Periodic Classification of Elements
Ionization Enthalpy& Electrongain Enthalpy

(C) IONISATION ENERGY / IONISATION POTENTIAL

The amount of energy required to remove the most loosely bound electron from an isolated gaseous atom is called ionisation energy.

The process may be represented as :

$$A(g) + I.E. \rightarrow A^+ + e^- \qquad I.E._1 \ / \ I.P_1 \qquad \Delta H = +ve \text{ (endothermic)}$$

Ionisation energy is expressed either in terms of electron volts per atom (eV/atom) or kilo joules per mole of atoms (kJ/mol).

$$1 \text{ ev per atom} = 96.3 \text{ kJ mol}^{-1}$$

The ionisation energy defined above is more precisely the first ionisation energy (IE_1).

Successive Ionisation energies :

Once the first electron has been removed from the gaseous atom, it is possible to remove second electron from the monopositive ion.

The amount of energy required to remove the most loosely bound electron from the isolated nonpositive ion of the element is called second ionisation energy (IE_2). Similarly, the energy required to remove the outermost electron from isolated dipositive ion is called third ionisation energy ($I.E._3$).

$$A^+ (g) + I.E._1 \quad A^+(g) + e^- \qquad I.E._1$$

$$A^+ (g) + I.E._2 \quad A^{2+}(g) + e^- \qquad I.E._2$$

$$A^{2+} (g) + I.E._3 \quad A^{3+}(g) + e^- \qquad I.E._3$$

The second (I.E.2), third (I.E.3), fourth (I.E.4) etc. ionisation energies are collectively known as successive ionisation energies. It may be noted that :

$$\mathbf{IE_4 > IE_3 > IE_2 > IE_1}$$

Factors on which Ionisation Energy Depends:

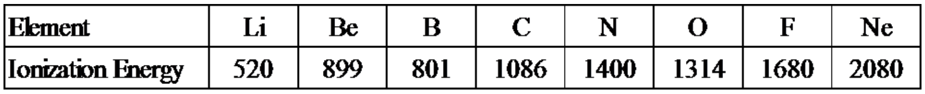
1. **Atomic Size:** I.E. decreases with increases in atomic size.
2. **Nuclear Charge:** I.E. increases with increase in nuclear charge.

3. **Screening Effect of the Inner Electrons :** Larger the number of electrons in the inner shells, greater is the screening effect on the outermost electron and hence lower is the ionisation energy.
4. **Penetration Effect :** Penetration power of various sub-shells of a particular energy level is in the order s > p > d > f. Therefore, for the same shell it is easier to remove an electron from p-sub-shell than from s-sub-shell. Greater the penetration power, higher is the I.E.
5. **Electronic Configuration :** The elements having stable electronic configurations have relatively higher values of I.E. For example,
   (i) The noble gases have stable configuration (ns^2np^6). They have highest ionisation energies within their respectively periods.
   (ii) The elements like N($1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$) and P($1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p_x^1$, $3p_y^1$, $3p_z^1$) have configurations in which orbitals belonging to same sub-shell are exactly half-filled. Such configurations are quite stable and consequently, their ionisation energies are relatively high.
   (iii) The elements like Be ($1s^2$, $2s^2$) and Mg ($1s^2$, $2s^2$, $2p^6$, $3s^2$) have all electrons paired. Such configurations being stable also result in the higher values of ionisation energy.

Variation across the period: In general, the value of ionisation energy increases with the increases in atomic number across a period. This can be attributed to the fact that in moving across the period, nuclear charge increases and atomic size decreases regularly and hence, the electrons are more tightly bound to the nucleus.

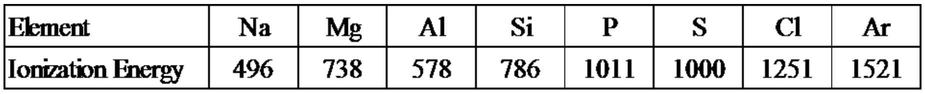
This trend can be seen in ionization energies (in kJ mol^{-1}) of elements belonging to 2nd and 3rd periods.

