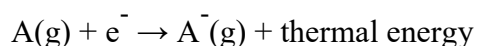


Electron Affinity

Definition: Electron affinity is defined as the change in energy (in kJ/mole) of a neutral atom (in the gaseous phase) when an electron is added to the atom to form a negative ion. In other words, the neutral atom's likelihood of gaining an electron.

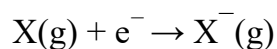


Unit: KJ mol⁻¹

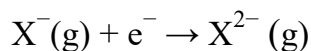
A chemical reaction that releases energy is called an exothermic reaction and a chemical reaction that absorbs energy is called an endothermic reaction. Energy from an exothermic reaction is negative, thus energy is given a negative sign; whereas, energy from an endothermic reaction is positive and energy is given a positive sign. When an electron is added to a neutral atom (i.e., first electron affinity) energy is released; thus, the first electron affinities are **negative**. However, more energy is required to add an electron to a negative ion (i.e., second electron affinity) which overwhelms any the release of energy from the electron attachment process and hence, second electron affinities are **positive**.

The higher an element's electron affinity, the more thermal energy is given off when an electron is added to an atom of the element.

First Electron Affinity (negative energy because energy released):



Second Electron Affinity (positive energy because energy needed is more than gained):



Factors affecting E.A

1. Atomic Size: The electron affinity decreases with increase in atomic size and increases with decrease in atomic size.

$$E.A \propto 1/\text{Size}$$

2. Effective Nuclear Charge : (Z_{eff})

Atomic size decreases with increase 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 E.A.

$$E.A \propto Z_{\text{eff}}$$

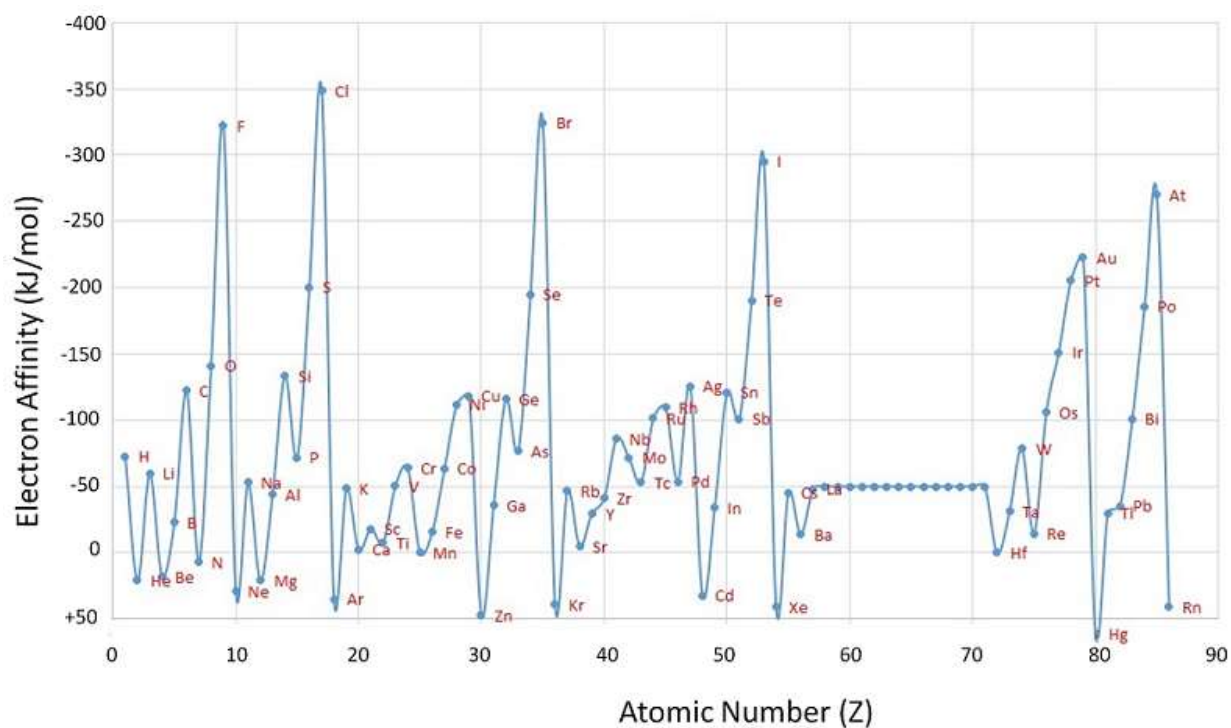
3. Shielding Effect : An increase in shielding effect decrease the nuclear charge. This result in decreased E.A.

$$E.A \propto 1/\text{Shielding effect}$$

4. Stability of half filled and fully filled orbitals :

Elements having half filled and fully filled electronic configuration have almost zero or negligible E.A.

Periodicity in electron affinity :



In Period : In general E.A value increases on moving from left to right in a period because effective nuclear charge increases.

