(3) Ionization Enthalpy(Δ_iH)

"The enthalpy change observed, when an electron is removed from the outermost shell of an isolated gaseous atom is called ionization enthalpy of the atom."

Ionization enthalpy is measured in eV/atom, kj/mole or kcal/mole. For example,

$M(g) + E \rightarrow M^+(g) + e^-$; $\Delta_iH = + E$

$H(g) + 13.6\ eV \rightarrow H^+(g) + e^-$; $\Delta_iH = + 13.6$ eV/atom

$Na(g) + 5.1\ eV \rightarrow Na^+(g) + e^-$; $\Delta_iH = + 5.1$ eV/atom

Ionization enthalpy is the measure of tendency of an element to remove electron. The larger the value of ionization enthalpy, lesser is the tendency of element to remove electron.

Ionization enthalpy is also the measure of potential difference applied for the removal of electron. Hence, it is also called ionization potential of the atom.

Ionization enthalpy also gives the idea of the metallic nature of the element. The larger the value of ionization enthalpy, lesser is tendency of element to remove electron and therefore lesser is metallic nature of the element.

Successive Ionization Enthalpy

There are certain atoms which can remove more than one electron and therefore, have successive ionization enthalpies namely first, second, third ------- ionization enthalpies, which are represented by Δ_iH_1, Δ_iH_2, Δ_iH_3, --------- respectively. For example,

$M(g) + E_1 \rightarrow M^+(g) + e^-$; $\Delta_iH_1 = + E_1$

$M^+(g) + E_2 \rightarrow M^{2+}(g) + e^-$; $\Delta_iH_2 = + E_2$

$M^{2+}(g) + E_1 \rightarrow M^{3+}(g) + e^-$; $\Delta_iH_3 = + E_3$

After removal of one electron mono-positive ion is obtained. In this ion the number of protons remains unchanged but number of electrons gets decreased. Hence, the value of effective nuclear charge (Z_{eff}) i.e. average number of protons attracting each electron, gets increased. Hence, electrons get more strongly attracted towards the nucleus and therefore, more energy is required for the removal of next electron. Hence, successive ionization enthalpies are always higher i.e. second ionization enthalpy is always higher than first ionization enthalpy and third

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ionization enthalpy is always higher than second ionization enthalpy and so on. Thus,

$$\Delta_iH_{(n+1)} > \Delta_iH_n$$

or $$\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3 < \text{----------}$$

Factors affecting Ionization Enthalpy

(1) **Atomic Size –** If atomic size is bigger**,** relatively lesser nuclear attraction operates on outermost electron and therefore, lesser energy is required for the removal of the electron. Thus, ionization enthalpy is lesser.

(2) **Nuclear Charge** - If nuclear charge is more**,** relatively more nuclear attraction operates on outermost electron and therefore, more energy is required for the removal of electron. Thus, ionization enthalpy is more**.**

(3) **Penetration Power of Orbitals**- The order of penetration power of different orbitals of a definite shell is as under-

s > p > d > f

Here, s orbital is most penetrating due to its highly compact size, while f orbital is least penetrating due to its highly diffused size.

If an electron is present in more penetrating orbital of a shell, it is more close to the nucleus and therefore remains more firmly held to the nucleus. Thus, more energy is required for the removal of electron i.e. ionization enthalpy is more**.**

(4) Screening or Shielding Effect – The electrons present between outermost shell and nucleus act like screen between two and therefore decrease nuclear attraction on outermost electrons. This effect is called screening or shielding effect.

