Electron Affinity (EA or $\Delta_{eg}H$)

Electron affinity (abbreviated as EA) is an atomic property which gives us an idea of the tendency of the element to accept the electron to form an anion. With the help of this property a number of properties of the elements like oxidising power and non-metallic (or electronegative) character can well be explained.

What is Electron Affinity ?

Electron affinity of an element is defined as the amount of energy released in adding an extra electron from outside to an isolated neutral gaseous atom in its lowest energy state (i.e. ground state) to convert it into a gaseous anion. Thus electron affinity of an atom, M(g) can be defined by the following process:

$$\underset{\text{Isolated gaseous atom}}{M(g)} + e^-(g) \rightarrow \underset{\text{Gaseous anion}}{M^-(g)} + \textit{Energy released} \ (= -EA_1)$$

Electron affinity defined above is strictly called **first electron affinity,** since it corresponds to the addition of *one* electron only. Hence it is represented as $-EA_1$ where negative (minus) sign represents the release of energy. It is also represented as E or Δ_{eg} H.

The above process which depicts the addition of an electron to a gaseous atom is an *exothermic process*, since in the addition of an electron energy is released.

Electron affinity is also called **electron affinity energy.** It is measured in electron volts, kilocalories or kilojoules. The values of electron affinity are shown by a negative (minus) sign which is placed before them. Negative sign represents the release of energy in the addition of an electron to $M(g)$ atom.

Values of first electron affinity (in KJ/mole) of *s*-and *p*-block elements are given in Table 4.10.

Second Electron Affinity

In addition to first electron affinity (E_1) defined above, second electron affinity (E_2) of some elements like O, S and Se is also known. *Second electron affinity of an element, M(g) is defined as the amount of energy required to add one more electron to its mono-negative anion, $M^-(g)$ to convert it into di-negative anion, $M^{2-}(g)$. Thus.*

$$M^-(g) + e\ (g) + \text{Energy supplied } (= +E_2) \rightarrow M^{2-}(g)$$

In the process of adding one more electron to $M^-(g)$ anion against the electrostatic repulsion between the extra electron being added to $M^-(g)$ and the negative charge on M^- (g) anion, energy, instead of being released, (as in case of first electron affinity) is supplied to $M^-(g)$ ion to convert it into $M^{2-}(g)$ ion. Thus the process of adding a second electron to $M^-(g)$ anion is an *endothermic process*. Second electron affinity is represented by a positive sign, since it represents the energy absorbed (*i.e.* supplied) and not released as in case of first electron affinity.

In the formation of a dinegative ion, $M^{2-}(g)$ from the neutral $M(g)$ atom, electrons are added one by one. Energy equal to first electron affinity (E_1) is

However, the general trend of variations of electron affinity of various elements can be discussed as follows :

(*a*) **In a period.** On moving from left to right in a period, the size of the atoms decreases and the effective nuclear charge increases. Both these factors favour an increase in the force of attraction exerted by the nucleus on the electron. Consequently the atom has a greater tendency to attract an extra electron from outside towards itself and hence its *electron affinity increases from left to right*. Thus the metals (*e.g.* alkali metals) which lie at the left hand portion of the periodic table have low values of electron affinity while the non-metals (*e.g.* halogens) which lie at the right hand portion of the periodic table have high values of electron affinity.

Exceptions. There are certain elements in each period which have abnormal values. For example in *2nd* period Li, Be, N and Ne have abnormal values. Similarly in *3rd* period Na, Mg, P and Ar have abnormal values. The abnormal values of Li and Na cannot be explained by simple mechanism while those of Be, N, Mg, P, Ne and Ar have already been explained.

(*b*) **In a group.** On moving down a group both the size of the atom and the effective nuclear charge increase. The increase in atomic size tends to decrease the electron affinity values while the increase in nuclear charge tends to increase the electron affinity values. The net result is that the effect produced by the progressive increase of the atomic size outweighs the effect produced by the progressive increase in nuclear charge and *consequently the electron affinity goes on decreasing as we move from top to bottom in a group* as is evident from EA values of (*i*) alkali metals (Group IA) (*ii*) C, Si and Ge (Group IVA) (*iii*) S, Se and Te (Group VIA) (*iv*) O, S and Se for two electrons (Group VI A) and (*v*) Cl, Br and I (Group VII A).

