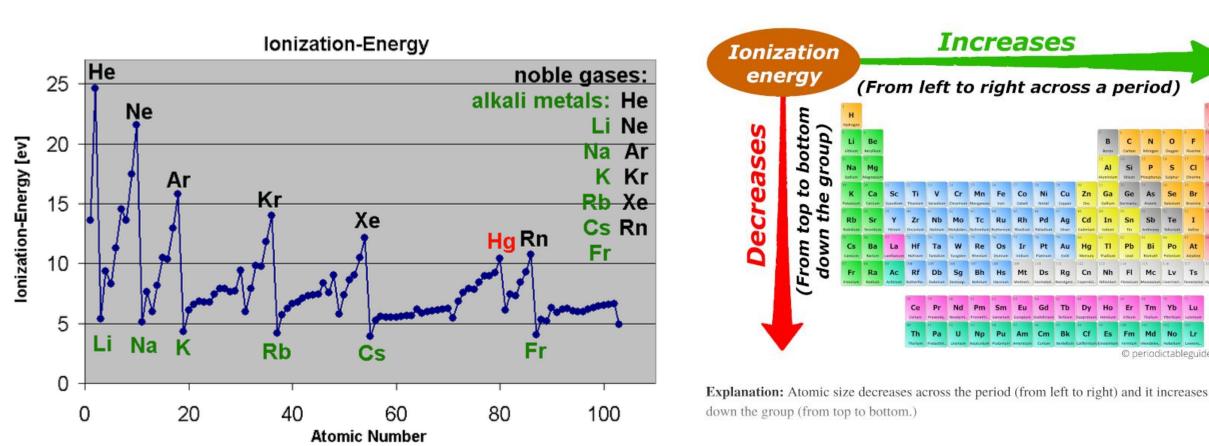
## Periodic variation of ionization energy:



Ionization energy is the energy required to remove an electron from a neutral atom in its gaseous phase.

The lower this energy is, the more readily the atom becomes a cation.

Therefore, the higher this energy is, the more unlikely it is the atom becomes a cation.

Generally, elements on the right side of the periodic table have a higher ionization energy because their valence shell is nearly filled.

Elements on the left side of the periodic table have low ionization energies because of their willingness to lose electrons and become cations.

Thus, ionization energy increases from left to right on the periodic table.

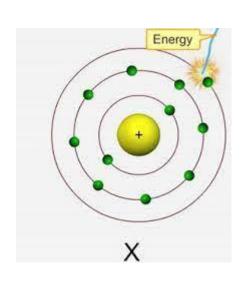
The ionization energy of the elements within a period generally increases from left to right. This is due to valence shell stability.

The ionization energy of the elements within a group generally decreases from top to bottom. This is due to electron shielding.

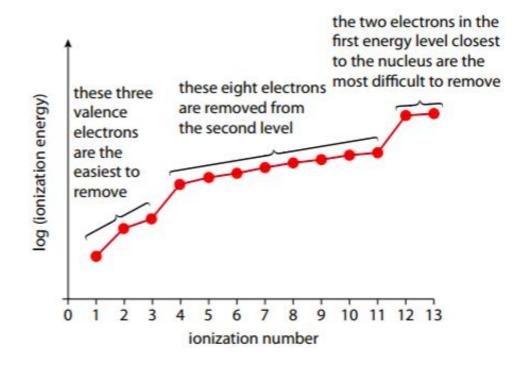
The noble gases possess very high ionization energies because of their full valence shells as indicated in the graph. Note that helium has the highest ionization energy of all the elements.

$$Al(g) \to Al^+(g) + e^-$$
 580kJ/mol ? Kcal/mol  $Al^+(g) \to Al^{2+}(g) + e^-$  1815kJ/mol ? Kcal/mol  $Al^{2+}(g) \to Al^{3+}(g) + e^-$  2740kJ/mol  $Al^{3+}(g) \to Al^{4+}(g) + e^-$  11600kJ/mol

IE3>IE2>IE1 because removing an electron from a positive charge species is difficult.



$$n = 1/2/3/4$$
 to  $n = \infty$ 



Prove IE =  $13.6 (Z^{*2}/n^2)$ 

### **Specific features:**

Inert gas occupy peak positions.

Alkali metals at the bottom positions.

In the transition series, the variation is not so marked having a slight increasing tendency, but at the endings there is sharp increase.

In the lanthanide, slight increasing trend is there.

#### **Factors governing Ionization energies:**

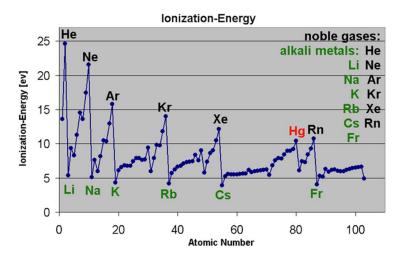
Effective nuclear charge

Radius of species

Screening power of the electron clouds

Penetrating power of the orbital from which the electron is to be knocked out

Relative stabilities of the starting and end point of the species from the standpoint of half-filled and fulfilled character of Orbitals involved.



