e^- \rightarrow F^-(g)$ $\quad EA = \Delta H - IE$
$= 4.3 - 0.82 = 3.5\ \text{eV}$

14. Both CO and N_2O are neutral oxides. So they cannot be acid anhydrides.

17. Let $X \longrightarrow X^+ e^-$
$\therefore$ IE (energy absorbed) = a eV per atom
and $X + e^- \longrightarrow X^-$
$\therefore$ EA (energy released) = – b eV per atom

Now $\frac{N}{2}$ number of X^- will lose two electrons to give $\frac{N}{2}$ X^+

$\therefore$ $X^- \longrightarrow X + e^-$
$\therefore$ energy absorbed = + b eV per atom.
$X \longrightarrow X^+ + e^-$
$\therefore$ energy absorbed = + a eV per atom.

$$\therefore \quad a \times \frac{N}{2} + b \times \frac{N}{2} = \frac{806.4 \times 1000}{1.6 \times 10^{-19}}\ \text{eV}$$

$$\text{or} \quad (a + b) = \frac{806.4 \times 1000 \times 2}{1.6 \times 10^{-19} \times 6 \times 10^{23}} = \frac{806.4 \times 2}{1.6 \times 60} = 16.8$$

$$\chi_M = \frac{IE + EA}{2} = \frac{16.8}{2} = 8.4$$

$\therefore$ Mulliken's electronegativity = 8.4

Pauling's electronegativity $= \frac{8.4}{2.8} = 3.0$

18. E.N. on Pauling scale $= \frac{7}{2.8} = 2.5$

E.N. on Pauling scale for 2nd element $= \frac{1.4}{2.8} = 0.5$

Electronegativity difference $\Delta = 2.5 - 0.5 = 2$

$\therefore$ % ionic character $= 16\Delta + 3.5\,\Delta^2 = 16 \times 2 + 3.5 \times 2^2$

$= 32 + 14 = 46\%$

25. The block of an element depends on the type of subshell which receive the last electron.

$Z = 19$, $[Ar]^{18}\,4s^1$. As last electron enter in 4s-subshell, so it belongs to s-block.

$Z = 25$, $[Ar]^{18}\,3d^5\,4s^2$. As last electron enter in 3d-subshell, so it belongs to d-block.

$Z = 31$, $[Ar]^{18}\,3d^{10}\,4s^2\,4p^1$. As last electron enter in 4p-subshell, so it belongs to p-block.

$Z = 38$, $[Kr]^{36}\,5s^2$. As last electron enter in 5s-subshell, so it belongs to s-block.

$Z = 42$, $[Kr]^{36}\,4d^4\,5s^2$. As last electron enter in 4d-subshell, so it belongs to d-block.

$Z = 54$, $[Xe]^{54}$. As last electron enter in 5p-subshell, so it belongs to p-block.

$Z = 64$, $[Xe]^{54}\,6s^2\,5d^1\,4f^7$. As last electron enter in 4f-subshell, so it belongs to f-block.

For $103 \le Z \le 118$, Group number $= Z - 100$. So, for element with $Z = 105$, Group number $= 5$ (d-block).

So, s-block : 19, 38 ; p-block : 31, 54 ; d-block : 25, 42, 105 ; f-block : 64.

27 As spin magnetic moment $= \sqrt{n(n+2)} = 1.73$;

So, $n = 1$

Since atom has only one unpaired electron, hence it must be ${}_{29}Cu$ $[{}_{29}Cu = [Ar]^{18}\,3d^{10}\,4s^1]$.

Hence element below it in Modern periodic table has atomic number $29 + 18 = 47$.

34 **(a)** Ionization enthalpy decreases on moving down the group. However, value of Sn is less than Pb due to Lanthanide contraction.

(b) Electronegativity decreases from B to Al as expected, and then increases marginally due to discrepancies in atomic sizes.

35. Electronegativity of A $= \frac{400 + 80}{130} \approx 3.7$

Electronegativity of B $= \frac{300 + 90}{130} = 3$

Therefore A has higher electronegativity.

36. $X_A - X_B = 0.208\left[E_{AB} - \sqrt{E_{AA}\,.\,E_{BB}}\right]^{1/2}$

$= 0.208\left[6 - \sqrt{4 \times 1}\right]^{1/2} = 0.2$

% ionic character $= 16(X_A - X_B) + 3.5\,(X_A - X_B)^2$

$= 3.34\%$

37. "6s" subshell do not participate in bonding due to inert pair effect. Due to participation of two less electrons, an oxidation state, 2 less than normal oxidation state, starts appearing in elements of 13th, 14th & 15th group of Modern periodic table.

