Chemical Periodicity

Periodic Table of Elements

Study the chemistry of all elements individually is extremely difficult and tedious. The periodic table provides a systematic and extremely useful framework for organizing a lot of information available on the chemical behavior of the elements into a few simple and logical patterns. This gave rise to classify the elements into families having similar physiochemical properties.

*Periodic table may be defined as the arrangements of various elements according to their properties (physical/chemical) in a tabular form.*

Need for classification of elements:
There were only few elements known in the literature before 17th Century. Later on, many elements were discovered in nature and fabricated, hence the number of known elements increasing. It was thought that elements must be properly classified in order to make a systematic study of elements, and understand or predict the properties of all the known elements. This concept evolves the development of periodic table.

The following are the advantages of classification of elements.
(1) To study and understand the elements in a systematic manner
(2) To correlate the properties of elements and classify them.
(3) To know the type of different compounds that different element can form

On or before 17th century all the known elements were classified into metals and non-metals.

History of periodic table development
The periodic table was originally constructed to represent the patterns observed in the chemical properties of the elements.

All earlier attempts on the classification of elements were based on atomic mass. Several chemists have for long tried to classify the elements and to find patterns in their properties.

Johann Dobereiner (1829): The German Chemist, who noticed several groups of three elements having similar properties and are called triads, and he try to fit this rule for other known elements, it become very clear that the rule works for only few elements.

*The law states that, the elements are arranged orderly in increasing atomic mass. the atomic mass of the middle element was found to be approximately equal to the arithmetic mean of the other two elements.*
John Alexander Newlands (1864): English chemist, started arranging the elements in their order of increasing atomic weight and found that every eighth elements have the similar properties of first element, just like the eighth note scale in an octave of music. He called it the law of octaves. It worked well for the lighter elements (up to Ca) but failed when applied to heavier elements.

Lother-Meyer’s (1869): He plotted atomic volumes versus atomic weights of elements and obtained a curve with series of peaks. He pointed out that elements occupying similar positions in the curve possessed similar properties.

- Alkali metals such as Na, K, Rb which have similar properties occur as peaks of the curve.
- Halogen elements like F, Cl, Br, which have similar properties occur at the rising or the ascending part of the curve.
- Noble gasses such as Ne, Ar, Kr which have similar properties occur just before the alkali elements.
- H and He seem to be exception to the rule
Dimitri Mendeleev (1869): Russian Chemist, first time published the periodic law, with 63 chemical elements (known at the time).

The properties of elements are a periodic function of their atomic weights, i.e., if the elements are arranged in the increasing order of their atomic weights, the properties of the elements (i.e., similar elements) are recur after definite intervals or periods.

Important features of the Table
(1) Mendeleev's Periodic table forms vertical columns and horizontal rows for elements.
(2) Vertical columns are called groups. There are eight groups in the table (Group I to Group VIII). Elements of a group are similar in properties.
(3) All groups from I to VII are divided into sub-groups A and B (i.e., I_A, I_B, II_A, II_B etc.). Group VIII has no sub-groups.
(4) Horizontal rows are known as periods. There are seven periods (1 to 7).
(5) Elements of the same period differ in properties.
(6) Sub-group elements also differ in properties.
$\text{I}_A = \text{Na}$ (highly reactive metal); $\text{I}_B = \text{Cu}$ (noble metal)

Merits of Mendeleev's Periodic Table
(1) Correction of atomic weights: Many doubtful atomic weights were corrected using Mendeleev's periodic table, Example, atomic mass of beryllium was corrected from 13.5 to 9. Similarly, with the help of this table, atomic masses of indium, gold, platinum etc. were also corrected.
(2) Vacant places for undiscovered elements: Mendeleev left vacant places in his table for elements to be discovered, (Ga, Ge etc.). Not only that, he also predicted properties of those elements.
which were when Mendeleev proposed his periodic table. He named these elements **eka-aluminium** (Ga) and eka-silicon (Ge) because he believed that they should be similar to Al and Si. Mendeleev's predictions were found to be true when the elements were actually discovered.

<table>
<thead>
<tr>
<th></th>
<th>Mendeleev's predicted properties</th>
<th>Actual properties</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gallium (eka-aluminium)</strong></td>
<td>Atomic mass About 68 amu</td>
<td>69.72 amu</td>
</tr>
<tr>
<td>Melting point</td>
<td>Low</td>
<td>29.8 °C</td>
</tr>
<tr>
<td>Density</td>
<td>5.9 g/cm³</td>
<td>5.90 g/cm³</td>
</tr>
<tr>
<td>Formula of oxide</td>
<td>X&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Ga&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>Formula of chloride</td>
<td>XCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>GaCl&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Mendeleev's predicted properties</th>
<th>Actual properties</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Germanium (eka-silicon)</strong></td>
<td>Atomic mass About 72 amu</td>
<td>72.64 amu</td>
</tr>
<tr>
<td>Density</td>
<td>5.5 g/cm³</td>
<td>5.35 g/cm³</td>
</tr>
<tr>
<td>Formula of oxide</td>
<td>XO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>GeO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Formula of chloride</td>
<td>XCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>GeCl&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

**Defects of Mendeleev's Periodic Table**

1. Hydrogen has placed in both Group I (alkali metals) and Group VII (halogens).
2. Some elements are placed in reverse order by ignoring their increasing atomic weights like
   
   a. Ar (Z = 18, at. wt. = 40) precedes K (Z = 19, at. wt. = 39.0)
   
   b. Co (Z = 27, at. wt. = 59.9) precedes Ni (Z = 28, at. wt. = 58.6)
   
   c. Te (Z = 52, at. wt. = 127.6) precedes I (Z = 53, at. wt. = 126.9)
   
   d. Th (Z = 90, at. wt. = 232.12) precedes Pa (Z = 91, at. wt. = 231)
3. Many dissimilar elements are placed in same group. E.g. Highly reactive alkali metals (Li to Cs) are with noble coinage metals (Cu, Ag, Au), Mn is grouped with halogens
4. Many similar elements are placed in different groups. E.g. copper and mercury; silver and thallium; and barium and lead.
5. Metals like Mn; Tc, Re were placed with non-metals and halogens (F to I) in Group VII.
6. Group VIII has three elements at a place (Fe, CO, Ni), (Ru, Rh, Pd) and (Os, Ir, Pt), instead of one element.
7. Isotopes (different molecular weight of same elements) have got no places in Mendeleev's periodic table.
8. Lanthanides are not placed in same group

**MODERN PERIODIC TABLE**

**Henry Mosley (1914):** British Physicist, found that there was a very prominent linear relationship between the atomic numbers of heavy elements and square roots of the frequency of their most
intense characteristic X–ray lines \((Z \propto \sqrt{\nu})\), rather atomic weight versus square roots of the frequency. Hence he convinced, atomic number is a more fundamental property of an element than its atomic weight. Mendeleev’s Periodic Law was, therefore, accordingly modified. This is known as the **Modern Periodic Law** and can be stated as

*The physical and chemical properties of the elements are periodic functions of their atomic numbers.*

Therefore, the elements were, then, arranged in increasing order of their atomic numbers. In this table sub groups are separated and so the table becomes longer in size. hence, it is also known as long form of the periodic table.

**Main Features of the Modern Periodic Table:**

1. It has **groups/family** (vertical row / top to down) and **periods** (horizontal row. left to right) like Mendeleev’s Periodic table.
2. It has **nine groups, I to VIII and zero** (Noble gases were known when the table was made and kept in Zero group) and **seven periods**
3. Groups from I to VII are divided into sub-groups of A and B, whereas groups Zero and VIII has no sub-groups.
4. Elements from atomic number 84 (Polonium) onwards are radioactive. A few others having lower atomic number are also radioactive, e.g. Tc is radioactive.
5. Elements after atomic number 92 (Uranium) are all synthetically made by nuclear reactions.

<table>
<thead>
<tr>
<th>Period</th>
<th>Nature</th>
<th>Number of Elements</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Shortest Period</td>
<td>2</td>
<td>H and He</td>
</tr>
<tr>
<td>2</td>
<td>Short period</td>
<td>8</td>
<td>Li to Ne</td>
</tr>
<tr>
<td>3</td>
<td>Short period</td>
<td>8</td>
<td>Na to Ar</td>
</tr>
<tr>
<td>4</td>
<td>Long period</td>
<td>18</td>
<td>K to Kr</td>
</tr>
<tr>
<td>5</td>
<td>Long period</td>
<td>18</td>
<td>Rb to Xe</td>
</tr>
<tr>
<td>6</td>
<td>Longest period</td>
<td>32</td>
<td>Cs to Rn</td>
</tr>
<tr>
<td>7</td>
<td>Incomplete</td>
<td>Depends as on</td>
<td>Fr to ---</td>
</tr>
</tbody>
</table>

**Defects of Long Form of Periodic Table:**

Although the long form of the periodic table is superior to Mendeleev’s periodic table in many respects, it retains some of the defects as such. For example:

1. The problem of the position of hydrogen remains unsolved.
2. Like the Mendeleev’s table, it fails to accommodate the lanthanides and actinides in the main body of the table.
3. The arrangement is unable to reflect the electronic configuration of many elements.
**IUPAC Table**

It is simply a changed version of the long form of the modern periodic table. **IUPAC** (The International Union of Pure and Applied Chemistry) committee recommended it in 1984. In most of the text, people commonly use the IUPAC group numbers rather other format to avoid the conflict / confusion.

**Main Features of IUPAC Table**

1. In this the old notations of 18 groups, I_A- VII_A, I_B – VII_B and VIII has renamed as 1 to 18 to avoid confusion arising out of A and B notion of the groups.
2. Elements of group 1, group 2 and groups 13 to 17 have all their inner shells completely filled. These are s- and p- block elements.
3. Elements of group 18 are noble gases. They have all their orbitals completely filled.
4. Elements belonging to group 3 to group 12 have their inner (n-1)d or (n-2)f orbital partially filled (these are d- and f-block elements / transition and inner-transition elements).
5. Some sections of the periodic table have traditional names, as shown in Fig.
Fig: Numbering Schemes and Names for Parts of the Periodic Table.

IUPAC recommendation for the naming heavy elements, Atomic Numbers Greater than 100

The naming of the new elements had been traditionally the privilege of the discoverer (or discoverers) and the suggested name was ratified by the IUPAC. In recent years, this has led to some controversy. For example, both American and Soviet scientists claimed credit for discovering element 104. The Americans named it Rutherfordium whereas Soviets named it Kurchatovium. To avoid such problems, the IUPAC has recommended that a systematic nomenclature be derived directly from the atomic number of an atom.

Few elements of atomic numbers greater than 100 have given trivial names and corresponding two letter symbols approved by IUPAC. The status of those elements names and symbols are not going to affect by IUPAC recommendation of systematic naming.
The Commission on Nomenclature of Inorganic Chemistry recommended some procedure to elements based on their atomic number and that names should accord with the following principles:

1. The names should be short and obviously related to the atomic numbers of the elements.
2. The names should end in 'ium' whether the element was expected to be a metal or otherwise.
3. The symbols for the systematically named elements should consist of three letters.
4. The symbols should derived directly from the atomic numbers and be visually related to the names as far as possible.

The Commission recommends the use of **three-letter symbols** because any systematically derived set of two-letter symbols will tend to duplicate some of the two-letter symbols of elements.

