Periodic properties of Atoms

Modern Periodic law: Physical and Chemical properties of the elements are periodic function of their atomic numbers.

Modern periodic table contains seven periods and eighteen groups. Elements are placed in four different blocks depending on their electronic configuration. The blocks are termed as s, p, d and f-blocks as the differentiating electrons are placed s, p, d and f orbital respectively. The s and p blocks elements are called representative elements, d-block elements are called transition elements and f-block elements are termed as inner transition elements (Lanthanide and actinide)

IUPAC name of elements of atomic number 100 or higher:

To overcome the controversies on naming the newly synthesized elements IUPAC introduced a new method of naming these elements.

Rule: According to the atomic number of an element the following numerical roots are used serially.

0	1	2	3	4	5	6	7	8	9
nil	un	bi	tri	quad	pent	hex	sept	oct	enn

The roots are put together and at the end 'ium' is used to complete the name of elements. (Repetition of letter 'i' is avoided for bi and tri)

For example:

100: Unnilnilium, 104: Unnilquadium, 110: Ununnilium, 112: Ununbium

Calculation of effective nuclear charge (Z_{eff} or Z^*)

Slater's rule: Slater proposed a set of empirical rules to estimate shielding contributions by electrons in different orbitals. It is used to calculate Z_{eff} by formulae, $Z_{eff} = Z - \sigma$ where Z = nuclear charge and σ = screening constant.

(i) The electrons of the atoms are divided into groups like (1s), (2s 2p), (3s 3p), (3d), (4s 4p), (4d), (4f), (5s 5p), (5d), (5f)......

(ii) Electrons in groups on the right side do not screen inner electron, so shielding contribution is zero.

(iii) Each other electron in same group: 0.30 for 1s group and 0.35 for other groups

(iv) If the electron under consideration belongs to (ns np) group then all electrons with principal quantum number less by one unit contribute 0.85 each and remaining electrons in the left contribute 1.00 each.

(v) If the electron under consideration belongs to (nd) or (np) group then all electrons with principal quantum number less by one unit: 1.0 each.

Example:

The ground state configuration of Zn (Z = 30) is $(1s)^2$, $(2s\ 2p)^8$, $(3s\ 3p)^8$, $(3d)^{10}$, $(4s)^2$

(i) 1s electron: $\sigma = 0.30$ and $Z_{eff} = 30 - 0.30 = 29.70$

(ii) 2s or 2p electron: $\sigma = (7 \times 0.35) + (2 \times 0.85) = 4.15$ and $Z_{eff} = 30 - 4.15 = 25.85$

(iii) 3s and 3p electrons: $\sigma = (7 \times 0.35) + (8 \times 0.85) + (2 \times 1) = 11.25$ and $Z_{eff} = 30 - 11.25 = 14.75$.

(iv) 3d electrons: $\sigma = (9 \times 0.35) + (18 \times 1) = 21.15$ and $Z_{eff} = 30 - 21.15 = 8.85$

(v) 4s electrons: $\sigma = (1 \times 0.35) + (18 \times 0.85) + (10 \times 1) = 25.65$ and $Z_{eff} = 30 - 25.65 = 4.35$

Size of the Atom:

Atomic Volume: The atomic volume is the volume of one mole of atoms of an element. Atomic volume (c.c./mole) = $\frac{\text{Atomic weight}}{\text{Density}}$. The density of the elements first increases and then decreases along a period because binding force depends on the number of valence electron provided by each atom, whether on moving down the group density increases because number of neutrons and protons increases. Atomic weight increases both in along the period and group but extent of increase down the group is large compared to along the period. That's why variation of atomic volume is not simple. It is found that the Gr-1 elements have highest atomic volume because of lowest density as they have only one valence electron.

Atomic radius:

van der Waals radius: The half of the shortest distance between two non-bonded atoms. For example, in solid xenon, inter-atomic distance is 436 pm. The vander Waals radius is to be 218 pm.

Metallic radius: The half distance of the two nearest neighbour atom in a metallic crystal of specific geometry and coordination number (C.N.) of metal. It depends on the C.N., as the C.N. increases, crowding of the atoms introduce more electronic repulsion and resulting larger value of metallic radius. Goldschmidt suggested relative scale of metallic radius based on the 12-coordinated radius as unity.

C.N.	4	6	8	12
Relative radius	0.88	0.96	0.97	1

Problem 1: The interionic distance between two sodium atoms in C.N. 8 is 370 pm. Calculate the metallic radius of Na in C.N. 12.