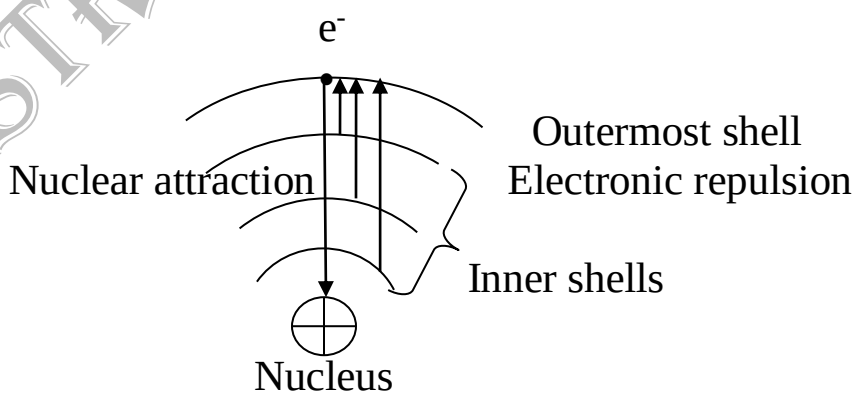


Fig.- Screening Effect

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Screening effect is expressed in terms of screening co-efficient, S. It is related with effective nuclear charge (Z_{eff}) and total nuclear charge (Z_{total}) of the atom as per the following relation-

$$Z_{eff} = Z_{Total} - S$$

Here, the larger the value of screening co-efficient, S, more stronger is the screening effect.

The order of screening effect of different orbitals of a definite shell is as under-

s > p > d > f

Here, s orbital has strongest screening effect due to its highly compact size, while d and f orbitals have very weak screening effect due to their highly diffused size.

If screening effect is stronger, lesser nuclear attraction operates on outermost electrons. Hence, lesser energy is required for the removal of electron i.e. ionization enthalpy is lesser**.**

(5) Stable Electronic Configuration - Half-filled (s^1, p^3, d^5, f^7) and full-filled (s^2, p^6, d^{10}, f^{14}) configuration of sub-shells, have extra stability and therefore, require more energy for the removal of electron. Thus, the elements having more stable half-filled and full-filled configurations of sub-shells, have more value of their ionization enthalpy. For example,

(a) Inert gases have highest ionization enthalpy in their respective period.

(b) Ionization enthalpy of Be is exceptionally higher than that of B.

(c) Ionization enthalpy of N is exceptionally higher than that of O.

Q. Give the reason-

Ionization enthalpy of Be is found to be exceptionally higher than that of B.

Ans. The electronic configuration of Be and B are as under-

Be (4) = $1s^2, 2s^2$

B (5) = $1s^2, 2s^2, 2p_x^1, 2p_y^0, 2p_z^0$

Here, in case of Be, electron is removed from more penetrating, completely filled 2s orbital. Hence, it requires relatively more energy for the removal of electron and has exceptionally higher value of its ionization enthalpy.

On the other hand, in case of B, electron is removed from less penetrating 2p orbital, where p sub-shell is neither half-filled nor full-filled. Hence, it requires

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relatively lesser energy for the removal of electron and has relatively lesser value of its ionization enthalpy.

Q. Give the reason-

Ionization enthalpy of N is found to be exceptionally higher than that of O.

Ans. The electronic configuration of N and O are as under-

N (7) = $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$

O (8) = $1s^2$, $2s^2$, $2p_x^2$, $2p_y^1$, $2p_z^1$

Here, in case of N, electron is removed from 2p sub-shell having more stable half-filled electronic configuration. Hence, it requires relatively more energy for the removal of electron. Thus, it has exceptionally higher value of its ionization enthalpy.

On the other hand, in case of O, electron is also removed from 2p orbital but it has neither half-filled nor full-filled electronic configuration. Hence, it requires relatively lesser energy for the removal of electron. Thus, it has relatively lesser value of its ionization enthalpy.

Q. Give the reason-

Ionization enthalpy of inert gases is found to be highest in respective period.

Ans. Inert gases have highly stable completely filled electronic configuration. Hence, they require highest energy for the removal of electron and therefore have highest value of their ionization enthalpy.