1. The name is derived directly from the digits of atomic number of the element using the following numerical roots:

<table>
<thead>
<tr>
<th>Atomic number</th>
<th>Roots</th>
<th>Name</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>un, nil, un</td>
<td>Unnilunium</td>
<td>Unu</td>
</tr>
<tr>
<td>102</td>
<td>un, nil, bi</td>
<td>Unnilbiunium</td>
<td>Unb</td>
</tr>
<tr>
<td>103</td>
<td>un, nil, tri</td>
<td>Unniltrium</td>
<td>Unt</td>
</tr>
<tr>
<td>104</td>
<td>un, nil, quad</td>
<td>Unnilquadrium</td>
<td>Unq</td>
</tr>
<tr>
<td>105</td>
<td>un, nil, pent</td>
<td>Unnilpentium</td>
<td>Unp</td>
</tr>
<tr>
<td>106</td>
<td>un, nil, hex</td>
<td>Unnilhexium</td>
<td>Unh</td>
</tr>
<tr>
<td>107</td>
<td>un, nil, sept</td>
<td>Unnilseptium</td>
<td>Uns</td>
</tr>
<tr>
<td>108</td>
<td>un, nil, oct</td>
<td>Unniloctium</td>
<td>Uno</td>
</tr>
<tr>
<td>109</td>
<td>un, nil, enn</td>
<td>Unnilennium</td>
<td>Une</td>
</tr>
<tr>
<td>110</td>
<td>un, un, nil</td>
<td>Ununnilium</td>
<td>Uun</td>
</tr>
<tr>
<td>111</td>
<td>un, un, un</td>
<td>Unununium</td>
<td>Uuu</td>
</tr>
<tr>
<td>900</td>
<td>enn, nil, nil</td>
<td>Ennilnilium</td>
<td>Enn</td>
</tr>
</tbody>
</table>

2. The roots are put together in the order of the digits, which make up the atomic number and terminated by 'ium' to spell out the name. The final 'n' of 'enn' is omitted when it occurs before 'nil', and the final 'i' of 'bi' and of 'tri' when it occurs before 'ium'. Therefore, symbol of the element is composed of the initial letters of the numerical roots, which make up the name.

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Electronic configurations of elements and the periodic table: ([http://dx.doi.org/10.1021/ed020p21](http://dx.doi.org/10.1021/ed020p21)) (Recall the knowledge of quantum number and orbitals studied earlier semester)

(a) **Electronic Configurations in Periods**: The period indicates the value of **n** (principle quantum number, refers to energy level of orbitals) for the outermost or valence shell. In other words,
successive period in the Periodic Table is associated with the filling of the next higher principal energy level \((n = 1, n = 2, \text{etc.})\). It could be seen, that the number of elements in each period is twice the number of atomic orbitals available in the energy level that is being filled.

There are seven periods and each period starts with a different principal quantum number.

The first period corresponds to the filling of electrons in the first energy shell \((n = 1)\). Now this energy level has only one orbital \((1s)\) and, therefore, it can accommodate two electrons. This means that there can be only two elements (hydrogen, \(1s^1\) and helium, \(1s^2\)) in the first period.

The second period starts with the electron beginning to enter the second energy shell \((n = 2)\). Since there are only four orbitals (one 2s and three 2p- orbitals) to be filled, it can accommodate eight electrons. Thus, second period has eight elements in it. It starts with lithium \((Z = 3)\) in which one electron enters the 2s-orbital. The period ends with neon \((Z = 10)\) in which the second shell is complete \((2s^2, 2p^6)\).

The third period begins with the electrons entering the third energy shell \((n = 3)\). It should be noted that out of nine orbitals of this energy level (one s, three p and five d) the five 3d-orbitals have higher energy than 4s-orbitals. As such only four orbitals (one 3s and three 3p) corresponding to \(n = 3\) are filled before fourth energy level begins to be filled. Hence, third period contains only eight elements from sodium \((Z = 11)\) to argon \((Z = 18)\) and so on given in the table...

<table>
<thead>
<tr>
<th>Period</th>
<th>Principal quantum shell ((n))</th>
<th>Orbitals being filled up</th>
<th>Electrons to be accommodated</th>
<th>Number of electrons</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td>(n=1)</td>
<td>1s</td>
<td>2</td>
<td>2</td>
<td>Short periods</td>
</tr>
<tr>
<td>Second</td>
<td>(n=2)</td>
<td>2s, 2p</td>
<td>2+6</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Third</td>
<td>(n=3)</td>
<td>3s, 3p</td>
<td>2+6</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Fourth</td>
<td>(n=4)</td>
<td>4s, 3d, 4p</td>
<td>2+6+10</td>
<td>18</td>
<td>Long periods</td>
</tr>
<tr>
<td>Fifth</td>
<td>(n=5)</td>
<td>5s, 4d, 5p</td>
<td>2+6+10</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Sixth</td>
<td>(n=6)</td>
<td>6s, 4f, 5d, 6p</td>
<td>2+14+10+6</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>Seventh</td>
<td>(n=7)</td>
<td>7s, 5f, 6d, 7p</td>
<td>2+14+10+6</td>
<td>32</td>
<td></td>
</tr>
</tbody>
</table>

(b) **Group wise Electronic Configurations**: Elements in the same vertical column or group have similar valence shell electronic configurations, the same number of electrons in the outer orbitals, and similar properties. For example, the Group 1 elements (alkali metals) all have \(ns^1\) valence shell electronic configuration as shown below.

<table>
<thead>
<tr>
<th>Atomic number</th>
<th>Symbol</th>
<th>Electronic configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Li</td>
<td>(1s^22s^1) (or) [He] (2s^1)</td>
</tr>
<tr>
<td>11</td>
<td>Na</td>
<td>(1s^22s^22p^63s^1) (or) [Ne] (3s^1)</td>
</tr>
<tr>
<td>19</td>
<td>K</td>
<td>(1s^22s^22p^63s^23p^64s^1) (or) [Ar] (4s^1)</td>
</tr>
<tr>
<td>37</td>
<td>Rb</td>
<td>(1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^1) (or) [Kr] (5s^1)</td>
</tr>
<tr>
<td>55</td>
<td>Cs</td>
<td>(1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^66s^1) (or) [Xe] (6s^1)</td>
</tr>
<tr>
<td>87</td>
<td>Fr</td>
<td>[Rn] (7s^1)</td>
</tr>
</tbody>
</table>

CHEM0202

P Sasikumar
Types of elements: *s*-, *p*-, *d*-, *f*- Blocks: The aufbau principle and the electronic configuration of atoms provide a theoretical foundation for the periodic classification. The elements in a vertical column of the periodic table constitute a group or family and exhibit similar chemical behavior. Even though, helium belongs to the s-block but it’s positioning in the p-block along with other group 18 elements is justified because it has a completely filled valence shell (1s²) and as a result, exhibits properties characteristic of other noble gases.

The other exception is hydrogen. It has a one 1s- electron and hence can be placed in-group 1 (alkali metals). It can also gain an electron to achieve a noble gas arrangement and hence it can behave similar to a group 17 (halogen family) elements. Because it is a special case, we shall place hydrogen separately at the top of the Periodic Table.

We will briefly discuss the salient features of the four types of elements marked in the periodic table.
The elements of group 1 (alkali metals) and group 2 (alkaline earth metals) which have ns\(^1\) and ns\(^2\) outermost electronic configuration belong to the s-block elements. They are
all reactive metals with low ionization enthalpies. They lose the outermost electron(s) readily to form 1+ (in the case of alkali metal) or 2+ ions (in the case of alkaline earth metals). The metallic character and the reactivity increase as we go down the group. The compounds of the s-block elements, with the exception of those of beryllium are predominantly ionic.

**p-Block Elements:** The p-Block Elements comprise those belonging to groups 13 to 18 and together with the s-block electronic are called the Representative Elements or Main Group Elements. The outermost electronic configuration varies from ns²np¹⁶ in each period. Each period ends in a noble gas with a closed shell ns²np⁶ configuration. All the orbitals in the valence shell of the noble gases are completely filled by electrons and it is very difficult to alter this stable arrangement by the addition or removal of electrons. The noble gases thus exhibit very low chemical reactivity. Preceding the noble gas family are two chemically important groups of nonmetals. They are the halogens (groups 17) and chalcogens (group 16). These two groups of elements have higher negative electron gain enthalpies and readily add one or two electrons respectively to attain the stable noble gas configuration. The nonmetallic character increases as we move from left to right across a period and metallic character increases as we go down the group.

**The d-block Elements (Transition Elements):** These are the elements of group 3 to 12 in the center of the periodic table. These elements are characterized by filling of inner d orbitals by electrons and are therefore referred to as d-Block Elements. These elements have the outer electronic configuration (n-1)d¹⁰ns². They are all metals. They mostly form colored ions and exhibit variable valences. However, Zn, Cd and Hg, which have the (n-1)d¹⁰ns² electronic configuration, do not show most of the properties of transition elements in a way, transition metals form a bridge between the chemically active metals of s-block elements and less active metals of groups 13 and 14 and thus take their familiar name “transition elements”

**The f-Block Elements (Inner-Transition elements):** The two rows of elements at the bottom of the periodic table, called the Lanthanoids 58Ce-71Lu and Actinoids, 90Th-103Lr are characterized by the outer electronic configuration (n-2)f¹⁴(n-1)d⁰-10ns². The last electron added to each element is an f-electron. These two series of elements are hence called the inner transition elements (f-Block Elements). They are all metals within each series; the properties of the elements are quite similar. The chemistry of the early actinoids is more complicated than the corresponding lanthanoids, due to the large number of oxidation states possible for these actinoid elements. Actinoid elements are radioactive. Many of the actinoid elements have been made only in nano-gram quantities or less by nuclear reactions and their chemistry is not fully studied. The elements coming after uranium are called trans-uranium elements.
In addition to displaying the classification of elements into s-, p-, d-, and f-blocks, the periodic table shows another broad classification of elements based on their properties. The elements can be divided into **Metals and Non-metals**. Metals comprise more than 75% of all known elements and appear on the left side of the Periodic Table.

**Metals** are usually solids at room temperature (Mercury is an exception); they have high melting and boiling points. They are good conductors of heat and electricity. They are malleable (can be flattened into thin sheets by hammering) and ductile (can be drawn into wires).

In contrast, **nonmetals** are located at the top right hand side of the Periodic Table. Nonmetals are usually solids or gases at room temperature with low melting and boiling points. They are poor conductors of heat and electricity. Most non-metallic solids are brittle and are neither malleable nor ductile.

The elements become more metallic as we go down a group; the nonmetallic character increases as one goes from left to right across the Periodic Table. The change from metallic to non-metallic character is not abrupt as shown by the thick zig-zag line in the periodic table. The elements (e.g. germanium, silicon, arsenic, antimony and tellurium) bordering this line and running diagonally across the Periodic Table show properties that are characteristic of both metals and non-metals. These elements are called **Semi Metals or Metalloids**.

**Position of Hydrogen and Helium in Periodic Table**

The peculiar structure of the hydrogen atoms electron shell (1s\(^1\)) makes it difficult to decide what group of the periodic table to put hydrogen in. The fact, that hydrogen can lose an electron to form a cation H\(^+\) (proton), makes it similar to the alkali metals. The ability of hydrogen to gain an electron to form H\(^-\) ion is reminiscent of the types of reactions the halogens undergo. The position of hydrogen in the periodic table is, thus, anomalous.

Hydrogen shows significant analogies to two groups, namely:
(a) Group I - the alkali-metal group—with valence shell configuration ns\(^1\).
(b) Group 17 - the halogens, having the electronic configuration ns\(^2\)np\(^5\), one short of the next noble gas configuration.

(a) **Comparison with Alkali Metals**

**Resemblance with Alkali Metals:**
The hydrogen forms a cation H\(^+\), similar to Na\(^+\), K\(^+\), etc. indicates its similarity to the alkali metals.
Both hydrogen and alkali metals combine with a number of nonmetals.
The deference’s with alkali metals:
The ionization energy of hydrogen (1312 kJ/mol) is very high as compared to that of the alkali metals (520 to 374 kJ/mol for Li to Cs).
(ii) The electronegativity of hydrogen (2.1) is also high as compared to that of the alkali metals (0.9).
(iii) The alkali metals are highly reactive metallic element even at room temperatures. Hydrogen is less electropositive gas and inert at room temperature (in the absence of catalysts).
(iv) Alkali metal compounds are ionic and contain M⁺ ions, whereas hydrogen compounds are either covalent or contain solvated ions.

