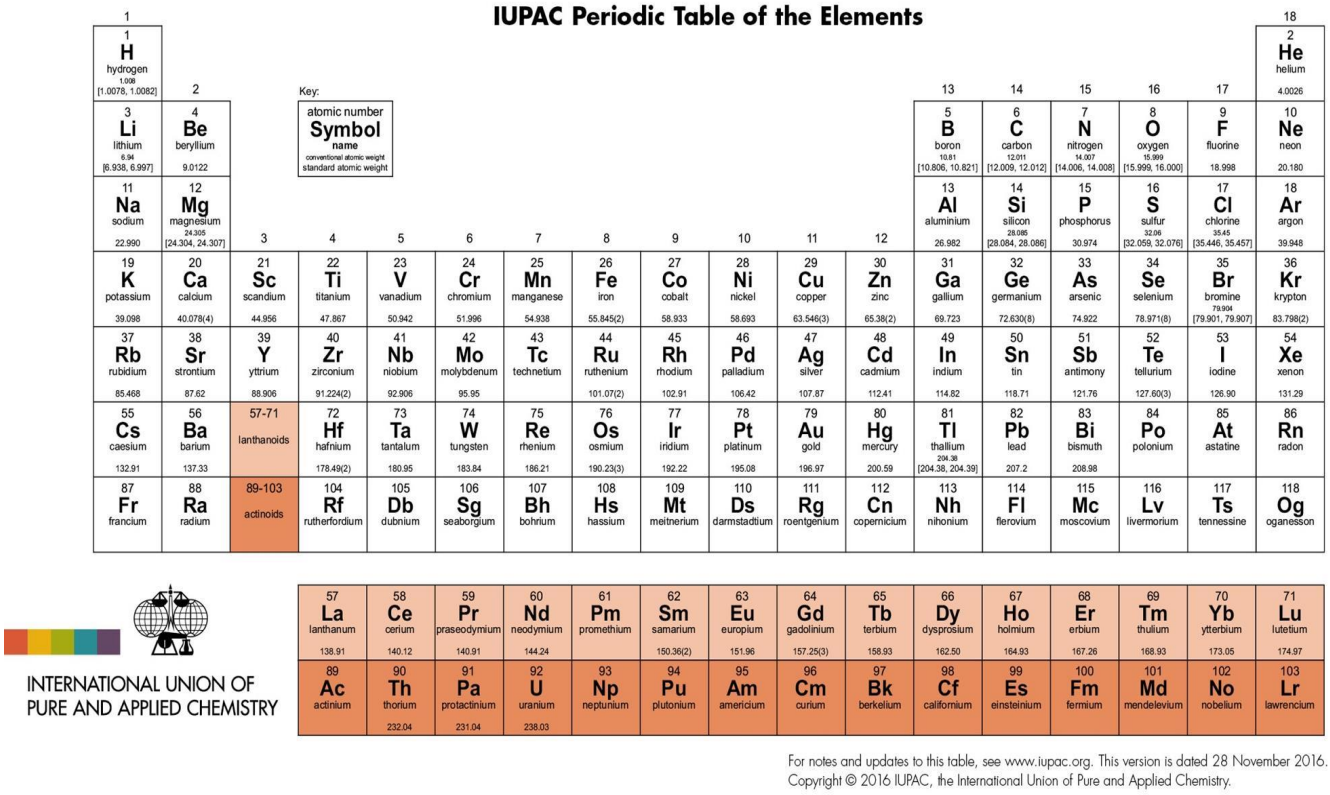
Chemical periodicity



BASICS OF PERIODIC TABLE

According to modern periodic law, the properties of elements are the periodic functions of their atomic numbers. In modern periodic table, the horizontal lines are periods and the vertical lines are groups. The periodic table has total 7 periods and 18 groups. If elements are arranged in increasing order of their atomic numbers, there is repetition of properties after 2, 8, 18, and 32 elements.There are two elements in the first period, eight elements in each of the second and third periods, eighteen elements in each of fourth and fifth period, thirty two elements in the sixth period and only nineteen elements till now in the seventh period.

Periodic classification of elements :

(i) s-block elements: The elements of the periodic table in which the last electron enters in s-subshell, are called s-block elements. It contains elements of group s^1 and s^2 and their general configuration is ns^{1-2}, where n represents the outermost shell. The total number of s-block elements are 14. IA group elements are known as alkali metals whereas the elements of II A group are known

as alkaline earth metals. Fr^{87} and Ra^{88} are radio active elements, H and He are gaseous elements and Cs and Fr are liquid elements among the s-block elements.

