Ionization energy is the quantity of energy that an isolated, gaseous atom in the ground electronic state must absorb to discharge an electron, resulting in a cation.

\[
\text{H(g)} \rightarrow \text{H}^+\text{(g)} + \text{e}^-\text{(g)}
\]

This energy is usually expressed in kJ/mol, or the amount of energy it takes for all the atoms in a mole to lose one electron each.

When considering an initially neutral atom, expelling the first electron will require less energy than expelling the second, the second will require less energy than the third, and so on. Each successive electron requires more energy to be released. This is because after the first electron is lost, the overall charge of the atom becomes positive, and the negative forces of the electron will be attracted to the positive charge of the newly formed ion. The more electrons that are lost, the more positive this ion will be, the harder it is to separate the electrons from the atom.

In general, the further away an electron is from the nucleus, the easier it is for it to be expelled. In other words, ionization energy is a function of atomic radius; the larger the radius, the smaller the amount of energy required to remove the electron from the outermost orbital.

For example, it would be far easier to take electrons away from the larger element of Ca (Calcium) than it would be from one where the electrons are held tighter to the nucleus, like Cl (Chlorine).

In a chemical reaction, understanding ionization energy is important in order to understand the behavior of whether various atoms make covalent or ionic bonds with each other. For instance, the ionization energy of Sodium (alkali metal) is 496KJ/mol (1) whereas Chlorine’s first ionization energy is 1251.1 KJ/mol (2). Due to this difference in their ionization energy, when they chemically combine they make an ionic bond. Elements that reside close to each other in the periodic table or elements that do not have much of a difference in ionization energy make polar covalent or covalent bonds. For example, carbon and oxygen make CO\textsubscript{2} (Carbon dioxide) reside close to each other on a periodic table; they, therefore, form a covalent bond. Carbon and chlorine make CCl\textsubscript{4} (Carbon tetrachloride) another molecule that is covalently bonded.

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**Periodic Table and Trend of Ionization Energies**

As described above, ionization energies are dependent upon the **atomic radius**. Since going from right to left on the periodic table, the atomic radius increases, and the ionization energy increases from left to right in the periods and up the groups. Exceptions to this trend is observed for alkaline earth metals (group 2) and nitrogen group elements (group 15). Typically, group 2 elements have ionization energy greater than group 13 elements and group 15 elements have greater ionization energy than group 16 elements. Groups 2 and 15 have completely and half-filled electronic configuration respectively, thus, it requires more energy to remove an electron from completely filled orbitals than incompletely filled orbitals.

Alkali metals (IA group) have small ionization energies, especially when compared to halogens or VII A group (see diagram 1). In addition to the radius (distance between nucleus and the electrons in outermost orbital), the number of electrons between the nucleus and the electron(s) you're looking at in the outermost shell have an effect on the ionization energy as well. This effect, where the full positive charge of the nucleus is not felt by outer electrons due to the negative charges of inner electrons partially canceling out the positive charge, is called shielding. The more electrons shielding the outer electron shell from the nucleus, the less energy required to expel an electron from said atom. The higher the
**Shielding Effect** the lower the ionization energy (see diagram 2). It is because of the shielding effect that the ionization energy decreases from top to bottom within a group. From this trend, Cesium is said to have the lowest ionization energy and Fluorine is said to have the highest ionization energy (with the exception of Helium and Neon).

Table 1: Showing the increasing trend of ionization energy in KJ/mol (exception in case of Boron) from left to right in the periodic table(8)

<table>
<thead>
<tr>
<th>Element</th>
<th>Ionization Energy (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>520</td>
</tr>
<tr>
<td>Be</td>
<td>899</td>
</tr>
<tr>
<td>B</td>
<td>800</td>
</tr>
<tr>
<td>C</td>
<td>1086</td>
</tr>
<tr>
<td>N</td>
<td>1402</td>
</tr>
<tr>
<td>O</td>
<td>1314</td>
</tr>
<tr>
<td>F</td>
<td>1680</td>
</tr>
</tbody>
</table>

Table 2: Showing decreasing trend of ionization energies (KJ/mol) from top to bottom (Cs is the exception in the first group) (8)

<table>
<thead>
<tr>
<th>Element</th>
<th>Ionization Energy (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>520</td>
</tr>
<tr>
<td>Na</td>
<td>496</td>
</tr>
<tr>
<td>K</td>
<td>419</td>
</tr>
<tr>
<td>Rb</td>
<td>408</td>
</tr>
<tr>
<td>Cs</td>
<td>376</td>
</tr>
<tr>
<td>Fr</td>
<td>398</td>
</tr>
</tbody>
</table>

1st, 2nd, and 3rd Ionization Energies

The symbol \( I_1 \) stands for the first ionization energy (energy required to take away an electron from a neutral atom) and the symbol \( I_2 \) stands for the second ionization energy (energy required to take away an electron from an atom with a +1 charge). Each succeeding ionization energy is larger than the preceding energy. This means that \( I_1 < I_2 < I_3 < ... < I_n \) will always be true.