38. Due to inert pair effect, Pb^{2+} is more stable as compared to Ge^{2+}. So Ge^{2+} has greater tendency to get oxidised to Ge^{4+} and hence has greater reducing capacity.

EXERCISE - 5

Part # I : AIEEE/JEE-MAIN

1. O^{2-} and F^- have two shells while Li^+ and B^{3+} have only one shell. Also, $O^{2-} > F^-$ (for isoelectronic species, as Z]increases, size decreases).

2. The addition of second electron in an atom or ion is always endothermic because of repulsion between two negative charges.

3. On moving left to right in a period, electronegativity increases. So non-metallic character increases.Thus, acidic strength of oxides increases and basic strength decreases.

4. CaO - basic, CO_2 and SiO_2 - acidic, SnO_2 - amphoteric, as it reacts with both acids and bases.

$SnO_2 + 4HCI \rightarrow SnCI_4 + 2H_2O$

$SnO_2 + 2NaOH \rightarrow Na_2SnO_3 + H_2O$

5. Nitrogen has half filled stable configuration, ns^2np^3. So, ionization enthalpy of nitrogen is greater than oxygen. On moving down the group, metallic radius increases due to increase in number of shells.

6. Lanthanide contraction is due to poor shielding of one of $4f$ electron by another in the sub-shell.

7. The atomic radii of the second and third transition series are almost the same. This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called **Lanthanide contraction** which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanide contraction is that the second and the third d series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm).

8.

Element :	B	S	P	F
I.E.(kJ mol^{-1}) :	801	1000	1011	1681

In general as we move from left to right in a period, the ionization enthalpy increases with increasing atomic number. The ionization enthalpy decreases as we move down a group. P ($1s^2, 2s^2, 3s^2\ 3p^3$) has a stable half filled electronic configuration than S ($1s^2, 2s^2, 2p^6, 3s^2, 3p^4$). For this reason, ionization enthalpy of P is greater than S.

9. In case of oxyacids of same element, higher is the oxidation state of the central atom, greater is the acidity. Hence, $HClO_4$ is a stronger acid than $HClO_3$. HNO_3 is a stronger acid than HNO_2.
Now greater is the electronegativity of central atom, greater is the acidity. Hence H_2SO_3 is a stronger acid than H_3PO_3.
Due to greater bond dissociation energy of H–F bond and molecular association due to hydrogen bonding in HF, HF is a weaker acid than HCl.

10. Lanthanoid contraction is due to ineffective shielding produced by larger f-subshell.

11. Due to the inert pair effect (the reluctance of ns^2 electrons of outermost shell to participate in bonding) the stability of M^{2+} ions (of group 14 elements) increases as we go down the group.

12. Down the group, ionic radii increases with increasing atomic number because of the increase in the number of shells. But across the period, the ionic radii decreases due to increase in effective nuclear charge as electrons are added in the same shell. Li^+ and Mg^{2+} are diagonally related but Mg^{2+} having higher charge is smaller than Li^+, so correct order is $Na^+ > Li^+ > Mg^{2+} > Be^{2+}$.

$Be^{2+} = 0.31$ Å
$Mg^{2+} = 0.72$ Å
$Li^+ = 0.76$ Å
$Na^+ = 1.02$ Å

13. HF < HCl < HBr < HI (on moving top to bottom, bond dissociation energy decreases, so acidic strength increases).
B < C < O < N (on moving left to right, Z_{eff} increases, so first ionization enthalpy increases ; N > O because N is half filled).
$CO_2 < SiO_2 < SnO_2 < PbO_2$ (on moving top to bottom, + 4 oxidation state becomes less stable due to inert pair effect). So oxidising power increases.
Since, (1), (3) and (4) are correct, so (2) is the answer.
In hydrides of 15th group elements, the basic strength decreases down the group and the correct order is :

$SbH_3 < AsH_3 < PH_3 < NH_3$

14. For isoelectronic species, ionic radii $\propto \dfrac{1}{\text{nuclear charge}}$.

So, correct order of ionic radii is ${}_8O^{2-} > {}_9F^- > {}_{11}Na^+ > {}_{12}Mg^{2+} > {}_{13}Al^{3+}$.

15. Gadolinium (${}_{64}Gd$) = $[Xe]^{54}\, 4f^7 5d^1 6s^2$

16. As metallic character of element attached to oxygen atom increases (on moving top to bottom or right to left in Modern periodic table), the difference between the electronegativity values of element and oxygen increases and thus basic character of oxides increases and vice-versa. Hence the increasing correct order of basic nature is $Al_2O_3 < MgO < Na_2O < K_2O$.