Periodicity of Ionization Enthalpy

On moving left to right in a period of periodic table, atomic size goes on decreasing while nuclear charge goes on increasing. Hence, electrons are more strongly attracted towards the nucleus. Thus, ionization enthalpy, in general, goes on increasing on moving left to right in a period from alkali metals to inert gases leaving some exceptions. For example,

The ionization enthalpy of the elements of Gr. 2, is found to be exceptionally higher than the elements of Gr. 3.

Similarly, ionization enthalpy of the elements of Gr. 15 is found to be exceptionally higher than the elements of Gr. 16.

If ionization enthalpies of some lighter elements are plotted against their atomic number, then inert gases occupy the apex, while the alkali metals occupy the niche. Thus, alkali metals have least ionization enthalpy while inert gases have the highest ionization enthalpy in a period of periodic table.

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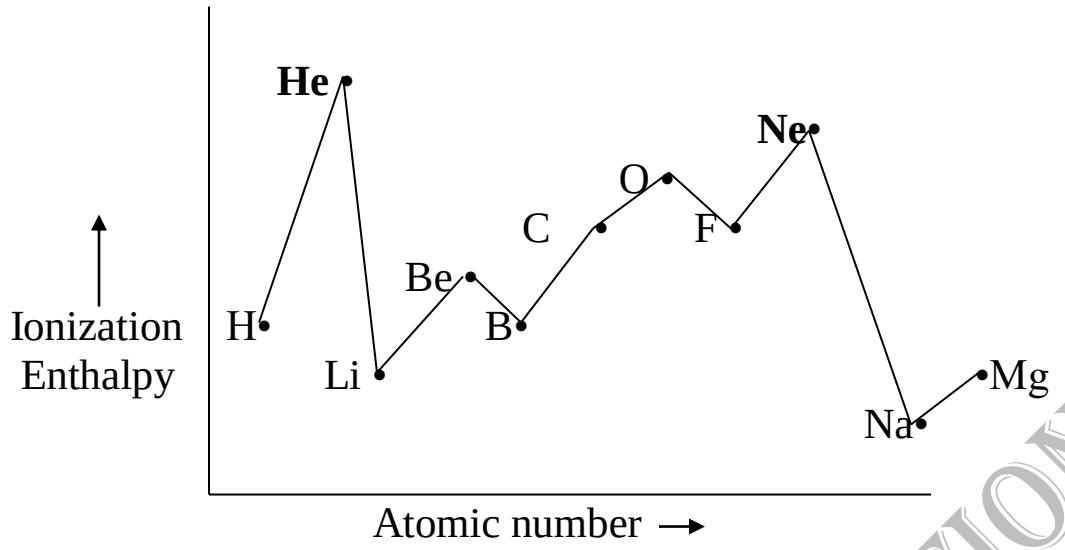


Fig. Plot of ionization enthalpies against atomic number

On moving top to bottom in a group of periodic table, atomic size goes on increasing due to addition of new shells one by one. Hence, nuclear attraction on outermost electrons goes on decreasing. Hence, lesser energy is required for the removal of electrons. Thus, ionization enthalpy goes on decreasing on moving top to bottom in a group.

(4) Electron Gain Enthalpy($\Delta_{e.g.}H$)

"The enthalpy change observed when an electron is added to the outermost shell of an isolated gaseous atom is called electron gain enthalpy of the atom."

Electron gain enthalpy is measured in eV/atom, kj/mole or kcal/mole. For example,

$$X(g) + e \rightarrow X^-(g) + E \; ; \; \Delta_{e.g.}H = -E$$

$$Cl(g) + e \rightarrow Cl^-(g) + e^- + 3.61 \text{ eV}; \; \Delta_{e.g.}H = -13.61 \text{ eV/atom}$$

Electron gain enthalpy is the measure of tendency of an element to gain electron. The larger the value of electron gain enthalpy, more is tendency of element to gain electron.

Electron gain enthalpy is also the measure of non-metallic nature of the element. The larger the value of electron gain enthalpy, more is tendency of element to gain electron and therefore more is non-metallic nature of the element.