(ii) p-block elements: The elements of the periodic table in which the last electron enters in p-subshell are called p-block elements. p-block contains elements groups 13, 14, 15, 16, 17 and 18 of the periodic table. The general configuration of p-block elements are ns^2np^{1-6} (where n = 2 to 6). The total number of p-block elements in the periodic table is 30 (excluding He). Most of these elements are non-metals, some are metalloids and few others are heavy elements which exhibit metallic character.

(iii) d-block Elements: The elements of the periodic table in which the last electron gets filled up the d-orbital called d-block elements. The general electronic configuration is $(n-1)d^{1-10}$, ns^{1-2}. The d-block contains elements of group 3 to 12 of the periodic table. In d-block elements, the electron get filled up in the d-orbital of penultimate shell, that is why, these elements are known as Transition elements. The total d-block elements in periodic table is 33. Out of all the d-block elements mercury is the only liquid elements.

(iv) f-block Elements: The elements of the periodic table in which the last electron gets filled up in the f orbital are called f-block elements. There are 28 f-block elements in the periodic table. The elements from atomic number 58 to 71 are called lanthanides because they come after lanthanum (57). The elements from atomic number from 90 to 103 are called Actinides because they come after actinium (39). All the actinium elements are radioactive. The general electronic configuration of these elements is $(n-2)f^{1-14}(n-1)d^{0-1}$, ns^2. All the elements after atomic number 92 (i.e., U^{92}) are transuranic elements.

The types of elements:

(i) Inert gases: The general electronic configuration of these elements are $ns^2\ np^6$. These have filled s and p orbitals of the outermost shell. So, these elements are stable and rarely take part in a reaction. Helium is also inert gas but its electronic configuration is $1s^2$.

(ii) Representative elements: s and p-block elements except inert gases are called representative elements. Outermost shell of these elements is incomplete.

(iii) Transition elements: These elements have partially d-orbitals in neutral state or in any stable oxidation state. The outermost electronic configuration is similar to d-block elements, i.e., $(n-1)d^{1-10}ns^{1-2}$.

(iv) Inner transition element: In these elements last three shells i.e, last, penultimate and prepenultimate shells are incomplete. These are related to III B i.e., group -3. Their outermost electronic configuration is similar to f-block elements i.e, $(n-2)f^{1-14}$, $(n-1)s^2$,(n-1)p6, $(n-1)d^{0-1}ns^2$.

Effective Nuclear Charge :

Due to screening effect, the valency electron experiences less attraction towards nucleus. This brings decrease in the nuclear charge (Z) actually present on the nucleus. The reduced nuclear charge is termed as effective nuclear charge and is represented by Z*.

$Z^* = (Z - \sigma)$

where, Z = atomic number

σ = screening constant

It is observed that magnitude of effective nuclear charge increases in a period when we move from left to right but in a subgroup of normal element the magnitude of effective nuclear charge remain almost same.

The Screening Effect or Shielding Effect :

In a multielectron atom, the electrons of the valency shell are attracted towards the nucleus and also these electrons are repelled by the electron present in the inner shells. On account of this, the actual force of attraction between the nucleus and the valency electrons is somewhat decreased by the repulsive forces acting in opposite direction. This decrease in the force of attraction exerted by the nucleus on the valency electrons due to the presence of electrons in the inner shells, is called screening effect or shielding effect.

The magnitude of the screening effect depends upon the number of inner electrons, i.e., higher the number of inner electrons, greater shall be the value of screening effect. The screening constant is represented by the symbol (σ) is determined by the **Slater's rule**.

Slater's rules

Effective nuclear charges, Z_{eff} , experienced by electrons in different atomic orbitals may be estimated using Slater's rules. These rules are based on experimental data for electron promotion and ionization energies, and Z_{eff} is determined from the equation: $Z_{eff} = Z - \sigma$.

The screening constant (σ) is estimated as follows.

(i) Write the electronic configuration of element in the following order and group them as.

: (1s), (2s, 2p), (3s, 3p), (3d), (4s, 4p), (4d), (4f), (5s, 5p) etc.

Chemical periodicity

For ns or np orbital electrons:

Electron in any group higher in this sequence than the electron under consideration contribute nothing to σ.