(b) Comparison with Halogens
Resemblance with Halogens: Hydrogen accepts one electron forming the hydride ion, H⁻, which has the noble gas configuration, ls².
The Main Similarities are:
(i) In the elementary state both hydrogen and the halogens form diatomic molecules. Both are nonmetallic elements. Solid hydrogen resembles iodine closely.
(ii) The ionization energy of hydrogen is of the same order as that of the halogens.
(iii) Hydrides and halides are similar in their properties. Electrolysis of molten hydrides and halides liberate the nonmetal at the anode.
(iv) The compounds of hydrogen with carbon, silicon, germanium, etc. are similar to the corresponding halide, e.g. SiH₄, and SiCl₄, CH₄ and CCl₄, etc.
(v) Hydrogen halides and inter-halogen compounds have similar properties.
The Main Difference with Halogens:
(i) The formation of H⁻ from H₂ is an endothermic process. Thus, it is apparent why the halogens are very reactive and hydrogen is inert at room temperature.
(ii) The hydride ion H⁻ is very large and easily polarizable as compared to the halides.
(iii) The maximum coordination number of halogens is seven (IF₇) whereas that of hydrogen is two.
(iv) In polynuclear complexes the halides act as bridging ligands; the hydride ion cannot act as a bridging ligand.
(v) Halogens do not show anything similar to hydrogen bonding.
It is evident from this discussion that the position and it is desirable to accord it a special place in the periodic table. Thus, hydrogen can be placed separately in periodic table

Similarly, you might wonder why Helium is placed in group 18 along with noble gases on right-hand side of the Periodic Table, rather than right next to hydrogen. Even though helium only has two
valence electrons, while the rest of the Group 18 elements have eight valence electrons, helium is placed on the top of the 18 column since *helium's chemical behavior is similar to the chemical behavior of the other noble gases* because it has a completed outer energy level.

1. like the other noble gases the valence shell of helium is complete
2. The valance of helium is zero similar to other elements in group 18, As a result, it is **chemically inert** (like the noble gases in group 18)
3. like other noble gases helium also monoatomic.

Hence helium is placed on the top of the 18 column.

**Relationships in the Periodic Table**

**(A) Group relation**

Elements of a particular group are have similar properties.

e.g.

Group1 ——> Li Na K Rb Cs
Group2 ——> Be Mg Ca Sr Ba etc., are similar.

However, first element of representative groups (i.e., s and p-block) differ from rest of the group members, Example, Li, Be, B, C, N, O, and F differ from their other group members respectively.

Li differ from Na, Be from Mg, etc. This difference is due to:

1. Small size (of the first member)
2. High electronegativity (of the first member)
3. Non-availability of d orbitals in the valence shell of these elements i.e., 2nd period elements).

Valence orbitals are s and p only.

**(B) Periodic / Horizontal relationship**

1. Elements of Group VIII (or 8, 9 and 10 of IUPAC table) have horizontal similarity

   Fe CO Ni ———> Ru Rh Pd ———> Os Ir Pt

2. Transition elements form a horizontal series. Ti, V, Cr, Mn, Fe, Co, Ni, etc and are similar
3. Lanthanides i.e., elements from Ce to Lu, are similar in many ways.

**(C) Diagonal relationship**

Some elements placed diagonally in the figures are similar properties
Li is similar to Mg, Be to Al and B to Si. It is known as diagonal relationship. Diagonal similarity is due – either having similar ionic radii $Li^+ = 0.76\text{Å}$, $Mg^{2+} = 0.72\text{Å}$ and or to similar ionic potential

$$\text{Ionic pot.} = \frac{\text{Charge}}{\text{ionic radius}}$$

$Be^{2+} = 6.6$, $Al^{3+} = 6.0$

**Periodicity in the Periodic Table**

**Effective Nuclear Charge ($Z^*$ or $Z_{eff}$)**

Most of the inherent properties of atoms depending on valence shell electronic configuration and on how strongly are they attracted to the nucleus. The attractive force between an electron and the nucleus depends on

(i) Magnitude of the nuclear charge

(ii) The average distance between the nucleus and the electron. i.e. the force increases as the nuclear charge increases and decreases as the electron moves farther from the nucleus.

Understanding the attraction between the electron and the nucleus in a hydrogen atom is straightforward because we have only one electron and one proton. However, in a multi electronic atom the situation become complicated. In addition to the attraction of each electron to the nucleus, also they experience the repulsion from other electrons. These electron–electron repulsions cancel some of the attraction of the electron to the nucleus. Hence, electron experiences less attraction than it would if the other electrons were not there.

**In essence, each electron in a multi-electron atom of the inner shells put a screen of negative charge on the nucleus. Therefore, outer electrons experience lesser attractive effect of nucleus. The actual nuclear charge an outer electron experiences is called ‘Effective Nuclear Charge’ ($Z^*$ or $Z_{eff}$).** Because the full attractive force of the nucleus has been decreased by the electron repulsions, we see that the effective nuclear charge is always less than the actual nuclear charge $Z^* < Z$.

It is given as, $Z^* = Z - \sigma$, where $Z =$ atomic number, $\sigma =$ screening (or shielding) constant. Thus, if $\sigma$ is known, $Z^*$ can be calculated. $\sigma$ is calculated using Slater’s rule.
Screening (or shielding) constant ($\sigma$)

The decrease in the attractive force exerted by the nucleus on the valence-shell electron, due to the presence of the electrons lying between the nucleus and valence-shell electrons, (called intervening electrons) is called shielding effect or screening effect.

Factors Affecting the Magnitude of Shielding Effect

1. Number of inner-shell electrons or inner shells.

   i.e $\sigma$ a No. of electrons

Greater is the number of inner-shell electrons or inner shells, greater is the magnitude of shielding effect caused by the inner electrons on the valence-shell electron.

E.g. Elements of group 1 (alkali metal), moving down the group with the increase of the number of inner shells and electrons in them, the shielding effect caused by these electrons on the valence-shell electron also increases from Li to Cs as shown.
2. Type of the orbital occupied by the electrons. Due to the shape of the orbitals, an electron in an s-orbital of a given shell penetrates the nucleus more strongly than that in a p-orbital of the same shell.

Thus for a given shell the penetration power (or penetration effect) of an ns electron is greater than that of an np electron (ns > np). The penetration power of an np electron is greater than that of an nd electron (np > nd) which has higher penetration power than an nf electron (nd > nf). Thus the penetration power of an electron in ns, np, nd and nf orbitals of a given n\textsuperscript{th} shell is in the following order:

(The values of 1 for all the orbitals are also given)

\[ \text{Penetration power decreasing} \rightarrow \]

\[ \text{Value of } n : \quad \text{same} \]

\[ \text{Value of } l : \quad 0 \quad 1 \quad 2 \quad 3 \]

\[ \text{Increasing} \rightarrow \]

The above order indicates that s-electrons are more tightly bound with the nucleus than p-electrons which, in turn, are bound more tightly than d-electrons and so on. Due to greater penetration power of s-electron, it screens the nucleus more effectively than a p-electron and a p-electron screens the nucleus more effectively than a d-electron and so on. Thus the order in which an electron in the intervening ns, np, nd and nf orbitals screens the nucleus (i.e. nuclear charge) is as

\[ \text{Screening power decreasing} \rightarrow \]

\[ ns > np > nd > nf \]

An electron present in nth orbital is more effectively screened by the electrons in the (n-1)\textsuperscript{th} orbital while the same electron is more effectively shielded by the other electron present in the same orbital. For example, in Li atom (ls\textsuperscript{2}, 2s\textsuperscript{1}) 2s\textsuperscript{1} electron is more effectively screened by the two electrons present in ls orbital, while in He atom (ls\textsuperscript{2}) one of the two electrons in 1s orbital is not effectively screened by the other electron present in the same orbital i.e. 1s orbital

**Applications of Shielding Effect**

(i) The concept explains several inherent properties of an atom. For example, it explains decrease on ionization potential values down the group.
(ii) This concept also explains *huge decrease* in the value of ionization potential, when we proceed from an inert gas to an alkali metal.

**Calculation of \( a \) and \( Z^* \) by Slater’s Rules**

The rules are:

1. Orbitals are grouped in the following way; (1s) (2s2p) (3s3p) (3d) (4s4p) (4d) (4f) (5s5p) (6s6p)……….. etc.
2. Now select the electron for which the value of \( \sigma \) is to be calculated. For this calculation add up the contributions to \( \sigma \) for the other electrons as stated below:
   
   (i) \( \sigma = 0 \), for \( e \) in question or \( e \) chosen to be calculated (i.e., \( e \) of \( n^{th} \) orbit) or electrons in the higher group of outside the electron chosen (i.e., \( n + 1 \))
   
   (ii) \( \sigma = 0.35 \) per electron for rest of the group electrons.
   
   (iii) \( \sigma = 0.3 \), for a 1s electron screening another 1s electron.
   
   (iv) \( \sigma = 0.85 \) per electron for all electrons in \( (n-1)^{th} \) group.
   
   (v) \( \sigma = 1 \), per electron for all electrons in \( (n-2)^{th} \) or lower groups.

*In case of electron being shielded of \( nd \) or \( nf \), all electrons lying to the left of \( nd \) or \( nf \) group, \( \sigma = 1 \) per electron.*

In summary:

<table>
<thead>
<tr>
<th>Electron group</th>
<th>All higher groups / out side</th>
<th>Same group</th>
<th>Group with ( (n-1) )</th>
<th>Group with ( (n-2) ) or lower</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>0</td>
<td>0.3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ns, np</td>
<td>0</td>
<td>0.35</td>
<td>0.85</td>
<td>1</td>
</tr>
<tr>
<td>nd, nf</td>
<td>0</td>
<td>0.35</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

**Example 1.**

Calculate the effective nuclear charge experienced by the valance shell electron in potassium atom.

The electronic configuration of K atom \((Z = 19)\) is \( ls^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1 \) and magnitude of \( Z^* \) experienced by valance shell i.e. in this case \( 4s \) electron can be calculated as follows

**Step 1:** Orbitals grouping \((ls^2) (2s^22p^6) (3s^23p^6) (4s^1)\)

**Step 2:** Calculation for 4s orbital \((ls^2) (2s^22p^6) (3s^23p^6) (4s^1)\)

\[ \sigma = [(1\times10)+(0.85\times8)+(0.35\times0)] = 10+6.8+0 = 16.8 \]

Therefore \( Z^* = 19-16.8 = 2.2 \)

Similarly for some other atoms as follows

<table>
<thead>
<tr>
<th>Atom</th>
<th>Orbitals grouping</th>
<th>( \sigma )</th>
<th>( Z^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^3 )Li</td>
<td>( 1s^2 2s^1 )</td>
<td>((0.85\times2) + (0.35\times0) = 1.7 )</td>
<td>3-1.7 = 1.3</td>
</tr>
</tbody>
</table>

CHEM0202

P Sasikumar
### Variation of Screening Effect in the Periodic Table

Due to increase of number of inside or intervening electrons, screening constant $\sigma$ as well as shielding effect also getting increases.

<table>
<thead>
<tr>
<th>Elements of group IA</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value of Z</td>
<td>3</td>
<td>11</td>
<td>19</td>
<td>37</td>
<td>55</td>
</tr>
<tr>
<td>Value of $\sigma$</td>
<td>1.7</td>
<td>8.8</td>
<td>16.8</td>
<td>34.8</td>
<td>52.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Elements of 2nd period</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value of Z</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Value of $\sigma$</td>
<td>1.70</td>
<td>2.05</td>
<td>2.40</td>
<td>2.75</td>
<td>3.10</td>
<td>3.45</td>
<td>3.80</td>
<td>4.15</td>
</tr>
</tbody>
</table>

Since number of *intervening electrons increases* both down the group as well as across the period, the magnitude of *screening effect also increases* in the same direction on proceeding down the group and from left to right in a period as given in the above table.

### Variation of Effective Nuclear Charge $Z^*$ in the Periodic Table

**In group:** Down the group, the values of effective nuclear charge remain almost the same (See the table we calculated for alkali metals already, for Li 1.3 and remaining elements of the group 2.2; similarly alkaline earths, for Be 1.85 and remaining elements 2.85)

**In period:** The values of effective nuclear charge increase across the period

When we move across the period the atomic number(i.e.nuclear charge) as well as valence electron increases by one however valence electron cause the effective repulsion equal to 0.35.

Therefore the effective nuclear charge increases by $\text{1-0.35 = 0.65}$ from member to member. i.e.each next atom is greater the effective nuclear charge by 0.65 than the previous atom (refer the below table period 2 and 3).

### Applications of Effective Nuclear Charge:

1. This explains why 4s orbital filled before 3d orbital
Example: for $^{19}$K the electronic configuration is $(1s^2)(2s^22p^6)(3s^23p^6)(4s^1)$, but not $(1s^2)(2s^22p^6)(3s^23p^6)(3d^1)$ This can be explained using the concept of effective nuclear charge.