#### **Ionization Energies of Transition Metals & Lanthanides**

As we noted, the first ionization energies of the transition metals and the lanthanides change very little across each row. Differences in their second and third ionization energies are also rather small, in sharp contrast to the pattern seen with the s- and p-block elements. The reason for these similarities is that the transition metals and the lanthanides form cations by losing the ns electrons before the (n-1)d or (n-2)f electrons, respectively. This means that transition metal cations have  $(n-1)d^n$  valence electron configurations, and lanthanide cations have  $(n-2)f^n$  valence electron configurations. Because the (n-1)d and (n-2)f shells are closer to the nucleus than the ns shell, the (n-1)d and (n-2)f electrons screen the ns electrons quite effectively, reducing the effective nuclear charge felt by the ns electrons. As Z increases, the increasing positive charge is largely canceled by the electrons added to the (n-1)d or (n-2)f orbitals.

That the ns electrons are removed before the (n-1)d or (n-2)f electrons may surprise you because the orbitals were filled in the reverse order. In fact, the ns, the (n-1)d, and the (n-2)f orbitals are so close to one another in energy, and interpenetrate one another so extensively, that very small changes in the effective nuclear charge can change the order of their energy levels. As the d orbitals are filled, the effective nuclear charge causes the 3d orbitals to be slightly lower in energy than the 4s orbitals. The  $[Ar]3d^2$  electron configuration of  $Ti^{2+}$  tells us that the 4s electrons of titanium are lost before the 3d electrons; this is confirmed by experiment. A similar pattern is seen with the lanthanides, producing cations with an  $(n-2)f^n$  valence electron configuration.

Because their first, second, and third ionization energies change so little across a row, these elements have important horizontal similarities in chemical properties in addition to the expected vertical similarities. For example, all the first-row transition metals except scandium form stable compounds as M2+ ions, whereas the lanthanides primarily form compounds in which they exist as M3+ ions.

Q1. IE1 (N) (1403 KJ/mol) > IE1 (O) (1314 KJ/mol) But IE2 (N) (2856 KJ/mol) < IE2 (O) (3388 KJ/mol)

Similar things are observed for P and S.

Q2. Explain the case of Be and B / Ca and Mg / Al

Energy required to knock out an electron from an orbital follows the sequences as:

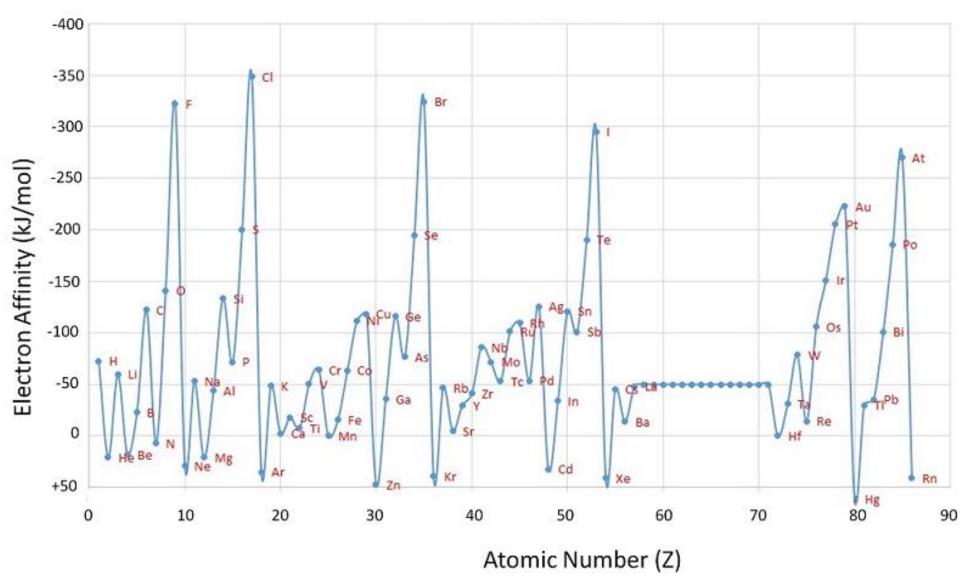
Why 
$$_{29}$$
Cu <  $_{30}$ Zn >  $_{31}$ Ga ? Similarly,  $_{47}$ Ag <  $_{48}$ Cd >  $_{49}$ In