Answer: r_8 = 370/2 = 185 pm. r_{12} = 185/0.97 = 191 pm

Problem 2: The interionic distance between two sodium atoms in C.N. 12 is 382 pm. Calculate the metallic radius of Na in C.N. 8.

Answer: r_{12} = 382/2 = 191 pm. r_8 = 191 x 0.97 = 185 pm

Covalent radius: The half of the internuclear distance between two atoms of same element forming single bond i.e., half of the bond distance.

Molecule	Bond distance (pm)	r_{cov} (pm) estimated	r_{cov} (pm) accepted
H_2	74	37	29
F_2	142	71	64

Schomaker-Stevenson relation: It is used to calculate covalent radius when two different atoms are joined by single covalent bond.

$r_{A-B} = r_A + r_B - 9(\chi_A - \chi_B)$ where χ terms represent the electronegativity.

$r_{A-B} = r_A + r_B - 7(\chi_A - \chi_B)^2$ a modified version of this relation is also used to calculate many bond lengths.

Periodic trend:

Co-valent atomic radii gradually decreases from left to right along the period as effective nuclear charge increases gradually whereas, down to a group, size increases as electron enters to new shell. But, few exceptions in size are also observed because of scandide contraction or lanthanide contraction.

Ionic radius: The radius of ions i.e., cation and anion is obtained from interionic distance in ionic crystals. It is the distance between the nucleus and outermost electron. The radius of cation is always smaller than the neutral atom while size of anion is higher than neutral atom. The extent of decrease or increase of size is also depends on charge of the ions.

Pauling's approach to calculate ionic radii:

It was assumed radii of isoelectronic ions are varied inversely with their effective nuclear

charge, i.e., $r = \dfrac{C}{Z_{eff}} = \dfrac{C}{Z - \sigma}$

Example: NaF

The interionic distance is 231 pm i.e., $r_{Na^+} + r_{F^-} = 231$

$r_{Na^+} = \dfrac{C}{11 - 4.5}$ and $r_{F^-} = \dfrac{C}{9 - 4.5}$ So, $r_{Na^+} + r_{F^-} = \dfrac{C}{6.5} + \dfrac{C}{4.5} = 231$

Or, $\dfrac{4.5C + 6.5C}{29.25} = 231$ or, C = 614.25

Therefore, $r_{Na^+} = \dfrac{614.25}{6.5} = 94.5$ and $r_{F^-} = \dfrac{614.25}{4.5} = 136.5$

[$_{11}Na^+$ or $_9F^-$: $(1s)^2 (2s2p)^8$ and $\sigma = (8 \times 0.35) + (2 \times 0.85) = 4.5$]

Size of divalent ions:

The ionic radii calculated by Pauling's method matched satisfactorily for univalent ions by

the other method and also with the observed values. But, the radii of multivalent ion do not

match. For this reason, an empirical formulae is introduced to calculate the ionic radii of

multivalent ions which is as follows: $r_c = r_1(Z)^{-2/(n-1)}$

Where, Z = charge, n = Born exponent and r_1 = radius of corresponding univalent ion

Example 1: The univalent radius of Ca^{2+} is 117 pm and S^{2-} is 219 pm. Calculate the effective

crystal radii of the ions. Given Born exponent (n) = 9 for both ions.

Answer: $r_c(Ca^{2+}) = 117 (2)^{-2/(9-1)} = 98.38$ pm and $r_c(S^{2-}) = 219 (2)^{-2/(9-1)} = 184.16$ pm

Example 2: The univalent radius of the oxide ion is 175 pm. Calculate the crystal radius of

O^{2-} ion. Given Born exponent (n) = 7.

Answer: $r_c(O^{2-}) = 175 (2)^{-2/(7-1)} = 139$ pm

Lanthanide contraction:

A prominent steady decrease of the metallic radii as well as ionic radii among the post lanthanum elements of 4f-series is observed, this phenomenon is popularly referred to as lanthanide contraction.

This steady decrease in size occurs due to filling of the 4f subshell. In the f-series the differentiating electron goes to the second penultimate shell in the (n-2)f subshell. The f-orbitals have very much low screening power because of their diffused shape and also have least penetrating power into the inner electron core. So, on successive addition of electron to f-subshell do not efficiently screen the next incoming electrons from the progressively increasing nuclear charge. Thus, the effective nuclear charge (Z*) experienced by the valence shell electrons gradually increases with the increase of atomic number along the series. This is why, contraction of spatial distribution of the orbitals and hence a gradual shrinkage in the atomic radii and ionic radii.