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Successive Electron Gain Enthalpy

There are certain atoms which can gain more than one electron and therefore have successive electron gain enthalpies namely first, second, third --------- electron gain enthalpies which are represented by $\Delta_{e.g.}H_1$, $\Delta_{e.g.}H_2$, $\Delta_{e.g.}H_3$, --------- respectively. For example,

$$X(g) + e \rightarrow X^-(g) + E_1 \; ; \; \Delta_{e.g.}H_1 = -E_1$$
$$X^-(g) + e \rightarrow X^{--}(g) - E_2 \; ; \; \Delta_{e.g.}H_2 = +E_2$$

After gaining of one electron mono-negative ion is formed. This negatively charged ion repels next incoming electron. Hence, energy is not released but absorbed during addition of second electron. Thus, second and higher electron gain enthalpies are always positive. For example,

$$O(g) + e \rightarrow O^-(g) + 1.47 \text{ eV} \; ; \; \Delta_{e.g.}H_1 = -1.47 \text{ eV/atom}$$
$$O^-(g) + e \rightarrow O^{--}(g) - 8.75 \text{ eV} \; ; \; \Delta_{e.g.}H_2 = +8.75 \text{ eV/atom}$$

Factors affecting Electron Gain Enthalpy

(1) **Atomic Size –** If atomic size is bigger**,** relatively lesser nuclear attraction operates on new incomming electron and therefore lesser energy is released in addition of electron. Thus electron gain enthalpy is lesser.

(2) **Nuclear Charge** - If nuclear charge is more**,** relatively more nuclear attraction operates on new incomming electron and therefore more energy is released in addition of electron. Thus electron gain enthalpy is more.

(3) Penetration Power of Orbitals- The order of penetration power of different orbitals of a definite shell is as under-

s > p > d > f

Here, s orbital is most penetrating due to its highly compact size while f orbital is least penetrating due to its highly diffused size.

If an electron enters in more penetrating orbital of a shell, it reaches more close to the nucleus and therefore feels more nuclear attraction. Thus, more energy is released in addition of electron and electron gain enthalpy is more**.**

(4) Screening or Shielding Effect

The order of screening effect of different orbitals of a definite shell is as under-

s > p > d > f

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Here, s orbital has strongest screening effect due to its highly compact size while d and f orbitals have very weak screening effect due to their highly diffused size.

If screening effect is stronger, then lesser nuclear attraction operates on new incoming electrons. Hence, more energy is released in addition of electron and electron gain enthalpy is more**.**

(5) Stable Electronic Configuration - Half-filled ($s^1.p^3,d^5,f^7$) and full-filled ($s^2.p^6,d^{10},f^{14}$) configuration of subshells have extra stability and therefore have lesser tendency to gain electron. Thus, the elements having more stable half-filled and full-filled configuration of subshells have lesser value of their electron gain enthalpy. For example,

(a) Inert gases have very high positive value of their electron gain enthalpy in their respective period. Here, energy is not released but absorbed during addition of electron.

(b) Elements of Gr. 2 have low positive value of their electron gain enthalpy due to their more stable half-filled electronic configuration of s-orbital.

(c) Elements of Gr. 15 have low negative value of their electron gain enthalpy due to their more stable half-filled electronic configuration of p-subshell.

Periodicity of Electron Gain Enthalpy

On moving left to right in a period of periodic table, atomic size goes on decreasing while nuclear charge goes on increasing. Hence, new incoming electron is more strongly attracted towards the nucleus and more energy is released in addition of new electron. Thus, negative value of electron gain enthalpy, in general, goes on increasing on moving left to right in a period. For example,

Halogens have most negative value of their electron gain enthalpy in respective period.