Consider following two electronic configurations

(i) $1s^2$, $2s^2p^6$, $3s^2p^6d^0$, $4s^1$ (4s orbital is filled before 3d orbitals)
(ii) $1s^2$, $2s^2p^6$, $3s^2p^6d^1$, $4s^0$ (3d orbitals get filled before 4s orbital)

Now let us calculate $Z_{\text{eff}}$ of valence shell for both configurations separately and compare.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$Z_{\text{eff}}$ Calculation for 4s orbital</th>
<th>$Z_{\text{eff}}$ Calculation for 3d orbital</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(1s^2)(2s^22p^6)(3s^23p^6)(4s^1)$</td>
<td>$\sigma = \left[ (1X10)+(0.85X8)+(0.35X0) \right] = 10+6.8+0 = 16.8$</td>
<td>$\sigma = \left[ (1X18)+(0.35X0) \right] = 18+0 = 18$</td>
</tr>
<tr>
<td>$Z_{\text{eff}} = 19-16.8 = 2.2$</td>
<td>$Z_{\text{eff}} = 19-18 = 1$</td>
<td></td>
</tr>
</tbody>
</table>

$Z_{\text{eff}}$ value is lower for 3d electron as compared to that on 4s electron makes it evident that in potassium atom 3d electron is less tightly bound to the nucleus than the 4s electron. Hence the additional electron in potassium atom prefers to enter 4s orbital rather than 3d.

(2) 4s electrons are removed prior to 3d electrons during conversion of 3d transition elements into cations.

Example: Let us consider the configuration of $^{24}$Cr $(1s^2)(2s^22p^6)(3s^23p^6)(3d^4)(4s^2)$, this atom converted to $^{24}$Cr$^{2+}$ and forms following two configurations

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$Z_{\text{eff}}$ Calculation for 3d orbital</th>
<th>$Z_{\text{eff}}$ Calculation for 4s orbital</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(1s^2)(2s^22p^6)(3s^23p^6)(3d^4)(4s^2)$</td>
<td>$\sigma = \left[ (1X18)+(0.35X3)+(0X2) \right] = 19.05$</td>
<td>$\sigma = \left[ (1X10)+(0.85X12)+(0.35X1) \right] = 20.55$</td>
</tr>
<tr>
<td>Therefore $Z_{\text{eff}} = 24-19.05 = 4.95$</td>
<td>Therefore $Z_{\text{eff}} = 24-20.55 = 3.45$</td>
<td></td>
</tr>
</tbody>
</table>

The greater value of $Z_{\text{eff}}$ value for 3d electrons suggest that 3d electrons are more tightly bound to the nucleus rather the 4s electrons. Therefore conversion of Cr atom to Cr$^{2+}$ ion accomplished by releasing the electrons easily from 4s orbital not from 3d.

(3) The increase in order of successive ionisation potentials ($I_1 < I_2 < I_3, \ldots$) of an atom very well explained on the basis of effective nuclear charge concept (explained latter in detail)

(4) Periodic variation of atomic radii in group as well as periods on periodic table cab be explained using $Z_{\text{eff}}$ value.

(5) The size of anion and cation compare with neutral atom can be explained on basis of $Z_{\text{eff}}$ value.

**e.g. (a) Size of the Cation is Smaller than that of its Parent Atom**

Cations are produced when atoms lose electrons ($\text{Na} \rightarrow \text{Na}^+ + e$; $\text{Al} \rightarrow \text{Al}^{3+} + 3e$), but there is no change in number of protons. Hence decrease the magnitude of shielding constant $\sigma$, as a result...
increasing effective nuclear charge $Z'$ of cation, which pulls the electron clouds much closer to the nucleus and reduce the size of cation than parental neutral atom.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Orbitals grouping</th>
<th>$\sigma$</th>
<th>$Z'$</th>
<th>Atomic / ionic radii Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1s$^2$ 2s$^1$</td>
<td>(0.85x2) + (0.35x0) = 1.7</td>
<td>3-1.7 = 1.3</td>
<td>1.22</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>1s$^2$ 2s$^0$</td>
<td>(0.3x1) + 0.3</td>
<td>3-0.3 = 2.7</td>
<td>0.66</td>
</tr>
<tr>
<td>Na</td>
<td>(1s$^2$) (2s$^2$sp$^6$) (3s$^1$)</td>
<td>(1X2)+(0.85X8)+(35X0) = 8.8</td>
<td>11-8.8 = 2.2</td>
<td>1.54</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>(1s$^2$) (2s$^2$sp$^6$) (3s$^3$)</td>
<td>(0.85X2)+(0.35X7) = 4.15</td>
<td>11-4.15=6.85</td>
<td>0.95</td>
</tr>
</tbody>
</table>

the size of various cations in different oxidation states derived from the same element decreases with the increase in their positive oxidation state. E.g. Fe$^{2+}$ (0.76 Å) > Fe$^{3+}$ (0.64 Å) and Pb$^{2+}$ (1.20 Å) > Pb$^{4+}$ (0.84 Å)

Among isoelectronic cations the cation which has highest charge is smallest in size, $r_{Na^+} > r_{Mg^{2+}} > r_{Al^3+}$

(b) Size of the Anion is bigger than that of its Parent Atom

Anions are produced when atom gains/added electrons (F + e → F$^-$; O + 2e → O$^{2-}$), but there is no change in nuber of protons. Hence increase the magnitude of shielding constant $\sigma$, as a result decreasing effective nuclear charge $Z'$ of cation, which pulls the electron cloud of the anion outward away from the nucleus and increase the size of anion than parental neutral atom.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Orbitals grouping</th>
<th>$\sigma$</th>
<th>$Z'$</th>
<th>Atomic / ionic radii Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>(1s$^2$) (2s$^2$sp$^5$)</td>
<td>(0.85x2) + (0.35x6) = 3.8</td>
<td>9-3.8 = 5.2</td>
<td>0.72</td>
</tr>
<tr>
<td>F$^-$</td>
<td>(1s$^2$) (2s$^2$sp$^6$)</td>
<td>(0.85x2) + (0.35x7) = 4.15</td>
<td>9-4.15 = 4.85</td>
<td>1.36</td>
</tr>
<tr>
<td>Cl</td>
<td>(1s$^2$)(2s$^2$2p$^6$)(3s$^2$3p$^5$)</td>
<td>(1X2)+(0.85X8)+(35X6) = 10.9</td>
<td>17-10.9 = 6.1</td>
<td>0.99</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>(1s$^2$)(2s$^2$2p$^6$)(3s$^2$3p$^6$)</td>
<td>(1X2)+(0.85X8)+(35X7) = 11.25</td>
<td>17-11.25=5.75</td>
<td>1.81</td>
</tr>
</tbody>
</table>

the size of various anion in different oxidation states derived from the same element increases with the increase in their negative oxidation state.

Among isoelectronic anions, the anion which has highest charge is largest in size $r_{N^3-} > r_{O^{2-}} > r_{F^-}$

(C) size of isoelectronic atoms and ions
Among isoelectronic cation and anion both, radii decreases with increase in nuclear charge.

<table>
<thead>
<tr>
<th>10 es</th>
<th>N⁻³</th>
<th>O⁻²</th>
<th>F⁻</th>
<th>Na⁺</th>
<th>Mg²⁺</th>
<th>Al³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protons</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>11</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>r (Å)</td>
<td>1.71</td>
<td>1.4</td>
<td>1.35</td>
<td>1.02</td>
<td>0.72</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Periodic Trends in Physical Properties

(1) Size of Atoms and Ions (Atomic and Ionic Radii)

Determination of atomic size is quite difficult since, size of the atom is very small typically in the order of Å unit. Secondly atom does not have a sharply defined boundary due to diffused nature (wave mechanical model) of electron cloud surrounded by a nucleus. Hence there is no practical practical way to determine the size of an individual atom. However, radii of atoms are determined in different combined states and influenced by the nature of neighboring atom:

(i) Covalent / atomic radius
(ii) Van der Waal’s radius
(iii) Ionic or Crystal radius

(i) Covalent / atomic radius (used for non-metals)

*Half of the bond length* (The distance between the nuclei of two bonded atoms) *between two similar covalently bonded atoms is defined as covalent radius.*

**Calculation of covalent radius r(A).**

In case of homonuclear diatomic molecules of A₂ type (e.g. F₂, Cl₂, Br₂ I₂, etc.), the bond length, d(A-A) is given by:

\[
d(A-A) = r(A) + r(A)
\]

\[
d(A-A) = 2 \times r(A)
\]

\[
r(A) = \frac{d(A-A)}{2}
\]

e.g. The Cl—Cl bond length is found 1.988 Å, so covalent radius of chlorine is 1.988/2 = 0.99 Å.

In case of heteronuclear diatomic molecule AB type, bond length, d(A-B) is given by
d(A-B) = r(A) + r(B)

r(A) and r(B) are the covalent radii of atoms A and B respectively. If we know the value of d(A-B) and r(B), the covalent radius of atom A r(A) can be calculated easily.

The single bond covalent radii are additive in nature, i.e., when the covalent radii of atoms in A₂ or AB molecules are added, we get the bond length, d(A-A) or d(A-B). This principle is called the principle of additivity of covalent radii. This principle has been used to calculate the covalent radii of the elements.

e.g. The C—C bond length d(C-C) is experimentally found to be 1.54 Å in diamond, so covalent radius r(C) of carbon is 1.54/2 = 0.77 Å.

The Si—C bond length d(Si-C) is experimentally found to be 1.93 Å in Carborundum, so covalent radius r(Si) of silicon is calculated as follows:

d(Si-C) = r(Si) + r(C) 
or r(Si) = d(Si-C) - r(C) 

= 1.93 - 0.77 = 1.16 Å.

**Characteristics of Covalent Radii**

(i) Single bond covalent radii are additive in nature.

(ii) The values of covalent radii change with the multiplicity of the bonds between the atoms. In case of atoms joined by double or triple covalent bonds, the covalent radius is called double bond covalent radius and triple bond covalent radius respectively. These radii are smaller than the single bond covalent radii due to greater overlapping of orbitals in the formation of double and triple covalent bonds.

C — C (1.54Å), C = C (1.33Å), C ≡ C (1.2Å)  
N — N (1.45Å), N = N (1.25Å), N ≡ N (1.10Å)

Therefore, double and triple bond radii are also defined (half the double bond length and triple bond length), e.g., Double bond radius of C = 1.33/2 = 0.665Å, Triple bond radius of N = 1.10/2 = 0.55Å. The double and triple bond radii of an atom are approximately **0.87 and 0.78 times the single bond radii**, respectively.

**Factors Affecting the Magnitude of Bond Length**

(a) The electronegativity difference of the bonded atoms, A and B. The increase in the amount of ionic character in A-B bond decreases the bond length, d(A-B).

By considering above point the bond distance of heteroatomic molecule rewritten as follows.

D(A-B) = r(A)+r(B)-0.09(Xₐ-Xₐ); Xₐ , Xₐ are the electronegativities of the elements A and B  
e.g. d(N-C) = r(N)+r(C), = (0.75 + 0.77), = 1.52 Å (calculated), this is deviate from experimentally found value 1.47 Å seen in (CH₃)₃N.
But value found using following modified formula have good agreement with experimental value,
\[
\text{D(N-C)} = r(N) + r(C) - 0.09(X_N - X_C) = [(0.75 + 0.77) - 0.09 (3.0 - 2.5)] = 1.475 \, \text{Å} \quad \text{(calculated using modified formula)}
\]

(b) **Hybridisation.** The shape of the molecule determined by hybridisation of orbitals in a molecule and also affect bond length. *Increase* of the percentage of *s-character* in a hybrid orbital, the *bond length decreases*. E.g. increase of the percentage of s-character from ethane (25 %) to acetylene (50 %) via ethylene (33.3 %), C-H and C-C bond lengths decrease in the same sequence.

Utility of Bond Length Determination

1. **Stability of a molecule** can be predicted and understood. 
   \[ \text{bond length} \propto \frac{1}{\text{Stability}} \] 
   A molecule with smaller bond length is more stable than that with large bond length.

2. **Bond order.** A molecule with smaller bond length has higher bond order. Thus the bond length can be used to infer the presence of \( \pi \)-bonding in a molecule. E.g. \( \text{(BF}_4^- \) ion, the B-F bond length has been found to be equal to 1.42 Å, while B-F bond distance found in \( \text{BF}_3 \) molecule is 1.29 Å. We know that in \( \text{(BF}_4^- \) ion four F atoms are linked with B atom by four \( \sigma \)-bonds. Thus the shortening of B-F bond distance in \( \text{BF}_3 \) molecule is due to the presence of \( \pi \)-character in B-F bonds. This character is produced by the donation of lone pair of electrons from the F atoms into the vacant 2p\(_z\) orbital of B atom (p\(\pi\)-p\(\pi\) bonding).