In group : In a group, E.A value decreases on moving from top to bottom because the atomic size increases.

Explanation: Electron affinity increases upward for the groups and from left to right across periods of a periodic table because the electrons added to energy levels become closer to the nucleus, thus a stronger attraction between the nucleus and its electrons. Remember that greater the distance, the less of an attraction; thus, less energy is released when an electron is added to the outside orbital. In addition, the more valence electrons an element has, the more likely it is to gain electrons to form a stable octet. The less valence electrons an atom has, the least likely it will gain electrons.

Electron affinity decreases down the groups and from right to left across the periods on the periodic table because the electrons are placed in a higher energy level far from the nucleus, thus a decrease from its pull. However, one might think that since the number of valence electrons increase going down the group, the element should be more stable and have higher electron affinity. One fails to account for the shielding affect. As one goes down the period, the shielding effect increases, thus repulsion occurs between the electrons. This is why the attraction between the electron and the nucleus decreases as one goes down the group in the periodic table.

As you go down the group, first electron affinities become less (in the sense that less energy is evolved when the negative ions are formed). Fluorine breaks that pattern, and will have to be accounted for separately. The electron affinity is a measure of the attraction between the incoming electron and the nucleus - **the stronger the attraction, the more energy is released.** The factors which affect this attraction are exactly the same as those relating to ionization energies - nuclear charge, distance and screening. The increased nuclear charge as you go down the group is offset by **extra screening** electrons. Each outer electron in effect feels a pull of 7+ from the center of the atom, irrespective of which element you are talking about.

Exceptions :

1. The electron affinity value of alkali metals is approximately zero because these elements have the tendency of losing the electron instead of gaining the electron.
2. The electron affinity value of alkaline earth metals is zero.
3. Electron affinity of nitrogen and phosphorus is lesser than the electron affinity of carbon and silicon respectively. It is due to the comparatively stable half filled configuration of N and P.

4. The electron affinity of inert gas elements is zero due to fully filled configuration.
5. Electron affinity of second period elements is smaller than the electron affinity 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 experiences comparatively more repulsion and the electron affinity value decreases.

Important Points :

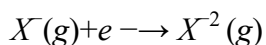
1. Elements having highest EA = Cl
2. Elements having zero EA = noble gases
3. The periodic trends of IE and EA are same in periodic table i.e both increase across the period both decrease down the group.
4. IE is an absorption of energy when e. is removed from an atom while EA is an emission of energy when e. is added to an atom.

Why is Fluorine an Anomaly?

The incoming electron is going to be closer to the nucleus in fluorine than in any other of these elements, so you would expect a high value of electron affinity. However, because fluorine is such a small atom, you are putting the new electron into a region of space already crowded with electrons and there is a significant amount of repulsion. This repulsion lessens the attraction the incoming electron feels and so lessens the electron affinity. A similar reversal of the expected trend happens between oxygen and sulfur in Group 16. The first electron affinity of oxygen (-142 kJ mol^{-1}) is smaller than that of sulfur (-200 kJ mol^{-1}) for exactly the same reason that fluorine's EA is smaller than chlorine's.

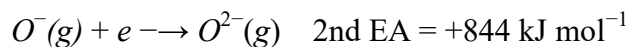
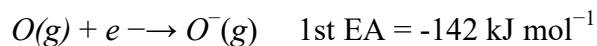
Second Electron Affinity

You are only ever likely to meet this with respect to the group 16 elements oxygen and sulfur which both form -2 ions. The second electron affinity is the energy required to add an electron to each ion in 1 mole of gaseous 1^- ions to produce 1 mole of gaseous 2^- ions. This is more easily seen in symbol terms.



It is the energy needed to carry out this change per mole of X^- .

Why is energy needed to do this? You are forcing an electron into an already negative ion. It's not going to go in willingly!



The positive sign shows that you have to put in energy to perform this change. The second electron affinity of oxygen is particularly high because the electron is being forced into a small, very electron-dense space.

Lanthanide contraction: The decrease in size (as of radii of atoms or ions or of atomic volumes) with increasing atomic number of the metals of the lanthanide series is termed as Lanthanide contraction.

Each succeeding lanthanides differs from its immediate predecessor in having one or more electron in the 4f (though there are some exceptions) and an extra proton in the nucleus of the atom. The 4f electrons constitute inner shells and are rather ineffective in screening the nucleus. This leads to a gradual increase in the attraction of the nucleus to the electrons in the outermost shell as the nuclear charge increases, and a consequent contraction in the atomic radius. In lanthanide contraction, the ionic radii of the lanthanides decrease progressively with increase atomic number from lanthanum ($\text{La}^{+3} = 0.115\text{nm}$) to Lutetium ($\text{Lu}^{+3} = 0.093\text{nm}$) (see Table 2). As the ionic radii contract along the lanthanide series, the ability to form complex ions increases and this is the basis of their separation on an ion exchange column.