On moving top to bottom in a group of periodic table, atomic size goes on increasing as new shells are added one by one. Hence, nuclear attraction on new incoming electrons goes on decreasing and therefore lesser energy is released in addition of electrons. Thus, negative value of electron gain enthalpy in general goes on decreasing on moving top to bottom in a group. However, electron gain enthalpy of the elements of II^{nd} period is found to be less negative than that of the elements of III^{rd} period.

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Q. **Give the reason-**

The electron gain enthalpy Cl is exceptionally found to be more negative than that of F.

Ans. The electronic configuration of F and Cl are as under-

F (9) = $1s^2.2s^2, 2p_x^2,2p_y^2,2p_z^1$

Cl (17) = $1s^2.2s^2,2p^6, 3s^2, 3p_x^2,2p_y^2,2p_z^1$

Here, in Fluorine atom very strong electronic repulsion operates amongst closely spaced electrons of p-orbitals of small sized second shell. Hence, new incoming electron feels relatively lesser nuclear attraction and therefore lesser energy is released in addition of new electron. Thus electron gain enthalpy has relatively lesser negative value.

On the other hand, in Chlorine atom electron enters in p- orbital of IIIrd shell where new incoming electron feels relatively more nuclear attraction and therefore more energy is released in addition of new electron. Thus, electron gain enthalpy has relatively more negative value.

Q. **Give the reason-**

The electron gain enthalpy S is exceptionally found to be more negative than that of O.

Ans. The electronic configuration of O and S are as under-

O (8) = $1s^2.2s^2, 2p_x^2,2p_y^1,2p_z^1$

S (16) = $1s^2.2s^2,2p^6, 3s^2, 3p_x^2,2p_y^1,2p_z^1$

Here, in Oxygen atom very strong electronic repulsion operates amongst closely spaced electrons of p-orbitals of small sized second shell. Hence, new incoming electron feels relatively lesser nuclear attraction and therefore lesser energy is released in addition of new electron. Thus electron gain enthalpy has relatively lesser negative value.

On the other hand, in sulphur atom electron enters in p- orbital of IIIrd shell where new incoming electron feels relatively more nuclear attraction and therefore more energy is released in addition of new electron. Thus, electron gain enthalpy has relatively more negative value.

(5) Electronegativity –

"The capacity of an atom to attract shared electron pair of a covalent bond towards itself is called Electronegativity of the atom"

Electronegativity is the measure of tendency of an atom to attract shared electron pair of a covalent bond towards itself. The larger the value of

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electronegativity larger is the tendency of atom to attract shared electron pair towards itself.

Electronegativity is the property of the bonded atoms. Its absolute value cannot be determined. Hence, its relative value is given for different elements. For doing so, the electronegativity of most electronegative Fluorine atom has been arbitrarily fixed to be 4.0 and that of Hydrogen has been fixed to be 2.1. The relative electronegativity of other elements are given with respect to these elements.

Factors affecting Electronegativity –

(1) Atomic Size- If atomic size is smaller, the electronegativity of the atom is larger.

(2) Nuclear Charge - If nuclear charge is more, the electronegativity of the atom is larger.

(3) Oxidation State – Higher the positive oxidation number of an element, more is its electronegativity.

(4) Hybrization State – If hybridized orbital has more s- character then the electronegativity of the element is higher.

For example, sp- hybridized triply bonded carbon atom of alkynes having highest s-character (50 % s- character) is more electronegative than sp^2- hybridized doubly bonded carbon atom of alkenes having 33.33 % s- character. In the same way, doubly bonded carbon atom of alkenes is more electronegative than sp^3- hybridized singly bonded carbon atom of alkanes having only 25 % s- character.

Periodicity of Electronegativity

On moving left to right in a period of periodic table, the value of electronegativity goes on increasing from alkali metals to halogens. It is because of the decrease of atomic size and increase of nuclear charge on moving left to right in a period.

On moving top to bottom in a group, the value of electronegativity goes on decreasing. It is because of increase of atomic size due to addition of new shells one by one.

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