$$_{79}$$
Au <  $_{80}$ Hg >  $_{81}$ Tl

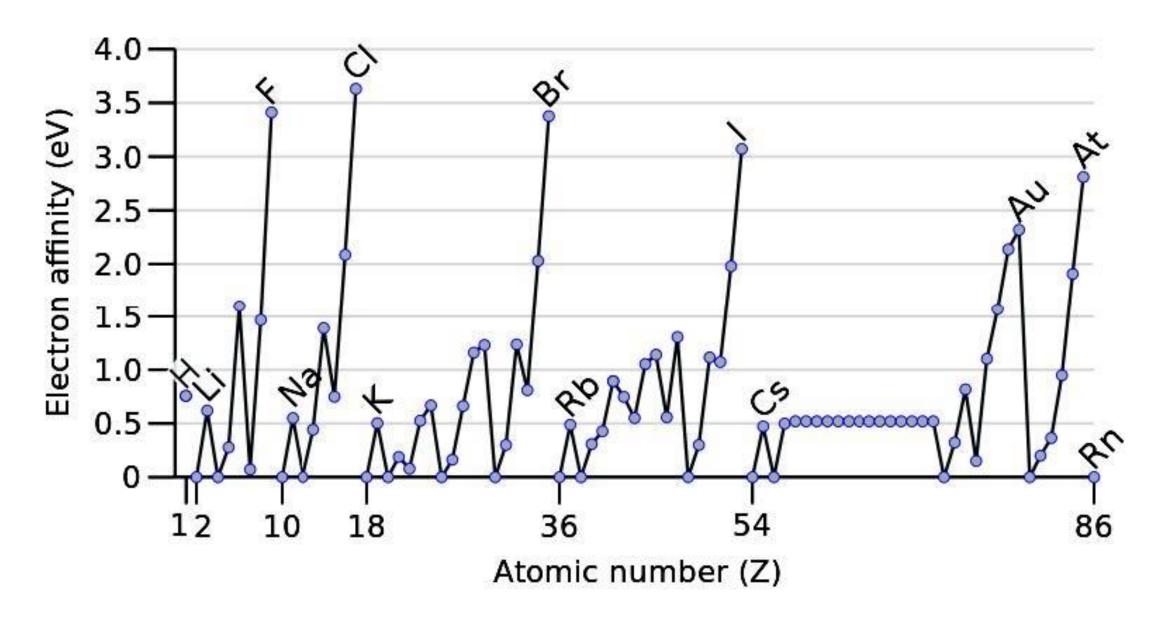
$$_{70}$$
Yb >  $_{71}$ Lu

## **Periodic variation of electron affinity:**

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.



# In eV unit:



Energy of an atom is defined when the atom loses or gains energy through chemical reactions that cause the loss or gain of electrons. 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.

An example that demonstrates both processes is when a person drops a book. When he or she lifts a book, he or she gives potential energy to the book (energy absorbed). However, once the he or she drops the book, the potential energy converts itself to kinetic energy and comes in the form of sound once it hits the ground (energy released).

**Usually,** 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.

First Electron Affinity (negative energy because energy released):

$$X(g)+e-\rightarrow X^{-}(g)$$

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

$$X^{-}(g)+e-\rightarrow X^{2-}(g)$$

### **First Electron Affinity**

Ionization 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 16 and 17 of the Periodic Table.

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. 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<sup>-1</sup>. By convention, the negative sign shows a release of energy.

When an electron is added to a metal element, energy is needed to gain that electron (endothermic reaction). Metals have a less likely chance to gain electrons because it is easier to lose their valence electrons and form cations. It is easier to lose their valence electrons because metals' nuclei do not have a strong pull on their valence electrons. Thus, metals are known to have lower electron affinities.

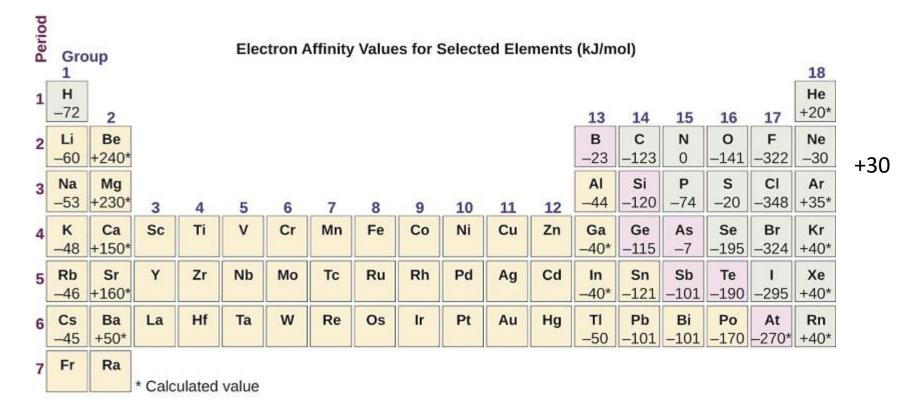
Why is energy needed to do this? You are forcing an electron into an already negative ion. It's not going to go in willingly!

O (g)+e
$$\rightarrow$$
O<sup>-</sup>(g)1st EA = -142 kJ mol<sup>-1</sup>

$$O^{-}(g)+e-\rightarrow O^{2-}(g)2nd EA = +844 kJ mol^{-1}$$

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.



This trend of lower electron affinities for metals is described by the Group 1 metals:

Lithium (Li): -60 KJ mol-1 Sodium (Na): -53 KJ mol-1

Potassium (K): -48 KJ mol-1

Rubidium (Rb): -47 KJ mol-1

Cesium (Cs): -46 KJ mol-1

Notice that electron affinity decreases down the group.

When moving down a group, the electron affinity generally decreases. This is because as you go down the period table, new valence shells are added increasing the atomic radius. The new orbital is further away from the nucleus, meaning the attraction between the positively charged nucleus and the new electron decrease. Thus, electron affinity decreases.