- The Relativistic effects on the 6s orbital of the lanthanides are also partly responsible for the lanthanide contraction.

Relativistic Effect

In heavier elements (Z > 80), relativistic variation of the mass of the electron becomes so prominent it causes an effective contraction in spatial distribution of the orbitals. This phenomenon is called relativistic effect.

According to Bohr model, the radial velocity v of an electron in an orbit of principal quantum number n is given by $v = \frac{Ze^2}{2\varepsilon_0 nh}$. For known values of ε_0, h and e, the velocity of 1s electron in H-atom (Z = 1, n = 1) will be 2.19 x 10^6 m s^{-1} = 0.0073c. But, when Z = 80 (Hg), the velocity of 1s electron will be 0.58c. According to the relativistic relation $m = \frac{m_0}{\sqrt{1-(\frac{v^2}{c^2})}}$ or, m = 1.2m$_0$, that means the mass of 1s electron in Hg increases about 20% relative to rest mass.

According to Bohr model, $r = \dfrac{Ze^2}{4\pi\varepsilon_0 mv^2}$, so radius of the orbit (r) will shrink, that is more closer to the nucleus.

Since, the velocity of an electron is inversely proportional to n, the relativistic effect will be most pronounced for electrons closer to the nucleus. According to wave mechanical model, this implies that the relativistic effect will be most pronounced for s-orbitals which penetrate most into inner electron core.

The relativistic effect becomes prominent in the sixth period, particularly on the 6s electrons. The contracted 6s orbital is lowered in energy and becomes largely separated from the 6p orbital. Properties of gold, mercury and last elements of p-block are largely influenced by the relativistic effect.

Q. Compare the size of H^-, F^-, Cl^- and Br^- ions?

Answer: Down to the group, the sizes of the elements are gradually increases because the last electron is entered into the shell having higher principal quantum number. So, order of size of halides will be $F^- < Cl^- < Br^-$. But, H^- is the only ion where electron to proton ratio (e/p) is 2 that results an appreciable electronic repulsion causes expanding of electron cloud. That's why, in spite of $1s^2$ configuration, the distance of electronic cloud from the nucleus is higher than in Br^-.

Q. Arrange the isoelectronic ions K^+, Ca^{2+}, S^{2-} and Cl^- in decreasing order of ionic sizes.

Answer: The cations have always smaller size compared to neutral atom because cations have more number of positive charge than the electron i.e. $\dfrac{proton}{electron} > 1$. Therefore, nucleus strongly attracts the outermost electron and decreases the size. Whereas, anions have larger size that the neutral atom because anions have less positive charge than the electron i.e. $\dfrac{proton}{electron} < 1$. Therefore, nucleus attracts the outermost electron weakly and increases the size. At the same time, neutral to mono-positive to di-positive ion Z^* is increased and neutral to mono-negative to di-negative anion Z^* is decreased. So, the decreasing order of size will be $S^{2-} > Cl^- > K^+ > Ca^{2+}$.

Ionisation energy: Minimum energy required to remove the most loosely bound electron from a free gaseous atom of the element in its ground state. It is expressed in kJ/mole.

$A(g) \xrightarrow{I_1} A^+(g) + e$; $A^+(g) \xrightarrow{I_2} A^{2+}(g) + e$; $A^{2+}(g) \xrightarrow{I_3} A^{3+}(g) + e$; and so on.....
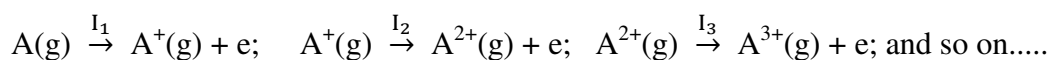
I_1, I_2 and I_3 term denotes the first, second and third ionisation energy respectively.

According to Bohr atomic model, $E_n = -R_H hc \frac{Z^2}{n^2}$ (R_H = Rydberg constant, h = Planck Constant, c = velocity of light, Z = atomic number), we can calculate the ionisation energy of an element. For example, ionisation energy of hydrogen is the E_1 x N_0 = (2.18 x 10^{-18}) x (6.023 x 10^{23}) = 1312 KJ/mole.

Problem: Estimate the fifth ionisation energy of boron if ionisation energy of H is 13.6eV.

