Ionization Energy (IE)

Ionization energy or ionization potential is an atomic property which is shown by the atoms of all the elements. This property gives us an idea of the tendency of the elements to lose the outer-most shell electron to form a cation. Ionization energy can be defined as; "*The ionization energy of an element is the minimum amount of energy required to remove an electron from a gaseous atom in its lowest energy state (ground state) to convert it into a unipositive gaseous cation*".

With the help of this property a number of other properties of the elements like *reducing power, metallic (or electropositive) character* etc. can be explained. Thus, ionization energy of an element X is the energy required to carry out the reaction;
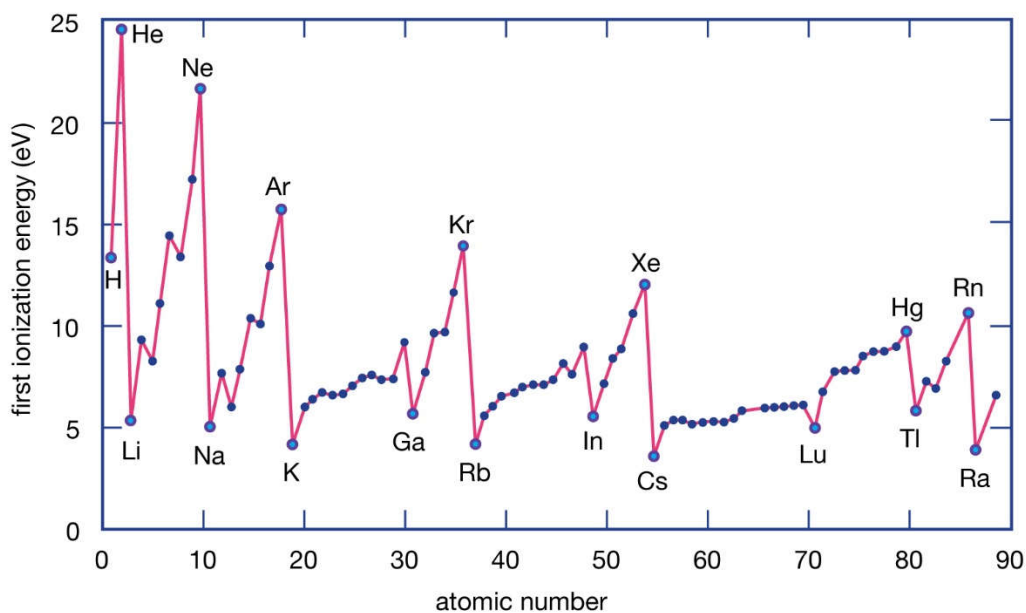
$$X_{(g)} \longrightarrow X^+ + e$$

Fig. 1. The variation of first ionization energies through the periodic table

Ionization energy is an atomic property which is shown by the atoms of all the elements. The magnitude of ionization energy is a measure of the effort required

to force an atom to give up an electron, or how "*tightly*" the electron is held in the atom. The higher the ionization energy, the more difficult is to remove the electron. With the help of this property, a number of other properties of the elements Ike reducing power, metallic character etc. can be explained.

Ionization energy is also called ionization potential, since it represents the amount of potential (voltage) required to remove the most loosely bound electron from the gaseous atom of an element to get a gaseous cation. Since in the gaseous phase the atom and the ion are isolated from all external influences, the ionization energy is exactly the energy with which the atom binds its electron. It, therefore, gives a quantitative measure of the stability of the isolated atom. *Ionization energies are usually expressed in electron volts (eV) per atom, or in kilo joules per mole of atoms (kJ mol^{-1}) or in kilo calories per mole as;*
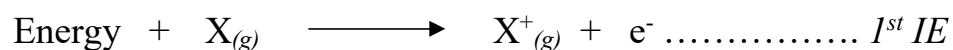
$$1 \text{ eV atom} = 96{:}48 \text{ kJ mol}^{-1} = 23.06 \text{ kcal mol}^{-1}$$

Table 1. First ionization energies (in kJ mol^{-1}) of representative elements.

Ionization energies of multi electron atoms

For multi electron atom, the amount of energy required to remove the first electron from the atom in the ground state,

$$\text{Energy} + X_{(g)} \longrightarrow X^+_{(g)} + e^- \dots\dots\dots\dots \textit{1}^{st} \textit{ IE}$$

It is called the *first ionization energy (I_1)*. In equation,

> *X   represents an atom of any element*
>
> *e   is an electron and*
>
> *g   denotes the gaseous state.*

Unlike an atom in the condensed phases (liquids and solids), an atom in the gaseous phase is virtually uninfluenced by its neighbours. The second ionization energy (I_2) and the third ionization energy (I_3) are shown in the following equations:

$$\text{Energy} + X^+_{(g)} \longrightarrow X^{2+}_{(g)} + e^- \quad \dots\dots \textit{2}^{nd} \textit{ IE}$$

$$\text{Energy} + X^{2+}_{(g)} \longrightarrow X^{3+}_{(g)} + e^- \quad \dots\dots.. \textit{3}^{rd} \textit{ IE}$$

This pattern continues for the removal of subsequent electrons with increasing ionization potential.

After an electron is removed from a neutral atom, the repulsion among the remaining electrons decreases. Removal of it second electron from a singly charged positive gaseous ion $X_{(g)}$ needs more energy than for the removal of the first electron. *This is so because attraction between the 'positive ion and electron is greater than between the neutral atom and the electron. Similarly, removal of a third electron from the ion is even more difficult.* Thus ionization energies always increase in the following order;

$$I_1 \quad < \quad I_2 \quad < I_3 \quad < .....$$

In comparing ionization energies; we must be careful to compare the energy for ionization of species with the same charge.