17. As we move in a group from top to bottom, electron gain enthalpy becomes less negative because the size of the atom increases and the added electron would be at larger distance from the nucleus.

Negative electron gain enthalpy of F is less than Cl. This is due to the fact that when an electron is added to F, the added electron goes to the smaller n = 2 energy level and experiences significant repulsion from the other electrons present in this level. In Cl, the electron goes to the larger n = 3 energy level and consequently occupies a larger region of space leading to much less electron-electron repulsion. So the correct order is Cl > F > Br > I.

18. Order of ionic radii $Ca^{2+} < K^+ < Cl^- < S^{2-}$

In isoelectronic species, as Z increases, size decreases.

19. Order of increasing ΔH_{IE_1} : Ba < Ca < Se < S < Ar

Ba < Ca ; Se < S : On moving top to bottom in a group, size increases. So ionisation enthalpy decreases.

Ar : Maximum value of ionisation enthalpy, since it is an inert gas.

20. $Na \longrightarrow Na^+ + e^-$ Ist I.E. = 5.1 eV

$Na^+ + e^- \longrightarrow Na$ Electron gain enthalpy of Na^+

Because reaction is reverse, so :

$\Delta_{eg}H = -5.1$ eV.

21. $CsI_3 \longrightarrow Cs^+ + I_3^-$

⇒ Cs cannot show +3 oxidation state.

⇒ I_2 molecules are too large to be accommodated in latice.

22. Isoelectronic species. If number of protons are more size will be less.

23. 3

24.
$$\left.\begin{array}{l} PH_3 \\ O_2 \\ B_2H_6 \\ H_2SO_4 \end{array}\right\} \text{All are covalent compounds}$$

KCl is ionic compound.

Part # II : IIT-JEE ADVANCED

1. The basic nature of oxides can be compared on the basis of the factors given below :

(i) If electronegativity difference between element and oxygen is less than 1.4, the oxide is generally acidic and if this difference is more than 1.4, the oxide is generally basic.

(ii) The basic character increases with increasing metallic character down the group and decreases across the period.

Hence the correct order of increasing Bronsted basicity is $Cl_2O_7 < SO_3 < CO_2 < B_2O_3 < BaO$.

2. In p-block elements (i.e. 14th group here), the lower oxidation state becomes more stable on going down the group due to inert pair effect. Thus, Pb^{4+} is less stable than Sn^{4+}. This makes the Pb^{4+} a stronger oxidising agent. Therefore, the statement-2 is incorrect.

MOCK TEST

1. (II) The d-block elements have general electronic configuration [noble] $(n-1)d^{1-10}\,ns^{0-2}$. It is configuration of copper which belongs to d-block and group number 11th.

2. $O^+ = 2s^2\,2p^3$ – half filled configuration has extra stability & $F^+ = 2s^2 2p^4$ partially filled less stable thus IE_2 of O > F. As nuclear charge increases the IE_2 increases. So IE_2 of N > C.

3. Due to small of F atom, the electron-electron repulsions in compact 2-p sub shell are large and hence the incoming electron is not accepted with the same ease as is the case with Cl (less electron - electron repulsions)

4. **(A)**, **(C)** and **(D)** are correct statements

(B) first decreases from B to Al and then increases marginally owing to discrepancies in atomic size of the element.

5. **(A)** As electronegativity increases the non-metallic character increases as tendency to form anion increases.

(B) It is bases on their SRP values. (Oxidising power may be cumulative effect of hydration energies, electronegativities, bond dissociation energies and electron gain enthalpies).

(C) C = – 121; Si = – 135 ; P = – 60 ; N = + 31 (all values are in KJ/mole). It depends on various factors like size of atom, nuclear charge, partially filled, half filled and completely filled electronic configurations.

6. Oxidation state ∝ electronegativity

Electronegativity increases with increase in oxidatioin state, so the \difference in electronegavitiy decreases (between element and oxygen) and acidic character increases.

7. **(A)** As screening effect increases, effective nuclear charge decreases thus valence shell electron is loosely bound. Hence I. E decreases.

(B) Be and Mg has ns^2 configuration (stable configuration)

(C) Due to lanthanide contraction

(D) $r_{\text{metallic}} > r_{\text{covalent}}$ (covalent bond formation involves the overlapping of orbitabls).