$B^{4+}(g) \rightarrow B^{5+}(g) + e$; B^{4+} is a hydrogen like system. $E = -R_H hc \frac{Z^2}{n^2} = -13.6 \times 5^2 = 340$ eV.
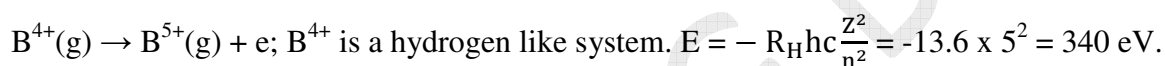
So, ionisation energy is 340 x 96.485 = 32804.9 kJ/mole

Controlling factors of ionisation energy:

1) Ionisation energy is increased with increase of effective nuclear charge (Z*), which depends on the screening capacity of inner orbitals.

2) It is decreased with increase of radial distance of the orbital i.e., size of the atom.

3) It depends on the penetrating nature orbital from which electron is removed. More energy is required to remove an electron from the orbital having high penetration power.

4) It also depends on the relative electron configuration before and after ionisation. For example, half field configuration has high ionisation energy.

   The energy order of ionisation energy is $I_1 < I_2 < I_3$ because more energy is required to removed an electron from positive charged ion compared to the neutral, or lower positive cation. At the same time, removal of an electron results in an increase of Z* and consequently, size of the species decreases.

Periodic trend of ionisation energy:

Generally, the ionisation energy decreases down to any group as size increases whereas along the period, ionisation energy is increased as size decreases with increase of Z*. Though few exceptions are observed, for example, Ga shows slightly higher ionisation energy than Al. Similarly, Tl also shows higher value of ionisation energy. In case of transition elements 6th period elements has higher ionisation energy than lighter congeners. For example, the order of I.E. for Gr. 5 element is V < Nb < Ta and Gr. 11 is Ag < Cu < Au.

For the second period elements, the trend of ionisation is as follows: Li < Be > B < C < N > O < F < Ne. This is because of stable electron configuration of Be and N.

Q. Compare the first ionization energy of Cu, Ag and Au.

Answer: As proceed down a group, the last electron enters to new shell of higher principal quantum number. Therefore, the size more precisely the radial distance of the orbital from which electron to be removed is increases and ionisation will be easier down the group. So, it is expecting the order of ionisation energy would be Cu > Ag > Au. But, Au has highest first ionisation energy than Cu and Ag. The electron configuration of Au is $[Xe]4f^{14} 5d^{10} 6s^1$. Due to improper screening of the inner 4f and 5d electron as well as relativistic effect, $6s^1$ electron is so stabilized that more energy is required to ionize it compared to the $4s^1$ or $5s^1$ electron of Cu or Ag. So, the actual order of first ionisation energy will be Au > Cu > Ag.

Calculation of ionisation energy using Slater's rule:

The energy of an electron in an atom according to Slater's treatment is $E = -13.6 \left(\frac{Z_{eff}}{n^*}\right)^2$ eV

Where Z_{eff} is effective nuclear charge and n* is effective principal quantum number. The value of n* is related with n is as follows:

n	1	2	3	4	5	6	7
N*	1.0	2.0	3.0	3.7	4.0	4.2	4.4

The ionisation energy of an atom or ion will be equal to the difference in energy between the energies of after and before ionisation i.e., $I = E_{M^+} - E_M$

Similarly, Electron affinity (E.A.) $= E_{X^-} - E_X$

Here, E tern is the sum of energies of all electrons in the species.

Calculation of first ionisation energy of Li:

$$E_{Li} = -13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{1s^2} - 13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{2s^1} \text{ and } E_{Li^+} = -13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{1s^2}$$

$$I = E_{Li^+} - E_{Li} = 13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{2s^1} = -13.6 \left(\frac{1.30}{2}\right)^2 \text{ eV} = 5.75 \text{ eV}$$

$[_3Li = (1s)^2 (2s)^1$ and Z_{eff} for 2s electron $= 3 - (2 \times 0.85) = 1.30]$

Calculation of first ionisation energy of O:

$$E_O = -13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{1s^2} - 13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{(2s2p)^6} \text{ and } E_{O^+} = -13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{1s^2} - 13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{(2s2p)^5}$$

$[_8O = (1s)^2 (2s2p)^6$ and Z_{eff} for (2s 2p) electron $= 8 - [(5 \times 0.35) + (2 \times 0.85)] = 4.55$ and