All other electrons in the same (ns, np) group contribute 0.35 each (except for 1s the value of σ is 0.30).

All the electrons in the (n-1) shell contribute 0.85 each.

All the electron in (n-2) or lower shell contributes 1.00 each.

For d or f-electrons :

All the electrons in the same group contribute 0.35 each.

All the electrons in the groups lying left of this group contribute1.00 each.

For example Screening Constant in Zn for (a) 4s- electrons, (b) 3d electron

Zn = $(1s)^2\ (2s\ 2p)^8\ (3s\ 3p)^8\ (3d)^{10}\ (4s)^2$

for 4s electron, σ = 10 × 1 + 18 × 0.85 + 1 × 0.35 = 25.65

for 3d electron, σ = 18 × 1 + 9 × 0.35 = 21.15

Question: Confirm that the experimentally observed electronic configuration of K, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$, is energetically more stable than the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$.

Answer: For K, Z = 19

Applying Slater's rules, the effective nuclear charge experienced by the **4s** electron for the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ is:

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

The nuclear charge, Z = 19

The screening constant, σ = (8 × 0.85)+(10×1.00) = 16.8

$Z_{eff} = 19 - 16.8 = 2.2$

The effective nuclear charge experienced by the **3d** electron for the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ is:

The screening constant, σ = (18 × 1:00) = 18.0

$Z_{eff} = 19 - 18.0 = 1.0$

Thus, an electron in the 4s (rather than the 3d) atomic orbital is under the influence of a greater effective nuclear charge and in the ground state of potassium, it is the 4s atomic orbital that is occupied.

Chemical periodicity

Periodicity in properties

periodicity refers to trends or recurring variations in element properties with increasing atomic number. The properties of elements are periodic functions of their atomic numbers. If elements are arranged in increasing order of their atomic number, there are repetition of properties of elements with similar properties after certain regular intervals is known as periodicity. The periodic repetition of properties is due to the recurrence of similar valence shell configurations after regular intervals.

Example of some periodic properties of atoms : (i) melting and boiling point (ii) dencity (iii) atomic radii and ionic radii (iv) ionization potential (v) electron affinity (vi) electronegetivity etc.

Aperiodicity: Not periodic; not occurring at regular intervals.

Atomic Size:

Atomic radius - It is the distance between atomic nucleus and the outermost shell containing electrons of the atom.

According to the Heisenberg.s uncertainity Principle, the position of a moving electron can not be accurately determined. So, the distance between the nucleus and the outermost electron is uncertain. So, the atomic radius can be determined indirectly from the internuclear distance between the two atoms in a gaseous diatomic molecule.This internuclear distance between the two atoms is called bond length.

The size of atoms decrease from left to right across a period in the periodic table.

For example, on moving from lithium to beryllium one extrapositive charge is added to the nucleus, and an extra orbital electron is also added. Increasing the nuclear charge results in all the orbital electrons being pulled closer to the nucleus.

The sizes of atoms increase downward along any group in the periodic table, due to the effect of extra shells of electron being added.

The chemical compounds are classified into following types according to the nature of chemical bond.

(i) Covalent molecule

(ii) Ionic molecule

(iii) Atomic crystals

(iv) Metals

The atomic radii of atoms of these compounds are classified as -

(i) Covalent radii (in covalent molecule)

(ii) Ionic radii (in ionic molecule)

(iii) Vander-Wall radii (in atomic crystals)

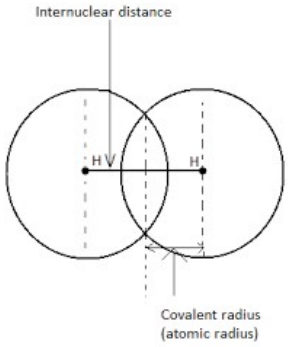
Chemical periodicity

(iv) Metallic radii (in metals)

(1) Covalent radii:

One half of the distance between the nuclei of two covalently bonded atoms in a homodiatomic molecule is called the covalent radius of the atom. The covalent bond must be single covalent bond. The covalent radius (r_A) of atom A in a molecule A_2 may be given as -

$r_A = d_{A-A}/2$, $d_{A-A} = r_A + r_A$



In heterodiatomic molecule AB, where the electronegativity of atoms A and B are different then covalent radii can be calculated as

For example, H-Cl

d_{HCl}= 1.31Å

r_{Cl^-} = 0.99Å

r_{H^+} = ?

we know that

$d_{HCl} = r_{Cl^-} + r_{H^+}$

r_{H^+} = 1.31 - 0.99 = 0.32 Å

(2) Ionic Radii:

It is defined as the distance between the nucleus and outermost shell of an ion. A positive ion is always smaller than the corresponding atom and the more electrons which are removed that is, the greater the charge on the ion, the smaller the ion becomes.