2nd Period Elements



Element	Li	Be	B	C	N	O	F	Ne
Ionization Energy	520	899	801	1086	1400	1314	1680	2080

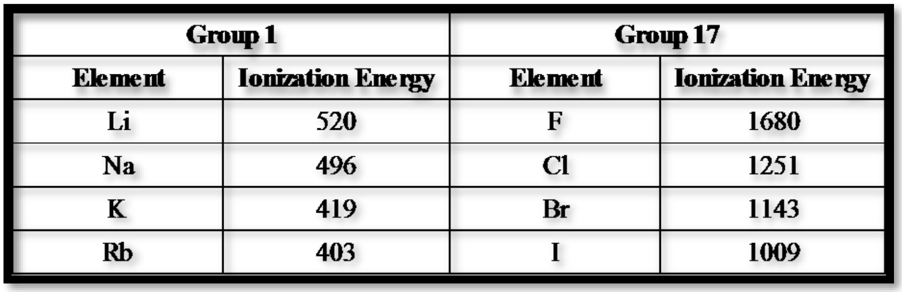
3rd Period Elements



Element	Na	Mg	Al	Si	P	S	Cl	Ar
Ionization Energy	496	738	578	786	1011	1000	1251	1521

Variation in a group: The value of ionisation energies decreases regularly with the increases in atomic number of shell and distance from the nucleus along a group.

We have already seen earlier, that the force of attraction between valence electrons and nucleus decrease in a group from top to bottom because of increase in atomic size due to addition of inner shells. Moreover, there is increase in shielding effect on outermost (valence) electrons due to increase in the number of inner electron. As a result, the electron becomes less and less firmly held to nucleus as we move down the group. Ionization energy decreases in a group from top to bottom. This can be seen from ioization energy values (in kJ mol^{-1}) of groups 1 and 17 elements given below :



Group 1		Group 17	
Element	Ionization Energy	Element	Ionization Energy
Li	520	F	1680
Na	496	Cl	1251
K	419	Br	1143
Rb	403	I	1009

$$\text{I.P.} \propto \frac{1}{\text{Atomic Size}}$$

$$\text{I.P.} \propto \text{Effective Nuclear Charge}$$

$$\text{I.P.} \propto \frac{1}{\textit{Screening Effect}}$$

Note : Half-filled and fully filled orbitals have greater ionisation potential.

(D) ELECTRON GAIN ENTHALPY / ELECTRON AFFINITY

Electron Gain Enthalpy may be defined as the amount of energy released when an electron is added to an isolated gaseous atom of the element.

The process may be expressed as :

$$A\ (g) + e^{-} \quad A^{-}(g) + E.A. \qquad \Delta H = -ve \ \text{(exothermic)}$$

The large value of electron reflects the greater tendency of an atom to accept the electron.

Units : The values of electron affinity are expressed either in electron volt per atom or kilo Joules per mole of atoms.

Factors Affecting Electron gain Enthalpy:

1. **Nuclear charge:** Greater the magnitude of nuclear charge, larger will be the value of electron affinity.
2. **Atomic size:** Larger the size of an atom, smaller will be the value of electron affinity.
3. **Electronic configuration:** Stable the electronic configuration of an atom, lesser will be its tendency to accept the electron and lower will be the value of its electron affinity.

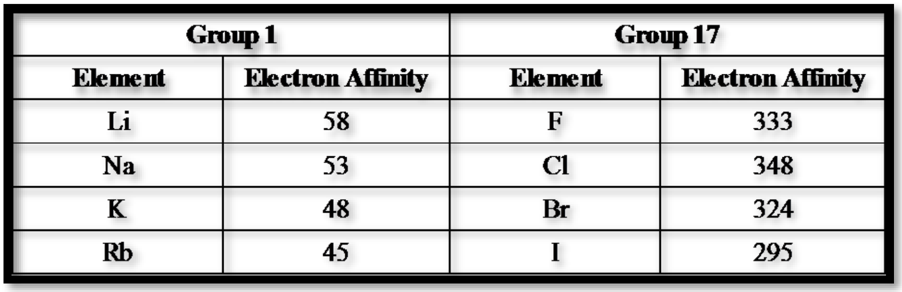
Variation in a period:

On moving across the period the atomic size decreases and nuclear charge increases. Both these factors result into greater attraction for the incoming electron, therefore, **electron affinity, in general, increases in a period from left to right.** However, some irregularities are observed in general trends. These are mainly due to the stable electronic configurations of certain elements. For example, electron affinities of noble gases like nitrogen, beryllium and magnesium are negative (regarded as zero) due to their stable electronic configurations.

Variation along a group:

On moving down a group, the atomic size and nuclear charge increase but the effect of increase in atomic size is much more pronounced that of nuclear charge and thus the additional electron feels less attraction by the nucleus.

Such trends in its values (in kJ mol^{-1}) for group 1 and group 17 elements are given below.



Group 1		Group 17	
Element	**Electron Affinity**	**Element**	**Electron Affinity**
Li	58	F	333
Na	53	Cl	348
K	48	Br	324
Rb	45	I	295

Consequently, electron affinity decreases from top to bottom in a group. However, electron affinities of elements of the second period are lower than those for the elements of the third period. This is possibly due to the strong inter electron repulsion forces operating within the relatively compact 2p-sub-shell.