(ii) **Van der Waal’s Radii (Collision Radius)**

*The distance between the nuclei of two non-bonded isolated atoms or the distance between two non-bonded atoms belonging to two adjacent molecules of an element in the solid state is called van der Waals distance while the half of this distance is called van der Waals radius.*

![Illustration of van der Waals radius of Cl atom in two non-bonded Cl atoms](image1)

![Illustration of van der Waals radius of Cl atom in two non-bonded adjacent Cl\(_2\) molecules](image2)
Comparison of van der Waals Radius with Covalent Radius
van der Waals radius of an element is higher than its covalent radius. The formation of covalent bond, atoms have to overlap (electron cloud) each other while in van der Waals forces the atoms/molecules simply come closer to each other and do not enter into overlapping (No bond formation) as illustrated in following fig.

(iii) Ionic Radius

The distance between the nucleus of an ion and the point where the nucleus exerts its influence on the electron cloud. This is calculated using internuclear distance between positive and negative ions in an ionic crystal.

Properties of Ionic Radii.

(i) The ionic radius of a particular ion is of more or less constant magnitude.
(ii) Ionic radii have an additive character.
\[ r(C^+) + r(A^-) = d(C^+ - A^-) \]

Pauling’s Univalent Method

This method considers isoelectronic cation and anion (NaF, Na\(^+\) & F\(^-\), 10 es.; KCl, K\(^+\) & Cl\(^-\), 18 es.; RbBr, Rb\(^+\), Br\(^-\), 36es and CsI, Cs\(^+\), I\(^-\), 54 es) ). Noble gas configuration

Based on following two assumption Pauling calculated the ionic radii.

(a) It is assumed that both anions and cations are contact with each other and the sum of their radii will be equal to the inter-nuclear (inter-ionic) distance between them.
\[ r(C^+) + r(A^-) = d(C^+ - A^-) \]

(b) For a given noble gas configuration, the radius of an ion is inversely proportional to its effective nuclear charge, i.e.
\[ r(C^+) \propto \frac{1}{Z_{eff} \ of \ C^+} \quad and \quad r(A^-) \propto \frac{1}{Z_{eff} \ of \ A^-} \]
combining relations gives
\[ \frac{r(C^+)}{r(A^-)} = \frac{Z_{eff} \ of \ A^-}{Z_{eff} \ of \ C^+} \]
Combinations of above equations may be used to deduce the value of \( r(C^+) \) and \( r(A^-) \), if the value of 
\( d(C^+ - A^-) \) is provided / known.

Example: \( d(K^+ - Cl^-) \) is found to be 3.14 Å, find the ionic radii of \( K^+ \) and \( Cl^- \)

Given \( r(K^+) + r(Cl^-) = d(K^+ - Cl^-) = 3.14 \text{ Å} \). Using slater rule we may calculate \( \sigma \) and subsequently the \( Z_{eff} \) for both \( K^+ \) and \( Cl^- \).

<table>
<thead>
<tr>
<th>ion</th>
<th>Slater group config.</th>
<th>( \sigma )</th>
<th>( Z_{eff} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K^+ )</td>
<td>((ls^2)(2s^22p^6)(3s^23p^6))</td>
<td>((1X2)+(0.85X8)+(0.35X7) = 11.25)</td>
<td>( 19-11.25 = 7.75 )</td>
</tr>
<tr>
<td>( Cl^- )</td>
<td>((ls^2)(2s^22p^6)(3s^23p^6))</td>
<td>((1X2)+(0.85X8)+(0.35X7) = 11.25)</td>
<td>( 17-11.25 = 5.75 )</td>
</tr>
</tbody>
</table>

\[
\frac{r(K^+)}{r(Cl^-)} = \frac{Z_{eff} \text{ of } Cl^-}{Z_{eff} \text{ of } K^+} = \frac{5.75}{7.75} = 0.74 \rightarrow (i)
\]

\( r(K^+) + r(Cl^-) = d(K^+ - Cl^-) \rightarrow (ii) \)

\( r(Cl^-) = d(K^+ - Cl^-) - r(K^+) \rightarrow (iii) \)

\( r(Cl^-) = d(K^+ - Cl^-) - 0.74r(Cl^-) \) [sub the value from (i)]

\( 1.74r(Cl^-) = 3.14 \)

\( \therefore r(Cl^-) = 1.8 \text{ Å} \)

Substitute \( r(Cl^-) \) in to (iii)

\( \therefore r(K^+) = 3.14 - 1.8 = 1.34 \text{ Å} \)

These values are good agreement with experimentally found values.

**Periodic Trends / Variation of Atomic and Ionic Radii**

(a) **In Period:** As we move across the period from left to right of the periodic table number of orbital remains same, however \( Z_{eff} \) increases as calculated by Slater's rules. The increased \( Z_{eff} \) pulls the electron cloud towards the nucleus and thereby reduce / decrease the size of the atoms and ions from left to right. In otherwords in going from left to right in a period, the atomic and ionic radii decrease with the increase of atomic number.

<table>
<thead>
<tr>
<th>Elements of 2\textsuperscript{nd} Period</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Z_{eff} )</td>
<td>1.30</td>
<td>1.95</td>
<td>2.60</td>
<td>3.15</td>
<td>3.90</td>
<td>4.55</td>
<td>5.20</td>
<td>5.85</td>
</tr>
<tr>
<td>Atomic (covalent) radius Å</td>
<td>1.23</td>
<td>0.90</td>
<td>0.82</td>
<td>0.77</td>
<td>0.75</td>
<td>0.73</td>
<td>0.72</td>
<td>0.71</td>
</tr>
<tr>
<td>Ionic radius Å (iso electronic)</td>
<td>0.60</td>
<td>0.31</td>
<td>0.20</td>
<td>0.15</td>
<td>0.11</td>
<td>0.09</td>
<td>0.07</td>
<td>--</td>
</tr>
<tr>
<td>( Li^+ )</td>
<td>( Be^{2+} )</td>
<td>( B^{3+} )</td>
<td>( C^{4+} )</td>
<td>( N^{5+} )</td>
<td>( O^{6+} )</td>
<td>( F^{7+} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) **In a group:** As going down a group the atomic and ionic radii both increase with the increase of atomic number.
Magnitude of $Z_{\text{eff}}$ of valence electron remains same except first element of every group on moving down the group (refere as discussed previously). Hence using the concept of $Z_{\text{eff}}$ one cannot explain the increase in the atomic or ionic radii of the elements down the group. However, the other factors such as number of shells or principal quantum number ($n$) can be used to explain the increase in atomic ionic radii. As the number of shells or principal quantum number ($n$) increases down the group the distance between nucleus and outer-most shell electrons get increase and their by increase the atomic and ionic radii. For example principle quantum number for Li atom is 2 and Cs is 6 hence size of the Cs is bigger than Li. In essence it is due to the progressive addition of a new shell (or the increase in the number of shells) that the atomic or ionic radii increase as move from top to bottom in a group.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$Z^*$</th>
<th>Electronic Configuration</th>
<th>Principle quantum number ($n$)</th>
<th>Atomic radii Å</th>
<th>Ionic ($M^+$) radii Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>3</td>
<td>1,3</td>
<td>2</td>
<td>1.3</td>
<td>0.60</td>
</tr>
<tr>
<td>Na</td>
<td>11</td>
<td>2,2,8,1</td>
<td>3</td>
<td>1.54</td>
<td>0.95</td>
</tr>
<tr>
<td>K</td>
<td>19</td>
<td>2,2,8,1,1</td>
<td>4</td>
<td>2.03</td>
<td>1.33</td>
</tr>
<tr>
<td>Rb</td>
<td>37</td>
<td>2,2,8,18,8,1</td>
<td>5</td>
<td>2.16</td>
<td>1.48</td>
</tr>
<tr>
<td>Cs</td>
<td>55</td>
<td>2,2,8,18,18,8,1</td>
<td>6</td>
<td>2.35</td>
<td>1.60</td>
</tr>
</tbody>
</table>

Exceptions

At several points in the periodic table the above trends are not followed.

(a) Radii of Al and Ga are similar (1.25 Å). it is due to presence of ten transition elements between Al and Ga. In transition elements (n-1)d orbitals are filled. The screening power $\sigma$ of d orbitals is very low (as seen already screening power $s>p>d>f$). Thus $Z_{\text{eff}}$ increases on outer shell electron on Ga and reducing its size. This is called d-orbital contraction.

(b) Similiarly, the atomic radii of 3rd transition series elements are almost equal to 2nd transition series elements due to lanthanide contraction. (The least screening power $\sigma$ of f orbitals).

(c) Variation of radii among transition series is small due to filling of electrons in inner orbitals, (n-1)d.
(d) Change in the radii of lanthanides is very small. It is due to the fact that electrons are filled in deep seated \((n - 2)f\) orbitals and \(f\) orbitals are least screening.

\[\begin{align*}
\text{Ce (1.65) } & \cdots \cdots \text{ Ga (1.61) } \cdots \cdots \text{ Lu (1.56)}; \\
\text{(Diff.} = 1.65 - 1.56 = 0.09\text{Å)}
\end{align*}\]

(2) Ionization Energy (IE) or Ionization Potential (IP) or Ionization Enthalpy (IE): is an atomic property and shown by the atoms. This property gives an idea of the tendency of the elements to lose the outer-most shell electron to form a cation. Several other properties of elements can be explained using IE of an element, such as redox power (reducing), metallic (or electropositive) character etc.

*The amount of energy needed to remove an outer most shell / valence shell electron (loosly bound compare to inner shell electron) from a free gaseous atom is known as “Ionization energy”.*

\[M(g) + \text{Energy} \rightarrow M(g)^+ + e\]

As removal of an electron is required the energy, the process is called *endothermic* process. If only one electron is removed from the neutral gaseous atom, the energy needed is called “first IE” and denoted as \(\Delta H\) or +I\(_1\) (+ sign gives the impression of absorption of energy). If the electron is further removed from gaseous univalent \(M(g)^+\), it is called “second IE” so on (successive / higher IE) and denoted as +I\(_2\), so on.

\[\begin{align*}
M(g) + I_1 & \rightarrow M(g)^+ + e \\
M(g)^+ + I_2 & \rightarrow M(g)^{2+} + e \\
M(g)^{2+} + I_3 & \rightarrow M(g)^{3+} + e \\
M(g) + (I_1 + I_2 + I_3) & \rightarrow M(g)^{3+} + 3e
\end{align*}\]

Ionization energy is determined experimentally, either from the spectra of the gaseous species or by discharge tube experiment technique. For all elements, successive IE increase in the order of:

\[I_1 < I_2 < I_3 < I_4 \ldots \text{ and so on. This trend can be explained using the concept of } Z_{\text{eff}}.\]

The cations are formed by removing the electrons from the atom/cation one by one

\[M(g) \rightarrow M(g)^+ \rightarrow M(g)^{2+} \rightarrow M(g)^{3+} \rightarrow M(g)^{4+} \ldots \rightarrow M(g)^{n+}\]

We were seen that cation or successive cation has lesser number of electrons than its parental atom or cation, but number of protons in the nucleus remains same as parental atom or cation. Hence the magnitude of \(Z_{\text{eff}}\) increases from \(M(g)\) to \(M(g)^{n+}\) and magnitude of the force of attraction between the nucleus and the valence shell electron cloud also increases (recall the periodicity of \(Z_{\text{eff}}\)). Therefore more energy required to remove an electron from valence shell, hence IE as follows, \(I_1 < I_2 < I_3 < I_4 \ldots \).
Atom/cation: 

\[ \text{M} (g) \rightarrow \text{M} (g)^+ \rightarrow \text{M} (g)^{2+} \rightarrow \text{M} (g)^{3+} \rightarrow \text{M} (g)^{4+} \cdots \rightarrow \text{M} (g)^{n+} \]

Factors Affecting the Magnitude of Ionisation Potential:

(i) **Effective nuclear charge** \((Z_{\text{eff}})\): Increase the magnitude of \(Z_{\text{eff}}\), greater is the force of attraction exerted by the nucleus on the valence electrons. Therefore, high energy required to overcome the force of attraction exerted by the nucleus on the valence shell electrons. In other words, greater the magnitude of \(Z_{\text{eff}}\), higher is the amount of energy (i.e. ionisation potential) needed to remove the valence shell electron. \(Z_{\text{eff}} \propto \text{IE}\)
Elements of 2nd Period

<table>
<thead>
<tr>
<th>Element</th>
<th>Z_{eff}</th>
<th>I_1 (KJ. mole^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1.30</td>
<td>520.3</td>
</tr>
<tr>
<td>Be</td>
<td>1.95</td>
<td>899.5</td>
</tr>
<tr>
<td>B</td>
<td>2.60</td>
<td>800.6</td>
</tr>
<tr>
<td>C</td>
<td>3.15</td>
<td>1086.4</td>
</tr>
<tr>
<td>N</td>
<td>3.90</td>
<td>1402.3</td>
</tr>
<tr>
<td>O</td>
<td>4.55</td>
<td>1314</td>
</tr>
<tr>
<td>F</td>
<td>5.20</td>
<td>1681</td>
</tr>
<tr>
<td>Ne</td>
<td>5.85</td>
<td>2080.7</td>
</tr>
</tbody>
</table>

- **Increasing**

(ii) **Atomic radii (r):** Increase the magnitude of atomic radii of an atom, i.e. the valence shell electrons are far from nucleus and hence Z_{eff} of valence shell electron get decreasing. Thus it is very easy to remove an electron from valence shell, *i.e. higher is the value of r of an atom, lower will be its ionisation energy.*

\[ r \propto \frac{1}{IE} \]

This fact has been used to explain the variation of ionisation potential values of the elements of a group and a period of the periodic table.