For example- Na = 1.54 Å, Na^+ = 0.95 Å

Mg = 1.36 Å, Mg^{+2} = 0.65 Å

Fe = 1.17 Å, Fe^{+2} = 0.780 Å (high spin), Fe^{+3} = 0.645 Å (high spin)

When a negative ion is formed , one or more electrons added to an atom, the effective nuclear charge is reduced and hence the electron cloud expand. So, Negative ions are bigger than the corresponding atom.

For example- F = 0.72 Å, F^- = 1.36 Å

Cl = 0.99 Å, Cl^- = 1.81 Å

Chemical periodicity

Isoelectric Series:

A series of atoms, ions and molecules in which each species contains same number of electrons but different nuclear charge is called isoelectronic series. In an isoelectronic series atomic size decrease with the increase of charge.

For example-	N^{3-}	O^{2-}	F^{-}	Ne	Na^{+}	Mg^{2+}
number of e^{-}	10	10	10	10	10	10

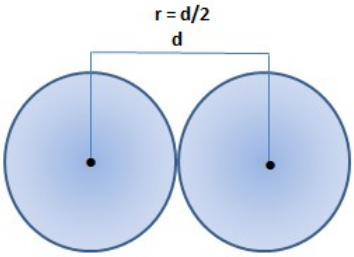
ionic radii ↓

(3) Metallic Radius:

Metals in their solid state consist of a close-packed arrangement of atoms. On half of the internuclear distance between the two closest metal atoms in the metallic crystal is called metallic radius.

Metallic radius > covalent radius

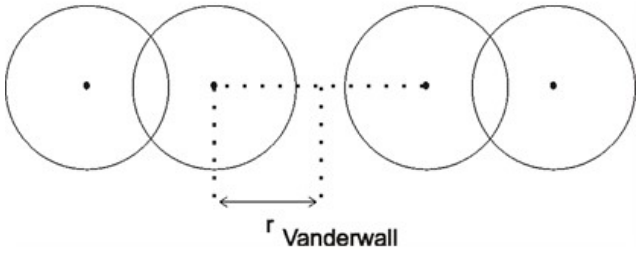
$r_{metallic} = d/2$



(4) Vanderwall.s Radius:

This is obtained from the shortest distance to which two nonbonded atoms can approach before repulsion between their electron clouds. It may be defined as half of the internuclear distance of two non bonded atoms of two adjacent

Molecules.



$r_{covalent} < r_{metallic} < r_{vw}$

Chemical periodicity

Ionization Potential:

The energy required to remove the most loosely bound electron from the outermost orbit of one mole of isolated gaseous atoms or ion of an element, is called Ionization energy (IE).

It is an endothermic process. Ionization energies are measured in KJ mol^{-1}. It is possible to remove more than one electron from most atoms. The first ionization energy is the energy required to remove the first electron and convert M to M^+ ; the second ionization energy is the energy required to remove the second electron and convert M^+ to M^{+2} the third ionization energy converts M^{2+} to M^{3+}, and so on.

I IP < II IP < III IP: as an electron is removed from an atom to form a mono-positive ion, the unchanged nuclear charge holds the remaining electrons more tightly. So, one requires greater energy to remove the second electron from the mono-positive ion. Hence, the second ionization potential is always greater than the first one.

Horizontal trends of ionization potential:

Increasing nuclear charge is accompanied by correspondingly more electrons in neutral atoms. Moving from left to right in the periodic table, the increase of nuclear charge has an effect that generally outweighs the screening from additional electrons. **Increasing Z_{eff} leads to an increase of IE across each period,** which is the most important single trend in the periodic table . At the same time, the atoms become smaller. As illustrated for the elements Li-Ne in *Fig. 1.* the IE trend across a period is not entirely regular. Irregularities can be understood from the electron configurations involved. Ionization of boron removes an electron from a 2*p* orbital, which is less tightly bound than the 2*s* involved in lithium and beryllium. Thus the IE of B is slightly less than that of Be. Between nitrogen and oxygen, the factors involved in Hund's rule are important. Up to three 2*p* electrons can be accommodated in different orbitals with parallel spin so as to minimize their mutual repulsion. For O $(2p)4$ and subsequent elements in the period some electrons are paired and repel more strongly, leading to IE values less than would be predicted by extrapolation from the previous three elements. The trends shown in *Fig. 1* are sometimes cited as evidence for a 'special stability' of filled and half-filled shells. This is a misleading notion. The general increase of IE across a period is entirely caused by the increase of nuclear charge. Maxima in the plot at filled shells $(2s)^2$ and half-filled shells $(2p)^3$ occur only because of the decrease after these points. It is the exclusion principle that controls such details, by forcing the next electron either to occupy another orbital type (as in boron) or to pair up giving a doubly occupied orbital (as in oxygen).