Example of how ionization energy increases as succeeding electrons are taken away.

\[
\text{Mg} \rightarrow \text{Mg}^+ + e^- \quad (I_1 = 738 \text{ kJ/mol})
\]

\[
\text{Mg}^+ \rightarrow \text{Mg}^{2+} + e^- \quad (I_2 = 1451 \text{ kJ/mol})
\]

See first, second, and third ionization energies of elements/ions in Table 3.
Table 3: Ionization Energies (kJ/mol)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
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<td>92010</td>
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<tr>
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<td>6130</td>
<td>9361</td>
<td>12180</td>
<td>15240</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>6913</td>
<td>9541</td>
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<td>10545</td>
<td>13627</td>
<td>17995</td>
<td>21700</td>
<td>25662</td>
</tr>
</tbody>
</table>

The Effects of Electron Shells on Ionization Energy

Electron orbitals are separated into various shells which have strong impacts on the ionization energies of the various electrons. For instance, let us look at aluminum. Aluminum is the first element of its period with electrons in the 3p shell. This makes the first ionization energy comparably low to the other elements in the same period, because it only has to get rid of one electron to make a stable 3s shell, the new valence electron shell. However, once you've moved past the first ionization energy into the second ionization energy, there is a large jump in the amount of energy required to expel another electron. This is because you now are trying to take an electron from a fairly stable and full 3s electron shell. Electron shells are also responsible for the shielding that was explained above.

Ionization Energy and Electron Affinity--Similar Trend

Both ionization energy and electron affinity have similar trend in the periodic table. For example, just as ionization energy increases along the periods, electron affinity also increases. Likewise, electron affinity decreases from top to bottom due to the same factor, i.e., shielding effect. Halogens can capture an electron easily as compared to elements in the first and second group. This tendency to capture an electron in a gaseous state is termed as electronegativity. This tendency also determines one of the chemical differences between Non metallic and metallic elements.
As indicated above, the elements to the right side of periodic table (diagram 3) have tendency to receive the electron while the one at the left are more electropositive. Also, from left to right, the metallic characteristics of elements decrease (4).

**Prediction of Covalent and Ionic Bonds**

The difference of electronegativity or ionization energies between two reacting elements determine the fate of the type of bond. For example, there is a big difference of ionization energies and electronegativity between Na and Cl. Therefore, sodium completely removes the electron from its outermost orbital and chlorine completely accepts the electron, and as a result we have an ionic bond (4). However, in cases where there is no difference in electronegativity, the sharing of electrons produces a covalent bond. For example, electronegativity of Hydrogen is 2.1 and the combination of two Hydrogen atoms will definitely make a covalent bond (by sharing of electrons). The combination of Hydrogen and Fluorine (electronegativity=3.96) will produce a polar covalent bond because they have small differences between electronegativity (5).

**Questions**

1) By looking at following electronic configuration of elements, can you predict which element has the lowest first ionization energy?

a. 1s$^2$ 2s$^2$ 2p$^6$

b. 1s$^2$ 2s$^2$ 2p$^4$

c. 1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$
2) The ionization energy of \( \text{Na}^{+3} \) ion is one of the following (7):

a. More than first ionization only
b. More than second ionization only
c. Sum of first and second ionization energies
d. Sum of first, second, and third ionization energies

3) Ionization energies and electron affinities are

a. Dependent upon each other,
b. Similar trend of increasing/decreasing along the periods and within the group of periodic table,
c. Inversely related with each other,
d. Indirectly related with each other

4) Ionization energy is the ability to capture an electron:

a. False,
b. True

5) The second ionization energy of Mg is greater than second ionization energy of Al:

a. False,
b. True

6) Which group would generally have the lowest first ionization energy?

a. Transition Metals
b. Alkali Metals
c. Noble Gases
d. Alkaline Earth Metals
e. Halogens

7) Sulfur has a first ionization energy of 999.6 kJ/mol. Rubidium has a first ionization energy of 403 kJ/mol. What bond do they form when chemically combined?

a. Covalent
b. Polar Covalent
c. Ionic

8) Ionization energy, when supplied to an atom, results in a(n)

a. Anion and a proton
b. Cation and a proton  
c. Cation and an Electron  
d. Anion and an electron

9) Low first ionization energy is considered a property of
   a. Metals  
   b. Nonmetals

10) Gallium has a first ionization energy of 578.8 kJ/mol, and calcium has a first ionization energy of 589.8 kJ/mol. According to periodic trends, one would assume that calcium, being to the left of gallium, would have the lower ionization energy. Explain, in terms of orbitals, why these numbers make sense.

Answers

10) Gallium has one electron in the 4p orbital, which can be expelled to reveal a more stable and full 4s orbital. Calcium, however, has a fully stable 4s orbital as its valence orbital, which you would have to disrupt to take an electron away from.

References
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4. General Chemistry: Principles and Modern Applications by Petrucci, Hardwood, Herring, and Madura
5. Principles of Modern Chemistry by Oxtoby, Gillis, and Campiont