(iii) **Principal quantum number (n):** Greater is the value of n for the valence shell electron of an atom, farther away this electron will be from the nucleus and hence lesser will be the force of attraction exerted by the nucleus on it. This means that lesser amount of energy will be required to remove the valence-shell electron. Thus with the increase of the value of n of the valence-shell electron, ionisation potential decreases and vice versa.

Thus with the **increase** of the principal quantum number (n) of the orbital from which the electron is to be removed, the magnitude of ionisation potential decreases.

\[ n \propto \frac{1}{IE} \]

This fact has been used to explain the variation of ionisation potential values of the elements of a group of the periodic table, Successive ionization potentials of an element, Ionisation potentials of inert gases as compared to those of alkali metals.

(iv) **Shielding of Screening effect (σ):** 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 ionisation potential to remove the valence-shell electron. *Thus with the increase of shielding effect, ionisation potential decreases.*

\[ σ \propto \frac{1}{IE} \]

This factor can be used to explain the variation of ionisation potential of the elements of a given group of the periodic table.

(v) **Half-filled and completely filled orbitals:** comparatively more stable and hence more energy is needed to remove an electron from such orbitals.
This factor can be used to explain some irregularities of ionisation potential of the elements of the periodic table. E.g. In 2nd period Be (Z = 4) has higher ionisation potential than B (Z = 5) and N (Z = 7) has higher value of ionisation potential than O (Z = 8). Similarly in other periods of elements also.

(vi) Nature of orbitals: The relative order of energy of s, p, d and f orbitals of a given nth shell is as: ns < np < nd < nf. Thus the orbital move farther from the nucleus and valence electrons are loosely held compare to inner shell electrons. Therefore the amount of energy required to remove an electron from nf-orbital is minimum compare to remove an electron from s-orbital.

the ionisation potentials of an electron in s, p, d and f-orbitals are as the following order : 
ns > np > nd > nf

This factor can be used to explain the Successive ionisation potentials of an element. E.g. 1st (I1) and 2nd (I2)ionisation potentials of B atom (ls2, 2s2 2p1) are: I1= 800.6KJ.mole⁻¹, I2 = 2427.0 KJ.mole⁻¹ and can be represented by the following equations :

\[ B (1s^2, 2s^2 2p^1) \xrightarrow{I_1} B^- (1s^2, 2s^2) \]

\[ B^- (1s^2, 2s^2) \xrightarrow{I_2} B^{2+} (1s^2, 2s^1) \]

Removal of 1st electrons is from 2P orbital, however removal of 2nd electron is from 2S orbital which required much more energy (both electrons are removed from same shell i.e. n = 2).

This factor can also be utilized to explain 1st ionisation potentials of two different elements as follows,

\[ Be (1s^2, 2s^2) \xrightarrow{I_1} Be^+ (1s^2, 2s^1) \]

\[ B (1s^2, 2s^2 2p^1) \xrightarrow{I_2} B^+ (1s^2, 2s^2) \]

Ionisation potential of Be is higher than that of B, since to remove an electron from a 2s-orbital of Be requires more energy than to remove the same from a 2p-orbital of B

**Variation of Ionisation Potential in a Period and a Group:**

(a) In group: Down the group, the values of the ionisation potential getting decreases.

Down the group, the values of effective nuclear charge remain almost the same. Hence using \( Z_{\text{eff}} \) we can’t explain the variation of IE.

Therefore variation of IE can be explained on the basis of some other concept as discussed above such as of atomic size (r), nature of orbital (the value of principal quantum number (n)) and magnitude of screening constant (\( \sigma \)).

<table>
<thead>
<tr>
<th>Atom</th>
<th>( Z^* )</th>
<th>Electronic Config.</th>
<th>n</th>
<th>rÅ</th>
<th>( \sigma )</th>
<th>IE, KJ.mole⁻¹</th>
</tr>
</thead>
</table>

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We were discussed that, all these \((r, n, \sigma)\) quantities increase on moving down a group and are inversely proportional to \(\text{IE}\). i.e. down the group ionisation potential decreases. E.g. the variation of ionisation potential values for the elements of group 1 elements shown in table,

**We were discussed that, all these \((r, n, \sigma)\) quantities increase on moving down a group and are inversely proportional to \(\text{IE}\). i.e. down the group ionisation potential decreases. E.g. the variation of ionisation potential values for the elements of group 1 elements shown in table,**

(b) In period: *In general, as we move from left to right in a period, the ionisation potential of the elements increases due to the successive increase in the nuclear charge (i.e. atomic number) and decreases in atomic size. However there are certain elements which show irregular trends.*

On passing period 2 elements from Li to Ne. We observed already that \(Z_{\text{eff}}\) increases and atomic size \((r)\) getting decreases. Therefore the ionization energy getting increases across the period from left to right. i.e. \(Z_{\text{eff}} \propto \text{IE} \) and \(r \propto \frac{1}{\text{IE}}\).

<table>
<thead>
<tr>
<th>Elements of 2nd Period</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Z_{\text{eff}})</td>
<td>1.30</td>
<td>1.95</td>
<td>2.60</td>
<td>3.15</td>
<td>3.90</td>
<td>4.55</td>
<td>5.20</td>
<td>5.85</td>
</tr>
<tr>
<td>Atomic Radii (Å)</td>
<td>1.23</td>
<td>0.90</td>
<td>0.82</td>
<td>0.77</td>
<td>0.75</td>
<td>0.73</td>
<td>0.72</td>
<td>0.71</td>
</tr>
<tr>
<td>(I_1) (KJ. mole(^{-1}))</td>
<td>520.3</td>
<td>899.5</td>
<td>800.6</td>
<td>1086.4</td>
<td>1402.3</td>
<td>1314</td>
<td>1681</td>
<td>2080.7</td>
</tr>
</tbody>
</table>

However Be and N show irregular trends as is evident from the fact that, although Be and N have smaller effective nuclear charges than their next elements namely B and O respectively (Be = 1.95, B = 2.60, N = 3.90, O = 4.55), these elements have higher ionization potential values than B and O respectively. These higher values can be explained as follows.

In case of Be \((ls^2, 2s^2)\) it is more difficult to remove an electron from the completely filled 2s-orbital while in case of B\((ls^2, 2s^22p^1)\) it easier to remove the same from a partially-filled 2p-orbital. Since to remove an electron from a 2s orbital of Be atom requires more energy than to remove the same from a 2p orbital of B atom, ionisation potential of Be is higher than that of B.

In case of N\((ls^2, 2s^2, 2p^3)\) it is more difficult to remove an electron from the half-filled 2p-orbital while in case of O\((ls^2, 2s^22p^4)\) it is easier to remove the same from a partially-filled 2p-orbital. Thus the ionization potential of N is higher than that of O.

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(3) **Electron Affinity (EA) or Electron Gain Enthalpy (Δ_{eg}H):** is an atomic property and shown by the atoms. This property gives an idea of the tendency of the elements to accept an electron to its outer-most shell to form an anion. Several other properties of elements can be explained using EA of an element, such as redox power (oxidizine), non-metallic (or electronegative) character etc.

*The amount of energy released when an electrons is added to an isolated neutral atom is known as “electron affinity”.*

\[ \text{M}_\text{(g)} + \text{e}_\text{(g)} \rightarrow \text{M}_\text{(g)}^- + \text{Energy Released} = -\text{EA}_1, \text{ first electron affinity, negative (minus) sign represents the release of energy / exothermic} \]

**Second Electron Affinity**

Similar to first electron affinity (EA₁) defined above, second electron affinity (EA₂) of some group 16 elements. Second electron affinity of an element can be defined as the amount of energy required to add one more electron to its mono-negative anion, M\(_{(g)}^- \) to convert it into di-negative anion, M\(_{(g)}^{2-} \). Thus

\[ \text{M}_\text{(g)}^- + \text{e}_\text{(g)} + \text{Energy supplied} = + \text{EA}_2 \rightarrow \text{M}_\text{(g)}^{2-} \]

In the process, *energy is supplied* rather releasing like EA₁ process. This is due to adding one more electron to M\(_{(g)}^- \) anion creates electrostatic repulsion between the extra electron being added and negative charge on M\(_{(g)}^- \) anion. To overcome this electrostatic repulsion energy being supplied. Hence it is very clear that, the process of \( \text{EA}_2 \) is endothermic (i.e. energy absorbed or supplied) and represented by positive sign.

Since EA₂ > EA₁, there is net absorption of energy in the formation of a dinegative ion, M\(_{(g)}^{2-} \) from the neutral M\(_{(g)} \) atom and the amount of energy absorbed in this process is equal E₂-E₁

\[ \text{M}_\text{(g)} + 2\text{e}_\text{(g)} + \text{Energy absorbed} = + \text{EA}_2 - \text{EA}_1 \rightarrow \text{M}_\text{(g)}^{2-} \]

**e.g.** formation of O\(_{(g)}^{2-} \) from O\(_{(g)} \) shown by the following equations:

\[ \text{O}_\text{(g)} + \text{e}_\text{(g)} \rightarrow \text{O}_\text{(g)}^- + \text{EA}_1 = -141 \text{ KJ.mole}^{-1} \text{ negative sign indicates the exothermic process} \]

\[ \text{O}_\text{(g)}^- + \text{e}_\text{(g)} + \text{EA}_2 = + 921 \text{ KJ.mole}^{-1} \text{ positive sign indicates the endothermic process} \rightarrow \text{O}_\text{(g)}^{2-} \]

On adding:

\[ \text{O}_\text{(g)} + 2\text{e}_\text{(g)} + \text{Energy} = + 921 - 141 = + 780 \text{ KJ.mole}^{-1} \rightarrow \text{O}_\text{(g)}^{2-} \]

Thus the total electron affinity for two electrons for oxygen atom = + 780 KJ.mole\(^{-1} \).
Factors Affecting the Magnitude of Electron Affinity

(i) Effective nuclear charge (Z_{eff}): Increase the magnitude of Z_{eff}, greater is the force of attraction exerted by the nucleus the additional electron towards valence shell of the atom and hence higher the amount of energy released upon the addition of an extra electron to neutral atom. Thus the atoms with higher effective nuclear charge have higher electron affinities. Z_{eff} \propto IE

(ii) Atomic radius (r): Larger the atomic radius, lesser the tendency of the atom to attract the additional electron towards itself, due to lesser the force of attraction exerted by the nucleus on the extra electron being added to the valence-shell of the atom and hence lesser the amount of energy released when the extra electron is added to the atom to form an anion. Thus smaller atoms have higher electron affinities. r \propto \frac{1}{EA}

(iii) Electronic configuration. the magnitude of electron affinity of an element can be explained by the following examples:

(a) Electron affinity values of the elements having completely filled valence-shell e.g. ns orbital of group 2 elements and ns^2p^6 noble gases (group 18) are completely filled. Addition of extra electron to this ns and ns^2p^6 orbitals are not possible, hence the elements of group 2 and 18 have practically zero electron affinity.