Chemical periodicity

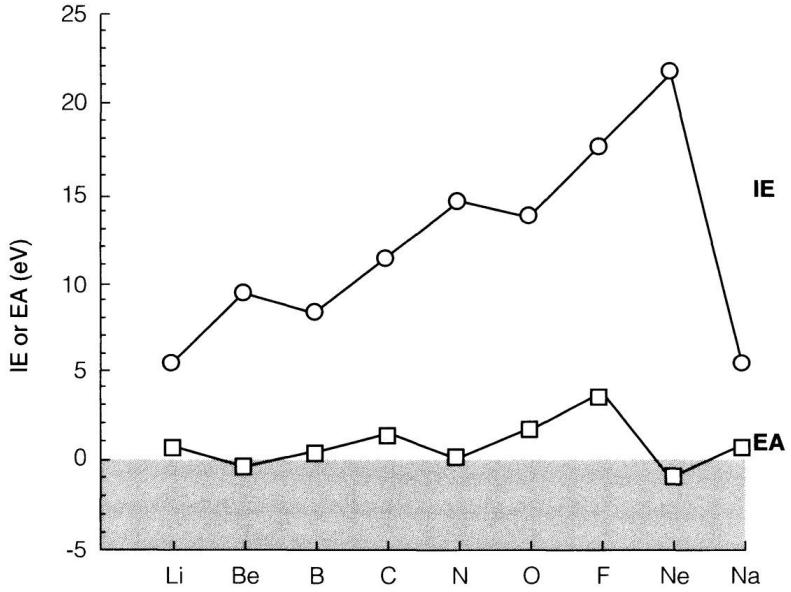


Fig. 1. Ionization energies (IE) and electron affinities (EA) for the elements Li-Na.

Vertical trends of ionization potential:

The IE generally decreases down each group of elements. *Fig2* shows this for hydrogen and the elements of group 1, all of which have the $(ns)^1$ outer electron configuration. The main influence here is the increasing value of principal quantum number *n.* The fall in IE is, however, much less steep than the simple hydrogenic prediction. There is a substantial increase of nuclear charge between each element, and although extra inner shells are occupied, they do not provide perfect shielding. Thus, contrary to what is sometimes stated, effective nuclear charge increases down the group. In the resulting balance between increasing n and increasing Z_{eff} the former generally dominates, as in group 1. There is, however, nothing inevitable about this, and there are occasions in later groups where Z_{eff} increases sufficiently to cause an increase of IE between an element and the one below it. *Fig. 2* also shows the group 11 elements Cu, Ag and Au, where an *ns* electron is also being ionized. The increase of IE along period 4 between K (Z=19) and Cu (Z=29) is caused by the extra nuclear charge of 10 protons, partly shielded by the 10 added 3*d* electrons. A similar increase occurs between Rb and Ag in period 5. In period 6, however, the 4*f* shell intervenes giving 14 additional elements and leading to a total increase of Z of 24 between Cs and Au. There is a much more substantial increase of IE therefore, and Au has a higher IE than Ag. Similarly irregular trends in IE may have some influence on the chemistry of *p*-block elements.