Factors Affecting Ionization Energies

The first ionization energy is a measure of the strength with which the nucleus holds the outermost electron. Thus, the magnitude of ionization energy depends upon:

1.   Effective Nuclear Charge

Greater is the magnitude of effective nuclear charge, greater is the electrostatic force of attraction exerted by the nucleus on the outer electrons. We know that on passing from left to right in a period, the effective nuclear charge increases by 0.65 at each next element. The increase in effective nuclear charge increases the magnitude of ionization potential as shown below for the elements of 2nd period (Note the abnormal values of Be and N as compared with those of Boron and Oxygen).

Elements of 2nd period : *Li   Be   Be   C   N   O   F   Ne*

Effective nuclear charge: *1.30* 1.95   2.60   3.25   3.55   4.55   5.20   *5.85*

Thus it would be more difficult to remove the outer shell electron from an atom with higher effective nuclear charge.

2.   Size of the Atom

Greater is the size of an atom, more far is the outermost shell electron from the nucleus and hence lesser will be the force of attraction exerted by the nucleus on the valence electron. With the increase of **radius (r)**, it would be more and more easy

to remove an electron from the outermost shell, i.e. higher is the value of r of an atom, lower will be its ionization energy. Thus with the increase of atomic size, it would be more and more easy to remove an electron from the outer-most shell.

3.   Shielding Effect

Greater is the magnitude of shielding effect working on the valence-shell electron, *smaller is the magnitude, of the force of attraction between the nucleus and valence shell electron* and hence lower is the amount of energy (ionization energy) to remove the valence-shell electron. In a multi- electron atom the electrons lying between the nucleus and the valence-shell (called intervening electrons) shield the outermost shell electron from the nucleus. The effect of shielding the valence-shell electron from the nucleus which is caused by the intervening electrons is called shielding or screening effect. The magnitude of shielding effect determines the magnitude of the force of attraction between the nucleus and the valence-shell electron. *Greater is the magnitude of shielding effect working on the valence-shell electron, smaller is the magnitude of the force of attraction between the nucleus and the valence-shell electron and hence lower is the amount of energy i.e. ionization potential)* to remove the valence shell electron. *Thus with the increase of shielding effect, ionization potential decreases.*

4.   The Extent of Penetration of Valence-Electrons

It has been found that the extent of *penetration of valence-electrons* in a given principal energy level decreases in the order:

$$s \quad > \quad p \quad > \quad d \quad > \quad f$$

This corresponds to the extent of binding of various electrons. An *ns* electron is more tightly bound than any *np* electron, which, in turn, is more tightly bound than any *nd* electron etc.

5.   The Nature of Configuration

According to Hund's rule, half-filled (ns^1, np^3, nd^5 or completely-filled (ns^2, np^6, nd^{10}) orbitals are comparatively more stable and hence more energy is needed to remove an electron from such orbitals. Similarly the higher value of ionization potential of Mg as compared to that of AI is because of the fact that in case of Mg the electron is to be removed from the completely-filled 3s-orbital while in case of AI the same is removed from the partially-filled 3p-orbital. Thus ionization energy of an atom 'having half-filled or completely filled atomic orbitals in its electronic configuration is relatively higher than that expected normally from its position in the periodic table.

Periodic Trends in Ionization Energies

(a)   Variation in a Group

When *we proceed from top to bottom in a group of representative element, the ionization energy values of the elements go on decreasing.* On descending a group toe size of the atom (i.e., the value of *principal quantum number*) and shielding effect caused by the intervening electrons on the valence-electrons increase, which result in the decrease of ionization energy.

The Group IA metals have very low first ionization energies, as is expected since these elements have only one "electron in their highest energy levels (….ns^1). The first electron added to a principal energy level is easily removed.

The first ionization energies for the ***Group IIA*** elements decrease in moving down the group but are significantly higher than those of Group IA elements in the same periods. This is due to the fact that Group IIA element have smaller atomic radii and high effective nuclear charges. Thus, their valence-electrons are held more tightly than those of the preceding alkali metals of the same period.

Moreover, *since a pair of electrons in an s-orbital is more stable than a single electron,* more energy is required to remove an electron from the filled outermost s-orbital of Group IIA elements than to remove the single electron from the half-filled outermost s-orbitals of the alkali metals.

(b)   Variation in a Period

In general, as *we move from left to right in a period, the ionization energies of the elements increases due to successive increase in the nuclear charge and decrease in atomic size.* Both effects are due to the fact that on moving across a period from one element to the other, electrons are being successively added to the same principal energy level while the nuclear charge is increasing. These electrons shield each other poorly from the increasing nuclear charge. As a result, there is an increase in the effective nuclear charge along the period. This causes a decrease in atomic radius and an increase in ionization energy along the period. However there are certain elements which show irregular trends.

Boron (B) has lower ionization energy than that of beryllium (Be). It is due to the fact that it has only single electron in its outermost p-orbital, hence it requires less energy to remove a p-electron than an s-electron from the same principal energy level since an np orbital is higher in energy than an ns orbital.

The ionization energy of oxygen is slightly less than that of nitrogen (N). The electronic configuration of nitrogen is *$1s^2$, $2s^2$, $2p^3$* in which the three p-orbitals are occupied by one electron each. The additional electron in oxygen must enter in one of these p-orbitals. It will then encounter repulsion and will therefore be less stable and easier to remove from the oxygen atom.

Similarly in the 3rd period higher ionization energies of Mg as compared to Al and P as compared to S can also be explained on the same line of arguments.