(b) Electron affinity values of N and P. The valence-shell electronic configuration of N and P are N = 2s^2p^3 ; P = 3s^2p^3. The 2p and 3p orbitals in N and P are half-filled and are quite stable. Thus the addition of any extra electron to 2p and 3p orbitals is not possible. Consequently N and P have very low electron affinity values (N = +20.1 KJ.mole^{-1}, P = -74 KJ.mole^{-1}).

(c) Electron affinity values of halogens. The valence-shell configuration of halogen atoms (ns^2p^5) has an one electron less to attaining the stable noble gas electronic configuration (ns^2p^6). Thus halogen atoms have a strong tendency to accept an extra electron and the addition an extra electron makes the configuration of the resulted halide ion similar to that of the noble gas. Consequently the halogen atoms have very high values of electron affinity.

Variation of EA in the Periodic Table
It is difficult to make general views due to the following reasons

(i) The electron affinities of only a very few atoms are known with certainty.

(ii) The elements completely filled orbitals such as group 2 and 18 elements have practically zero electron affinity values, and similarly half filled orbital of group 15 elements have very small values.

(iii) The elements of 2nd period of the periodic table do not follow the general trend of decrease of electron affinity values on moving from top to bottom in a group.
Still the general trend can be discussed certain extent as follows.
(a) **In a group:** EA depends on atomic radius \((r)\). As we have seen \(r \propto \frac{1}{EA}\) i.e. smaller the radius of the atom larger the EA and vice versa.

Atomic **radius increases** down the group from top to bottom. Hence EA **decreases in group from top to bottom**.

(b) **In a period:** Atomic **radius decreases** from left to right of the period. Hence EA **increases in period from left to right of the period**.

![Diagram showing EA and radius trends](image)

**Applications of Ionisation Potential and Electron Affinity**

1. **Tendency of elements to form cations and anions.** We were seen that greater the value of ionisation potential of an element, lower its tendency to lose the electron and hence to form cation. Thus the elements with low values of ionisation potential (e.g. alkali metals and alkaline earth metals) have a strong tendency to lose their outermost shell electron and form cations quite easily.

   The elements having high values IE (e.g. halogens) are not able to lose the electron and hence have no tendency to form cations.

   Similarly we were seen the greater the value of electron affinity of an element, greater its tendency to accept the electrons and hence to form anions. Thus the elements with high electron affinity values (e.g. halogens) have a strong tendency to accept an electron and hence form an anion quite easily while the elements with low electron affinity values (e.g. alkali metals and alkaline earth metals) are not able to accept an electron and hence have no tendency to form an anion.

![Diagram showing EA and ionisation potential trends](image)

2. **Reducing and oxidising power of elements.** A reducing substance (atom, ion or molecule) is that which loses one or more electrons and is thereby oxidized to a higher valency state. For example if
an element in its gaseous state, \( \text{M}_{(g)} \) loses one electron and is converted into \( \text{M}^+_{(g)} \) cation, the element \( \text{M}_{(g)} \) is said to be acting as a reducing agent.

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

(lower oxidation state) Reducing agent \hspace{1cm} Higher oxidation state

A substance having greater tendency to lose the electrons, act as strong reducing agent. We know very well that lower the value of ionisation potential of an element, greater its tendency to lose the electrons. Therefore a element have low values of ionisation potential are strong reducing agents.

Trend of ionisation potential of the elements decreases down a group and increases from left to right across the period. By correlating this property with the reducing power of the elements gives an idea that reducing power of an elements increases in going down a group and decreases as we move from left to right in a period.

Thus the elements lying at the extreme left of the periodic table have low values of ionisation potential are strong reducing agent, while those lying at the extreme right of the periodic table have high values of ionisation potential are weak reducing agents.

Simillarly one may understand the oxidising power (reverse the case of reducing agent) of an element in its gaseous state is determined by its tendency to accept the electrons. Greater its tendency to accept the electrons, greater its oxidising power. Again it is known that higher the value of electron affinity of an element in the gaseous state, greater its tendency to accept the electrons. Thus the elements (in the gaseous state) which have high electron affinity values are strong oxidising agents

In essence electron affinity of the elements decreases on down the group and increases from Left to right in a period, the oxidising power of the elements decreases on descending a group and increases from left to right in a period.

3. Metallic (electropositive or basic) and non-metallic (electronegative) character of elements can also be explained based of IE and EA.
Metallic or electropositive character of elements

Non-metallic or electronegative character of elements

(4) Electronegativity (EN): The relative tendency of an atom in a molecule (differs from electron affinity, it is defined for single atom in gaseous state) to attract shared bond pair electrons towards itself is called electronegativity.

Pauling noticed that, the dipole moment of HF (1.91) is quite greater than HCl (1.03). This shows that polarity in HF bond is larger than HCl bond (dipole moment, $\mu = qr$, q = charge at either end and r = bond length). That is F has higher tendency to attract bond pair electrons than Cl.

Note: electron affinity is atomic properties and tendency of an isolated gaseous atom to attract the electrons. Where as electronegativity represents the tendency of a bonded atoms in a molecule, and one of the atom attracts the bonding pair electron much better than another.

**Measurement of Electronegativity**

Number of arbitrary (no unit and with respect to some non-measurable standard value) scales are devised for measurement of electronegativity. These values are obtained based on several available experimental data like bond energy, dipole moment, ionisation potential and electron affinity. There are several scales are available to express the EN see table.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Method of Calculation or description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pauling</td>
<td>Bond energies</td>
</tr>
<tr>
<td>Mulliken</td>
<td>Average of EA and IE</td>
</tr>
<tr>
<td>Allred and Rochow</td>
<td>Electrostatic attraction $\alpha \frac{Z_{eff}}{r^2}$</td>
</tr>
<tr>
<td>Sanderson</td>
<td>Electron densities of atoms</td>
</tr>
<tr>
<td>Pearson</td>
<td>Average of EA and IE</td>
</tr>
<tr>
<td>Allen</td>
<td>Average energy of valence shell electron, configuration energy</td>
</tr>
<tr>
<td>Jaffé</td>
<td>Orbital electronegativities</td>
</tr>
</tbody>
</table>

However we may discuss more commonly used scales (Highlighted yellow) as below:

(i) **Pauling’s Electronegativity Scale, American Scientist (1932):** This scale is based on an empirical relation between the bond energy and the electronegativities of bonded atoms. He assigned arbitrarily a value of 4.0 to fluorine, the element considered to have the greatest ability to attract electrons.

Consider a bond A-B between two dissimilar atoms A and B of a molecule AB. Let the bond energies of corresponding bonds be represented as $E_{A-A}$, $E_{B-B}$ and $E_{A-B}$ respectively. It may be seen that the $E_{A-B}$ is almost higher than the geometric mean of the $E_{A-A}$, $E_{B-B}$ of A-A and B-B bonds i.e.,

$$E_{A-B} > \sqrt{(E_{A-A})(E_{B-B})}$$

The difference ($\Delta$) between $E_{A-B}$ and $\sqrt{(E_{A-A})(E_{B-B})}$ is related to the difference in the electronegativities (ionic-resonance energy) of A and B according to the following equation:
\[ \Delta_{A-B} = E_{A-B} - \sqrt{(E_{A-A})(E_{B-B})} \] (1) this is valid only electronegativities of A, B and C are in the order: \( \chi_A > \chi_B > \chi_C \)

Value of \( \Delta_{A-B} \) is **not an additive** property, i.e. Consider three covalent bonds viz. A-B, B-C and C-A, then the sum of \( \Delta A-B \) and \( \Delta B-C \) is not equal to \( \Delta C-A \) which means that: \( \Delta A-B + \Delta B-C \neq \Delta C-A \) (2)

However \( \sqrt{\Delta_{A-B}} \) is **nearly an additive** property, \( \sqrt{\Delta_{A-B}} + \sqrt{\Delta B-C} \approx \sqrt{\Delta C-A} \) (3)

\[ \sqrt{\Delta_{A-B}} \] Amount ionic character in A-B bond
\[ \chi_A - \chi_B \] Amount ionic character in A-B bond
\[ \therefore \sqrt{\Delta_{A-B}} \chi_A - \chi_B \]

\[ \chi_A - \chi_B = K \sqrt{\Delta_{A-B}} \] substitute is value in to equaltion (1)

\[ \therefore \chi_A - \chi_B = K \left[ E_{A-B} - \sqrt{(E_{A-A})(E_{B-B})} \right]^{\frac{1}{2}} \]

The value of the constant, K has been found to be equal to 0.208. This is comes from the conversion of experimental values of \( E_{A-B} \) measured in Kcals.mole\(^{-1}\) into eV

\[ \therefore \chi_A - \chi_B = 0.208 \left[ E_{A-B} - \sqrt{(E_{A-A})(E_{B-B})} \right]^{\frac{1}{2}} \]

This equation gives difference in electronegativity values between two bonded atoms, and utilized the arbitrarily electronegativity of hydrogen to be 2.1 and fluorine is 4, Pauling calculated electronegativities of other elements with the help of above equation. These values are arbitrary and only relative.

**Disadvantage of Pauling scale**

The disadvantage of Pauling’s scale is that bond energies are not known with any degree of accuracy for many solid elements.

e.g. Calculate the electronegativity of chlorine from the following data. \( E_{H-H} = 104 \) K cal mol\(^{-1}\); \( E_{Cl-Cl} = 36 \) K cal mol\(^{-1}\), \( E_{H-Cl} = 134 \) K cal mol\(^{-1}\)

According to Pauling’s equation

\[ X_{Cl} - \chi_H = 0.208 \left[ E_{Cl-Cl} - \sqrt{(E_{H-H})(E_{Cl-Cl})} \right]^{\frac{1}{2}} \]
\( \chi_{\text{Cl}} - 2.1 = 0.208 \times (134 -61.15)^{1/2} = 0.208 \times 8.53 \)
\( \chi_{\text{Cl}} = 1.77 \)
\( \chi_{\text{Cl}} = 1.77 + 2.1 = 3.87 \)

(ii) **Mulliken's Electronegativity Scale (1934):** He suggested that the electronegativity is related to its IE and EA. An atom having a high value of ionisation potential (i.e. small tendency to lose its valence-shell electron) and a high value of electron affinity (i.e. having a great tendency to attract an electron) has a high value of electronegativity.

Mulliken considers the formation of a covalent bond between two atoms A and B as follows. Suppose:

- \( \chi_A \) and \( \chi_B \) = Electronegativities of atoms A and B
- \( (\text{IE})_A \) and \( (\text{IE})_B \) = Ionisation potentials of atoms A and B
- \( (\text{EA})_A \) and \( (\text{EA})_B \) = Electron affinities of atoms A and B

According to Mulliken:

(a) If \( \chi_A > \chi_B \), then \( A^+B^- \) type of ionic compound can be obtained and its formation may takes place through the following steps;

Step (i) \( B - e^- \rightarrow \text{Energy supplied } = (\text{IE})_B \rightarrow B^+ \)
Step (ii) \( A + e^- \rightarrow A^- \rightarrow \text{Energy released } = (\text{EA})_A \)

\[ \text{On adding: } B + A + \text{Energy supplied } = (\text{IE})_B + (\text{EA})_A \rightarrow A^+B^- \]

\( \therefore \) Energy change in the formation of \( A^+B^- \) structure = \( (\text{IE})_B - (\text{EA})_A \)

(b) If \( \chi_B > \chi_A \), then \( A^+B^- \) type of ionic compound can be obtained and the energy change in the formation of \( A^+B^- \) structure = \( (\text{IE})_A - (\text{EA})_B \)

(c) If \( \chi_A = \chi_B \), then \( AB \) type of covalent compound can be obtained, other way both \( A^+B^- = A^+B^- \) i.e.

\( (\text{IE})_B - (\text{EA})_A = (\text{IE})_A - (\text{EA})_B \)

\( (\text{IE})_A + (\text{EA})_A = (\text{IE})_B + (\text{EA})_B \) ---- (i)

Based on relation (i) Mulliken suggested that electronegativity of an atom can be taken to be equal to the average of its IE and EA values,

\[ \chi_A = \frac{(\text{IE})_A + (\text{EA})_A}{2} \] ---- (ii)

Mulliken used IE and IA values measured in eV and values were found to be **2.8 times higher than Pauling values**. The values of ionisation energy and electron affinity are measured in kJ mol\(^{-1}\) and 1eV =96.48 kJ mol\(^{-1}\). Therefore the commonly accepted Pauling values are more nearly obtained by...
\[ \chi_A = \frac{(IE)_A + (EA)_A}{2 \times 2.8 \times 96.8} = \frac{(IE)_A + (EA)_A}{540} \] ----- (iii)

e.g.