Exceptions. Although the elements of *2nd* period of the periodic table have smaller size than the elements of *3rd* period, the EA values of some of the elements of *2nd* period are lower than the EA values of the elements lying just below them in *3rd* period. For example $B<Al$, $N<P$, $O<S$ and $F<Cl$. The lower values for the elements of *2nd* period are explained by saying that, due to the smaller size of the atoms of the elements of *2nd* period, the addition of an extra electron to these atoms produces high electron density round the resulted anions. This high electron density increases the repulsion between the electrons (called electron–electron repulsion) already present in the relatively compact *2p* orbital of the *2nd* shell of these atoms and the electron being added. Due to this electron–electron repulsion, the atoms of the elements of *2nd* period show lesser tendency to attract the extra electron from outside and hence lower values of electron affinity for these elements.

The variation of electron affinity of *s*- and *p*- block elements in a group and

1. Atomic radius. Larger the atomic radius, lesser the tendency of the atom to attract the additional electron towards itself, lesser the force of attraction exerted by the nucleus on the extra electron being added to the outer-shell of the atom and hence lesser the amount of energy released when the extra electron is added to the atom to form an anion. Thus *smaller atoms have higher electron affinities.*

2. Effective nuclear charge. Higher the effective nuclear charge, greater the tendency of the atom to attract the additional electron towards itself, greater the force of attraction exerted by the nucleus on the extra electron being added to the outer-shell of the atom and hence higher the amount of energy released when the extra electron is added to the atom. *Thus the atoms with higher effective nuclear charge have higher electron affinities.*

3. Electronic configuration. The effect of this factor on the magnitude of electron affinity of an element can be explained by the following examples :

(*a*) Electron affinity values of the elements of group IIA. *ns* orbital of the valence-shell of the atoms of these elements is completely filled and hence the addition of any extra electron from outside to this *ns* orbital is not possible. *Consequently the elements of group IIA have practically zero electron affinity.*

(*b*) Electron affinity values of N and P. The valence-shell electronic configuration of N and P are :

$$N \rightarrow 2s^2p^3 \; ; \quad P \rightarrow 3s^2p^3$$

$2p$ and $3p$ orbitals in N and P respectively are half-filled and hence are extra ordinarily stable. Thus the addition of any extra electron from outside to these orbitals is not possible. *Consequently N and P have very low electron affinity values* (N = + 20.1 KJ/mole, P = –74 KJ/mole).

(*c*) Electron affinity values of halogens. The valence-shell configuration of halogen atoms (ns^2p^5) has an appetite for one electron to stabilise its configuration by attaining the noble gas configuration (ns^2p^6) which is very stable. Thus halogen atoms have a strong tendency to accept an extra electron from outside and the addition an extra electron makes the configuration of the resulted halide ion similar to that of the noble gas and hence very stable. *Consequently the halogen atoms have very high values of electron affinity.*

(*d*) Electron affinity values of noble gases. The noble gases which have extra-ordinarily stable configuration namely ns^2p^6 show no tendency to accept the additional electron from outside. *Hence the electron affinity values of inert gases are practically zero.*

First electron affinity

Ionisation energies are always concerned with the formation of positive ions. Electron affinities are the negative ion equivalent, and their use is almost always confined to elements in groups 6 and 7 of the Periodic Table.

Defining first electron affinity

The first electron affinity is the energy released when 1 mole of gaseous atoms each acquire an electron to form 1 mole of gaseous 1- ions.

This is more easily seen in symbol terms.

$$X_{(g)} + e^- \longrightarrow X^-_{(g)}$$

It is the energy released (per mole of X) when this change happens.

First electron affinities have negative values. For example, the first electron affinity of chlorine is -349 kJ mol^{-1}. By convention, the negative sign shows a release of energy.

The first electron affinities of the group 7 elements

F	-328 kJ mol^{-1}
Cl	-349 kJ mol^{-1}
Br	-324 kJ mol^{-1}
I	-295 kJ mol^{-1}

Note: These values are based on the most recent research. If you are using a different data source, you may have slightly different numbers. That doesn't matter - the pattern will still be the same.