$_8O^+ = (1s)^2 (2s2p)^5$ and Z_{eff} for (2s 2p) electron $= 8 - [(4 \times 0.35) + (2 \times 0.85)] = 4.90]$

$$I = E_{O^+} - E_O = \left[6 \times 13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{(2s2p)^6}\right] - \left[5 \times 13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{(2s2p)^5}\right]$$

$$= \left[6 \times 13.6 \left(\frac{4.55}{2}\right)^2\right] - \left[5 \times 13.6 \left(\frac{4.90}{2}\right)^2\right] = 422.331 - 408.17 = 14.16 \text{ eV}$$

Electron affinity: The energy released due to the addition of an electron to the valence shell of a free gaseous atom of the element in its ground state. $A(g) + e \rightarrow A^-(g)$

It is also defined as the ionisation energy of $A^-(g)$ ion, that's why, electron affinity is also described as 'zeroth ionisation energy'. $A^-(g) \rightarrow A(g) + e$

Factor affecting electron affinity:

(i) Size of atom: Smaller atom has higher electron affinity as new added electron experience higher nuclear attraction force.

(ii) Effective nuclear charge: The element having higher effective nuclear charge for valence shell will have high electron affinity.

(iii) Nature of the orbital involved: If the electron is added to a orbital has high penetrating power, electron affinity value will be greater.

(iv) Nature of electron configuration: The relative configuration after and before addition of electron.

Periodic trend of electron affinity: It is increased along the period from left to right, reaching maxima at halogen and negative for inert element. Down to any group, electron affinity value is decreased because higher size as electron is added to the next higher shell i.e., at larger distance from the nucleus.

Q. Explain the electron affinity order. F < Cl; O < S; N < P; B < Al.

Though the nuclear attractive force towards the new added electron is higher for 2nd period element but, on addition of electron, the electron-electron repulsion is increased, due to smaller size. This repulsive force is not large in 3rd period element because of their larger size as well as they have vacant d-orbital to delocalize the extra negative charge. That's why 2nd period elements have lower electron affinity compared to the 3rd period element of same group.

Calculation of electron affinity using Slater's rule:

Calculate electron affinity of F:

$_9$F: $(1s)^2 (2s2p)^7$ and Z_{eff} for (2s 2p) electron = $9 - [(6 \times 0.35) + (2 \times 0.85)] = 5.2$

$_9$F$^-$: $(1s)^2 (2s2p)^8$ and Z_{eff} for (2s 2p) electron = $9 - [(7 \times 0.35) + (2 \times 0.85)] = 4.85$

$E_F = -13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{1s^2} - 13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{(2s2p)^7}$ and $E_{F^-} = -13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{1s^2} - 13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{(2s2p)^8}$

E.A. of F = $E_{F^-} - E_F = [7 \times 13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{(2s2p)^7}] - [8 \times 13.6 \left(\frac{Z_{eff}}{n^*}\right)^2_{(2s2p)^8}]$

$= [7 \times 13.6 \left(\frac{5.2}{2}\right)^2] - [8 \times 13.6 \left(\frac{4.85}{2}\right)^2] = 643.55 - 639.74 = 3.81$ eV

Electronegativity: It is defined as the ability of an atom to attract electrons towards itself in a chemical bond with another element. Electronegativity is not inherent property of an isolated atom because it depends on bonding environment of the atom. The different theoretical approach is developed to calculate electronegativity value of the elements.

(i) Pauling scale: According to Pauling, A-B bond is more stable than either A-A or B-B. This extra stability arises due to unequal sharing of bonding electron between A and B, giving rise to some ionic character. The extent of ionic character is depends on the unequal sharing of bonding electron which in turn arises due to difference in electron attracting powers of A and B in A-B bond. This property is termed as electronegativity.

The electronegativity of the elements is related to the extra stability as follows:

$|\chi_A - \chi_B| = 0.102\sqrt{\Delta}$ where χ terms represent electronegativity and Δ represent extra stability of A-B bond, measured as the difference between (i) the actual bond energy of A-B bond, E_{A-B} and (ii) the hypothetical bond energy of the A-B bond if it is fully co-valent, E_{cov} that is $\Delta = E_{A-B} - E_{cov}$ where $E_{cov} = (E_{A-A} . E_{B-B})^{\frac{1}{2}}$. Therefore, finally we can write,

$|\chi_A - \chi_B| = 0.102\sqrt{E_{A-B} - \sqrt{E_{A-A} . E_{B-B}}}$ (The bond energy is taken in kJmol^{-1})

$|\chi_A - \chi_B| = 0.208\sqrt{E_{A-B} - \sqrt{E_{A-A} . E_{B-B}}}$ (The bond energy is taken in kcalmol^{-1})

Q. Calculate the Pauling electronegativity of iodine. $\chi_A = 4.0$ and Bond energy of I-F = 278, I-I = 149 and F-F = 155 kJmol^{-1}.