8. Species having same number of electrons are called isoelectronic species.

9. **(B)** Addition of second electron to O^- is opposed by electrostatic repulsion due to same charge. Hence energy is given for the addition of IInd electron.

(D) Ar has stable electronic configuration ($ns^2\,np^6$). Hence energy has to be given to add an extra electron to form Ar^-

10. High electronegativity and small size, has only –1 oxidation state.

12. Both statements are true and **Statement-2** is the true explanation of the Statement-1. The magnitude of an element's electron affinity depends on the element's valence shell electrons configuration.

$_{25}Mn = [Ar]^{18}\, 3d^5\, 4s^2$ configuration, $_{24}Cr = [Ar]^{18}\, 3d^5\, 4s^1$ configuration, $_{26}Fe = [Ar]^{18}\, 3d^6\, 4s^2$ configuration

13. Statement-1 is false. Electron configuration $_{16}S^{2+} = 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^2$ and $_{15}P^{2+} = 1s^1\, 2s^2\, 2p^6\, 3s^2\, 3p^1$.

Sulphur gas higher nucler charge and smaller size than that of phosphorus so IE_3 of S > P .

$IE_3\,(P) = 2,912\,;\,(S) = 3,361$ KJmol^{-1}.

14. **S1** : Metal comprises more than 78% of all known elements.

S2 : Selenium is not a semi-metal.

S_3 and S_4 correct Statements.

15. Electronic configuratioin of element with Z = 56; $[Xe]^{54}\, 6s^2$

Electronic configuration of element with Z = 12 ; $[Ne]^{10}\, 3s^2$

As both have same valence shell electron configurations they belongs to s-block and same group i.e. 2nd, the alkaline earth metals.

16. If aufbau rule is not followed then 3d will be filled before 4s. So lkast electron of Ca-20 will go to 3d-subshell.

Hence the element will belong to d-block inplace of s-block.

17. When n = 4, the configuration will be $[Ar]^{18}\, 3d^1\, 4s^2$ and thus period is fourth and group number is third, (1 + 2 + 3).

18. Value corresponds to Noble gas. Hence, T is inert toward chemical reactivity.

19. Metal having low IE_1 and higher IE_2 corresponds to alkali metal. Hence, Q is most reactive metal (easily forms cation).

20. Non-metal having higher negative value of electron gain enthalpy corresponds to halogen. Hence R is more reactive non-metal (easily forms anion).

21. In a period the IE increases due to decrease in atomic size & increase in nuclear charge. But IE_1 of Mg is greater than Al due to more penetration power of S-sub shel electrons and stable $3s^2$ configuration (completely filled s-orbital).

22. All statements are correct.

23. Orbitals bearing lower value of n will be more closer to the nucleus and thus electrons will epxerience greater attraction from nucleus and so its removal will be difficult not easier.

24. ΔH_{eg} kJ mol^{-1} $\longrightarrow$ Cl = – 349 ; F = 328 ;

S = – 200 ; O = – 141

25. **(A)** Have same number of electrons – So isoelectronic species

(B) Has metallic as well as non-metallic properties-semi metal

(C) They belongs to group 18th elements i.e. noble gases. All have $ns^2\, np^6$ valence electrons configuration.

(D) Their oxides in water form strong alkalies and occur in earth crust.

26. **(A)** inter gases exist as monoatomic molecule. They have higest IE_1 and IE_2 and positive electron gain enthalpies.

(B) Alkali metal – IE_1 is low because of bigger size of atom and IE_2 is high due to noble gas configuration. As it has low IE_1, it can lose one electron easily and thus more electropositive. So it acts as strong reducing agents and their oxides are basic in nature. They have low negative value of ΔH_{eg} because of large size.

(C) IE_1 and IE_2 both high and negative value of electron gain enthalpy is very high because of high nuclear charge and small size of atoms, so it has a greater tendency to accept an additional electron. So it as a strong oxidising agent.

(D) As it has less negative value for ΔH_{eg} then **(C)** thus it will be least reactive non – metal (I).

27. **(A)** For isoelectronic species, the ionic size decreases with increase in nuclear charge. Hydration ∝ charge on anion and heavier hydrated ions move slowly. So it is not correct order.

(B) Heavier hydrated ions move slowly. Number of atomic shells increases, ionic size increases.

(C) Correct order ; as Cl has less inter electronic repulsions than F due to bigger size of 3p-subshell.

(D) Oxidation state increases, the electronegativity increases. For isoelectronic species ionisation energy and electron affinity increases with increasing nuclear charge.