Chemical periodicity

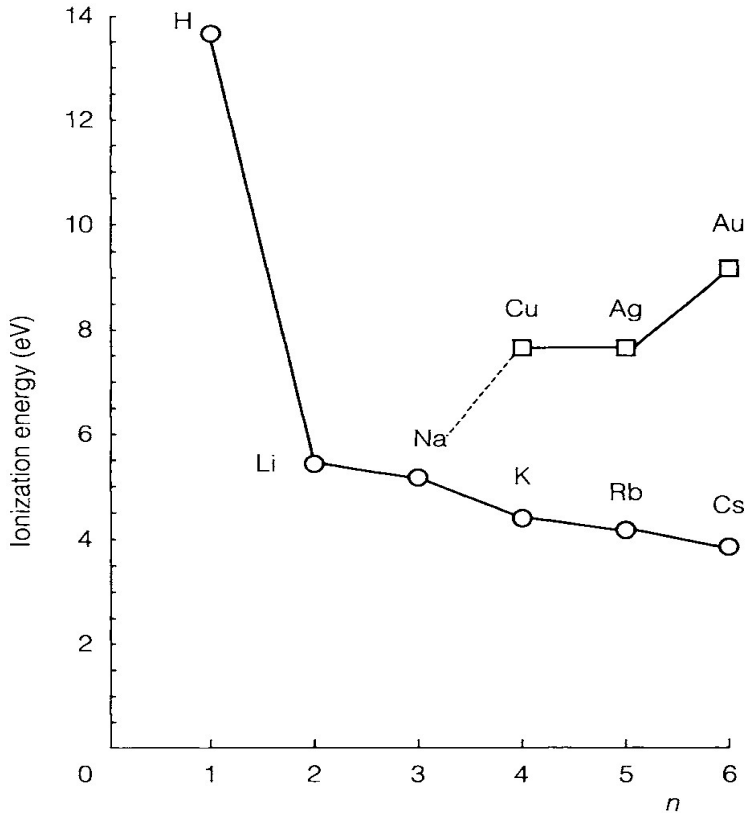


Fig. 2. Ionization energies for elements with $(ns)^1$ outer electron configurations.

Factors affecting ionization Potential :

(1) Size of Atom: The ionization energy decreases with increase in atomic size and increases with decrease in atomic size. As the size increases the outer most electrons lie farther away from the nucleus, hence the IP potential decreases (Li-Na-k-Rb-Cs)

IE ∞ 1/Size

(2) Effective Nuclear Charge: (Z_{eff}) Atomic size decreases with increases in effective nuclear charge because, higher the effective nuclear charge stronger will be the attraction of the nucleus towards the electron of the outermost orbit and higher will be the I.E.

IE ∞ Z_{eff}

(3) Penetration Power: In any atom, the s orbital is nearer to the nucleus in comparision to p, d, and f orbitals. Therefore, greater energy is required to remove an electron from s orbital than from p, d and f orbitals. Thus the decreasing order of ionization potential of s, p, d and f orbitals is as follows:

s > p > d > f

(4) Shielding effect: An increase in shielding effect, decreases the nuclear charge. This result in decrease of I.E

IE ∞ 1/ Shielding effect

(5) Stability of half filled and fully filled orbitals : The atoms whose orbitals are half filled (p^3, d^5,f^7) or fully filled (p^6, d^{10}, f^{14}) have greater stability than the others. Therefore, they require greater amount of energy for removing an electron. However, stability of fully filled orbitals is greater than that of the half filled orbitals.

Important Points:

1. In the periodic table the element having highest value of I.E is He.
2. The value of I.E of noble gases are extremely high, because the outermost orbitals are fully filled (ns^2, np^6) and provide great stability.
3. In a period, the elements having least value of I.E are alkali metals (group 1) and those having highest value are inert gas (group 18).

Application of ionization energy:

1. Metallic and non metallic characters

The elements having low value of ionization energy readily lose electron and thus exhibit greater metallic property.

2. Reactivity

Reactivity ∞ 1/ IE

Reactivity of metals is controlled by their I.E while reactivity of non metals (Halogens) is controlled by their electronegativity. So, halogens are highly reactive because of their higher electronegativity.

3. Basic Property

The elements having low value of Ionization energy readily lose electron and thus oxide and hydroxide of these elements have basic property.

For example

LiOH NaOH KOH RbOH CsOH

$\longrightarrow$

IE↓ Basicity↑

NaOH $Mg(OH)_2$ HOCl

$\longrightarrow$

IE ↑ Basicity ↓

Chemical periodicity

4. Reducing Nature :

The element having low value of ionization energy behave as strong reducing agent.

Reducing Power $\propto 1/$ Ionization Energy

For example-

Alkali Metals**:** Here solvation energy of Li is greater than Cs, so the reducing power is greater than Cs.

Li > Cs > Rb > K > Na

but, in gaseous phase - Cs > Rb > K > Na > Li, because in gaseous phase solvation energy is absent.