Ans: $|4.0 - \chi_I| = 0.102\sqrt{278 - \sqrt{149 . 155}}$ or, $\chi_I = 4.0 - 0.102\sqrt{(278 - 152)} = 4 - 1.145 = 2.855$

The Mulliken scale:

Electronegativity is the average value of ionisation energy and electron affinity, both is taken in electronvolt (eV) per atom. $\chi_M = \frac{1}{2}(I.E. + E.A.)$

Mulliken electronegativity is related with Pauling electronegativity as follows:

$\chi_P = 1.35\sqrt{\chi_M} - 1.37$

Q. Calculate Mulliken electronegativity of chlorine. I.E. = 13.0 eV per atom and E.A. = 4.0 eV per atm.

Ans: $\chi_{Cl} = \frac{1}{2}(13.0 - 4.0) = 4.5$

The Allred-Rochow scale:

The electronegativity of an atom is measured in terms of electrostatic force F exerted by the nucleus of the atom on an electron at a distance of covalent radius (r_{cov}). The force is expressed as: $F \propto \frac{Z^* e^2}{r_{cov}^2}$ (Z^* = effective nuclear charge)

Finally, for the adjustment with the Pauling scale, the value of electronegativity (χ_{AR}) are expressed by the relation: $\chi_{AR} = \frac{0.3590 Z^*}{(r_{cov}/\text{Å})^2} + 0.744 = \frac{3590 Z^*}{(r_{cov}/pm)^2} + 0.744$

Q. Calculate the electronegativity of bromine in Allred Rochow scale. r_{cov}= 114 pm.

Ans: Br = $(1s)^2 (2s2p)^8 (3s3p)^8 (3d)^{10} (4s4p)^7$

$Z^* = 35 - [(0.35 \times 7) + (0.85 \times 18) + (1.00 \times 10)] = 7.25$

$\chi_{AR} = \frac{3590 Z^*}{(r_{cov}/pm)^2} + 0.744 = \frac{3590 \times 7.25}{114^2} + 0.744 = 2.75$

Inert pair effect

The heavier p-block elements have an inherent tendency to show two units lower valency compared to their group valency expected from electron congiguration, is known as inert pair effect. If group valency if G, then heavier congener preferred to exhibit G-2 covalency.

The general electron configuration of p-block elements is $ns^2 np^x$ where $x = 1, 2, 3, 4$ for Gr-13, Gr-14, Gr-15 and Gr-16 respectively. It is observed that the heavier elements tend to keep ns^2 electron pair as non-bonding. That's why it is describe as inert pair effect.

For example,

Group -13: Group oxidation state is +3. But, Tl(I) is more stable compared to Tl(II), while Ga(III) is stable compare to Ga(I).

Group - 14: Group oxidation state is +4. The stability of +4 state is gradually decreases compared to +2 state. Pb(II) is more stable than (Pb(IV) state while Sn(IV) is more stable compared to Sn(II).That's why tetravalent lead compounds (PbCl4, PbO2) are potential oxidizing agent while Sn(II), Ge(II) are reducing agents.

Group 15: Group oxidation state is +5. That's why trivalent compounds for heavier congeners are more abundant while pentavalent compound is more frequent for lighter elements. Bi(V) compounds are unstable with respect to Bi(III) while Sb(V) is stable.

Inert pair effect is also observed in Hg, Au.

Reason for Inert pair effect:

(1) Lanthanide contraction: Due to lower screening capacity of $4f^{14} 5d^{10}$ orbital, Z^* is very high for valence shell electrons.

(2) Relativistic stabilisation of 6s orbital: The 6s orbital becomes contracted and so stabilized that it do not participate in bonding.

(3) Penetrating power: The $6s^2$ electron becomes inert due to the high penetrating power of 6s orbital.

Consequences of inert pair effect:

(i) $PbCl_4$ is oxidizing while $SnCl_2$ is reducing: Due to inert pair effect Pb(II) is stable compared to Pb(IV) while Sn(IV) is stable compared to Sn(II).

