Electron Affinity

(1) The amount of energy released when an electron is added to the outermost shell of one more of an isolated gaseous atom in its lower energy state.

(2) Electron affinity just defined is actually first electron affinity since it corresponds to the addition of one electron only. In the process of adding further electron, the second electron will be added to gaseous anion against the electrostatic repulsion between the electron being added and the gaseous anion. Sometimes energy instead of being released is supplied or the addition of an electron to an anion.

$$A_{(g)} + e^- \rightarrow A^-_{(g)} + E_1$$

$$A^-_{(g)} + e^- + \text{Energy supplied} \rightarrow A^{2-}_{(g)}$$

Factors affecting the electron affinity

(1) **Atomic size :** The value of electron affinity decreases with the increase in the size of atom since the nuclear attraction decreases down a group as the atomic number increases. Its value increases as we move along a period since the size of atoms decreases along a period. The lower value of F than Cl is due to the very small size of F in which negative charge is highly concentrated and repels the incoming electron thereby reducing the force of attraction of the nucleus towards the adding electron and hence decreasing the electron affinity. Thus, chlorine has a highest value of electron affinity.

(2) **Nuclear charge :** The value of electron affinity increases with increasing nuclear charge. Thus, its value increases with increase in nuclear charge along a period.

(3) **Screening or shielding effect :** The value of electron affinity increases with the decrease in shielding effect of inner electrons. Besides, the value of electron affinity also depends to some extent upon the type of orbital in which electron is added. The value is greater when electron enters '*s*' orbital and decreases successively for *p, d* and *f* orbitals.

(4) **Stability of half filled and completely filled orbitals :** The stability of half filled and completely filled degenerate orbitals of a sub shell is comparatively more, so it is difficult to add electron in such orbitals and lesser energy is released on addition of electron hence the electron affinity value will decrease.

Periodicity in Electron Affinity

(i) In general electron affinity value increases on moving left to right in a period because effective nuclear charge increases.

Exceptions

(a) The electron affinity value of alkaline earth metals of IIA group is zero.

(b) Electron affinity value of alkali metals of IA group is also approximately zero because these elements have the tendency of losing the electron instead of gaining the electron.

(c) Electron affinity values of nitrogen and phosphorous (VA) are lesser than the electron affinity values of carbon and silicon respectively. It is due to the comparatively stable half filled configuration (np^3) of nitrogen and phosphorus and the tendency to acquire the stable np^3 configuration by the gain of one electron in cation and silicon $(np)^2$

(d) The theoretical value of the electron affinity of zero group inert gas elements is zero due to stable $s^2 p^6$ configuration.

(ii) In a group on moving from top to bottom the electron affinity value of elements decreases because the atomic size increases.

(a) Electron affinity values of second period elements are smaller than the electron affinity values of third period elements. This unexpected behaviour can be explained by the very much high value of charge densities, of second period elements due to much smaller size. The electron being added experiences comparatively more repulsion and the electron affinity value decreases.

(b) The electron affinity of fluorine (Second period) is less than the electron affinity of chlorine (third period). 2*p*-orbitals in fluorine are much more compact than 3*p*-orbitals of chlorine. So the electron being added in 2*p*-orbitals experiences comparatively more repulsion and the electron affinity value decreases.