(ii) Tl exits as Tl(I) not as Tl(III) in most of thallium compounds: Due to inert pair effect $6s^2$ electron is reluctant to participate in bonding that's why only $6p^1$ electron involve in bonding.

(iii) Inertness of Hg: Electron configuration of Hg is $[Xe]_{54} \, 4f^{14} \, 5d^{10} \, 6s^2$. The $6s^2$ electron is so stabilized, it is reluctant to participate in bonding. That's why Hg is described as inert liquid. This configuration is also called noble liquid configuration.

(iv) Existence of Hg_2^{2+}: Hg^+ ions has configuration $[Xe]_{54} \, 4f^{14} \, 5d^{10} \, 6s^1$, that is one electron short to achieve noble liquid configuration. But, it may fulfilled by sharing 6s electron between two Hg^+ centre through formation of Hg-Hg bond in Hg_2^{2+} species.

(v) Oxidation state of Tl in TlX_3: Due to inert pair effect, Tl(I) is more stable than Tl(III). It is actually exists as $Tl^+X_3^-$ not as $Tl^{III}X_3$.

(vi) High electron affinity of Au: On addition of one electron to Au, it attains noble liquid configuration. Au $(4f^{14} \, 5d^{10} \, 6s^1)$ + e $\rightarrow$ Au$^-$ $(4f^{14} \, 5d^{10} \, 6s^2)$. That's why Au accepts one electron to form Au$^-$, auride ion. For this reason, CsAu, RbAu types of compound is obtained.

(vii) Aurophilicity: Along with the usual coordination number 2, Au(I) shows an additional tendency to introduce Au(I)-Au(I) interaction which can lead cyclization or dimerization. The other cationic species may interact with the Au(I) centre. This tendency is called Aurophilicity. For example, Au(I)-Hg(II), Au(I)-Ag(I), Au(I)-Tl(I), Au(I)-Pb(II) etc.

Such type of additional interaction may be explained considering relativistic effect. In such species 6s is contracted while 5d orbital becomes expanded, which is called relativistic expansion. Due to this relativistic expansion, some 5d electron may transfer to the contracted 6s orbital. These transferred electrons probably participate in additional bonding.

1. Calculate the screening constant (σ) for the 3d electron of iron (atomic number 26)

2. Comment on the relative ionic radii of O^{2-}, F^- and Na^+.

3. Calculate the electronegativity of chlorine in Mulliken's scale and hence find out the elctronegativity of the same element in Pauling scale. Electron affinity of Cl = 4.0 eV per atm and ionisation energy = 13eV per atom.

4. Although In and Tl occur in the same group if the periodic table, In shows +3 oxidation state in most of its compound, however , Tl is +1 oxidation state. Explain.

5. Calculate the first ionistion energy of oxygen using Slater's rule.

6. Ionisation energy of nitrogen is higrer than that of oxygen-Explain.

7. Why always second ionisation energy is greater than first ionisation energy?

8. Atomic volume of alkali metal is larger than other elements of a period - Explain.

9. Electron affinity of gold is very high – Explain.

10. After Ca, electron enters to 4s orbital then going to the 3d orbital. But, when a transition metal ionizes, the 4s electrons are removed first – Why?

11. What do you mean by ionic radius? Calculate the radii of K^+ and Cl^- ions using Pauling's methods. Given that d_{KCl} (Crystal) = 3.14Å.

12. What is inert pair effect? How does Tl form iodide in +1 oxidation state?

13. The drop of ionisation energy in N to O is larger than that for P to S – Explain.

14. Using Slater's rules calculate the effective nuclear charge for the following electrons :

(i) a 4s electron in Cu atom (Z=29), (ii) a 3d electron in Cu atom.

15. The interionic distance in RbBr is 342 pm. Use Pauling's method to calculate the radii of Rb^+ and Br^- (Atomic no of Rb is 37).

16. Electron affinity of Mn^{3+} is greater than that of Fe^{3+} - Explain.

17. Account for the decrease in first ionisation energy between P and S.

18. $SnCl_2$ is reducing while $PbCl_2$ is neither reducing nor oxidizing - Explain.

19. Explain the basis of electronegativity as described by Allred-Rochow scale.

20. Explain the similar size of Zr and Hf or Nb and Ta.

21. Size of Ga is smaller than Al. Explain.