Calculate the electronegativity values of fluorine and chlorine on Mulliken’s scale, given that

\( (\text{Ionisation potential})_F = 17.4 \text{ eV/atom} \) (Electron affinity)_F = 3.62 eV/atom, \( (IE)_Cl = 13.0 \text{ eV/atom} \) and \( (EA)_Cl = 4.0 \text{ eV} \)

Electronegativity of fluorine \( \chi_F = \frac{(IE)_F + (EA)_F}{2 \times 2.8} = \frac{17.4 + 3.62}{5.6} = 3.75 \)

Electronegativity of chlorine \( \chi_Cl = \frac{(IE)_{Cl} + (EA)_{Cl}}{2 \times 2.8} = \frac{13 + 4}{5.6} = 3.03 \)

**Advantage of Mulliken Scale:** Even though this method is based on ordinary theoretical basis, still experimental values are used to obtain the electronegativity of particular atom. This method also has advantage that different values can be obtained for different oxidation states of the same element.

**Disadvantage of Mulliken Scale:** Although Mulliken’s scale is less empirical than Pauling Scale, yet it suffers from a serious disadvantage that reliable electron affinity values of a few elements only known.

(iii) **Allred and Rochow’s Scale (1958):** On the basis of covalent radii Allred and Rochow suggested new scale of electronegativity.

According to this scale electronegativity of an atom is the force of attraction between the nucleus of one atom and an electron of an adjacent atom bonded to it and separated from the nucleus by the covalent radius.

Thus, if \( Z_{\text{eff}} \) is the effective nuclear charge, the effective nuclear charge felt by the electron under the influence of the nucleus is \( Z_{\text{eff}}e \) and the force of attraction between the nucleus and the electron is, therefore, equal to \( (Z_{\text{eff}}e) \frac{e}{r^2} \) where \( r \) is the distance (in Å) between the nucleus and the electron.

This force of attraction is equal to the electronegativity, \( \chi_A \) of an atom A. Thus :

\[ \chi_A = (Z_{\text{eff}}e) \frac{e}{r^2} = \frac{Z_{\text{eff}}e^2}{r^2} \]

In order to correlate Allred and Rochow’s electronegativity scale with Pauling’s scale. The Allred and Rochow’s values are plotted against Pauling’s values and the best straight line is drawn through the points. From the slope and the intercept of this line they obtained the following relation for the electronegativity values
\[ \chi_A = 0.359 \frac{Z_{\text{eff}}}{r^2} + 0.744 \]

e.g. 1. Find out the electronegativity of lead with the help of the given values: screening constant (\(\sigma\)) of Pb = 76.70, atomic number of Pb(Z) = 82 and covalent radius of Pb(r) = 1.53 Å

Solution. On substituting the values of \(\sigma\), Z and r in the following equation:

\[ \chi_{\text{Pb}} = 0.359 \frac{Z_{\text{eff}}}{r^2} + 0.744 = 0.359 \frac{5.3}{(1.53)^2} + 0.744 = 1.55 \]

2. Using Allred Rochow equation calculate electronegativity of Zn atom using following data. Covalent radius of Zn = 1.25 Å

3. Calculate the electronegativity of carbon atom using Allred Rochow method. The covalent radius of carbon is 0.77 Å

**Advantage of Allred and Rochow's Scale:** This method have advantage that \(Z_{\text{eff}}\) can be calculated using Slatter’s rule and covalent radius of many elements are experimentally well established, hence the electronegativity predicted by this method is widly accepted.

**Disadvantage of Allred and Rochow's Scale:** Few elements have the unreliable values of covalent radii and the electronegativity predicted using this method is not reliable for them.

**Important Note:** None of the electronegativity scales discussed above has a distinct advantage over the others. Drago (1960), who has critically examined various proposed scales, is of the view that *Pauling's scale* with all its limitations is the best one.

**Factors Affecting the Magnitude of Electronegativity:**

(a) **Size of the atom.** The smaller the size of an atom (have the nucleus quite closer to electron cloud), greater is its tendency to attract towards itself the shared pair electrons. Thus the smaller atoms have greater electronegativity values than the larger atoms. For example:

(i) Electronegativity values of the elements of **group 1 decrease down the group** from H(Z = 1) to Cs(Z = 55), since the atomic (covalent) radii of these elements increase in the same order.

(ii) Electronegativity values of the elements of **Period 2 increase across left to right increase** from Li C(Z= 3) to F(Z = 9), since the atomic (covalent) radii of these elements decrease in the same order.

(b) **Number of inner shells.** The atom with greater number of inner shells (i.e. the shells between the nucleus and the outer-most shell has less value of electronegativity than the atom with smaller number of inner shells. For example: **group 1 elements down the group number of inner shell increases** from H(principle quantum number n = 1) to Cs(n = 5), hence their electronegativity decreases in the same order.
(c) **Charge on the ion (Type of the ion)**. A cation attracts the electron pair more readily towards itself than the atom from which it has been derived. This is due to the smaller size of the cation as compared to its parent atom. Thus a cation, $M^+$ has higher electronegativity ($M^+ > M$) than its parent atom. Also the electronegativity increases with the increase in positive oxidation state ($M^{2+} > M^+ > M$).

The cations have the opposite trend and similar to opposite discussion applied.

(d) **Number and nature of atoms to which the atom is bonded**. We have seen that, since electronegativity of an atom is not the property of this atom in its isolated state, it depends on the number and nature of the atoms to which the atom is bonded. For this reason the electronegativity value of an atom is not constant. For example electronegativity value of P atom in $\text{PCl}_3$ molecule is different from that in $\text{PF}_3$ molecule in which the number and nature of the atoms both to which P atom is bonded change.

(e) **Ionisation energy and electron affinity**. The element, which have higher values of ionisation energy and electron affinity also have higher values of electronegativity. For example, the elements of group 17 (halogens) which have the highest ionisation energies and electron affinities also have the highest values of electronegativity. Similarly, the elements of group 1 (alkali metals) which have the lowest ionisation energies and electron affinities have the lowest values of electronegativity.

(f) **Type of hybridisation**. The magnitude of electronegativity of an atom also depends on the type of hybridisation which the atom undergoes in the formation of different bonds in the molecule. The magnitude of electronegativity increases as the s-character in hybrid orbitals increases.

**Periodic Trends of Electronegativity**

(a) **In a group**. Electronegativity decreases down the group from top to bottom (reason is increase in atomic radii down the group or increasing number of inner shell or Ionisation energy and electron affinity decrease down the group hence electronegativity also decrease in same order).

(b) **In a period**. Electronegativity increases from left to right in a period. It is because atomic radii decrease across a period or Ionisation energy and electron affinity increase across the period from left to right hence electronegativity also increase in same order.

**Note**: The variation of electronegativity values discussed above reveals that the which lie on the extreme right of the periodic table are the most electronegative (i.e. least electropositive) elements and the alkali metals which lie on the extreme left of the periodic table are the least electronegative (i.e. most electropositive) elements. Thus we see that the most electronegative element is fluorine which occurs at the top right hand corner and the least electronegative element is cesium which occurs at the bottom left hand corner of the periodic table. Being the most electronegative, $F$ does
not show any basic character, i.e., it has no tendency to form positive ions in any of its known compounds.

Applications of Electronegativity

(a) **Nature of bond.** The concept of electronegativity can be used to predict the nature of bond (polar, non-polar, ionic, etc) formed between two similar or dissimilar atoms.

(i) **Non-polar covalent bond.** Consider a molecule A-B. If the electronegativity difference between linked atoms are zero (|\(\Delta \chi\)| = |\(\chi_A - \chi_B\)| = 0) i.e. equally shared or electronegativity of both the elements are same, have the same tendency to attract the shared electron pair towards them. Hence the bond between A & B has no polarity or ionic character, i.e. non-polar covalent bond or simply covalent bond. E.g. homonuclear diatomic molecules such as H\(_2\), Cl\(_2\), …. etc

(ii) **Polar covalent bond.** Consider a molecule A-B. If the electronegativity difference between linked atoms are non-zero, but have smaller difference (|\(\Delta \chi\)| = |\(\chi_A - \chi_B\)| ≠ 0) i.e. not equally shared or electronegativity of both the elements are not same, then the shared electron pair partially displaced towards more electronegative atom. This partial displacement of shared electron pair towards more electronegative atom develops a fractional negative charge (denoted \(\delta^-\)) on it. Similarly an equal amont of fractional positive charge (denoted \(\delta^+\)) developed on less electronegative atom. Therefor constituted molecule denoted as A\(\delta^-\)–B\(\delta^+\) / A\(\delta^+\)–B\(\delta^-\) depending on their electronegativity. Hence the bond between A & B has partial polarity or partial ionic character, i.e. polar covalent bond. E.g. HCl denoted H\(\delta^+\)–Cl\(\delta^-\) (Cl is more electronegative than H and hece, shared electron pair attracted by Cl atom); in a molecule ClF, F is more electronegative than Cl and denoted as Cl\(\delta^+\)–F\(\delta^-\).

(iii) **Ionic or polar bond.** Consider a molecule A-B. If the electronegativity difference between linked atoms are non-zero, but have large difference (|\(\Delta \chi\)| = |\(\chi_A - \chi_B\)| ≠ 0) i.e. the shared electron pair almost completely displaced towards more electronegative atom. This electron pair displacement of shared electron pair towards more electronegative atom develops a negative charge (denoted -) on it. Similarly an equal amont of positive charge (denoted +) developed on less electronegative atom. Therefor constituted molecule denoted as A\(^-\)–B\(^+\) / A\(^+\)–B\(^-\) depending on their
electronegativity. Hence the bond between A & B is polar or ionic in nature, i.e. purely ionic bond. E.g. LiF denoted Li⁺F⁻, NaCl, denoted Na⁺Cl⁻ etc….

(b) **Percentage of ionic character in a polar covalent bond.** Consider a molecule A-B. The amount of ionic character in this bond depends on the difference of electronegativity values of A and B (|Δχ| = |χₐ-χₜ|). i.e. |Δχ| α amount of ionic character

Pauling has estimated the percentage of ionic character in various polar covalent bonds from known values and has derived the following conclusions:

<table>
<thead>
<tr>
<th>Mean value of χ</th>
<th>Δχ</th>
<th>Type of bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small</td>
<td>Zero</td>
<td>Metallic</td>
</tr>
<tr>
<td>Intermediate</td>
<td>Large</td>
<td>Ionic</td>
</tr>
<tr>
<td>Large</td>
<td>Zero</td>
<td>Covalent</td>
</tr>
</tbody>
</table>

(i) When |Δχ| = |χₐ-χₜ| = 1.7, the amount of ionic character in Aδ⁻–Bδ⁺ bond is 50% and that of covalent character is also 50%. Thus A-B bond is 50% ionic and 50% covalent.

(ii) When |Δχ| = |χₐ-χₜ| < 1.7, the amount of ionic character in Aδ⁻–Bδ⁺ bond is less than 50% and that of covalent character is more than 50%. Thus Aδ⁻–Bδ⁺ bond is predominantly covalent and hence is represented as A-B.

(iii) When |Δχ| = |χₐ-χₜ| > 1.7, the amount of ionic character in Aδ⁻–Bδ⁺ bond is more than 50% and that of covalent character is less than 50%. Hence Aδ⁻–Bδ⁺ bond is predominantly ionic and hence is represented as A-B⁺.

| |Δχ| = |χₐ-χₜ| | 0.6 | 0.8 | 1.2 | 1.7 | 2.2 | 2.8 | 3.2 |
|-----------------|-----------------|----|----|----|----|----|----|
| Increasing % of ionic Character in A-B | 10  | 15  | 30  | 50  | 70  | 86  | 92  |

Percentage of ionic character also explained using The Ketelaar triangle [https://dx.doi.org/10.1021%2Fed082p325](https://dx.doi.org/10.1021%2Fed082p325) (see fig.), triangle based on the difference in electronegativities (Δχ) of the elements in a binary compound and their average electronegativity (χ_mean). Different compounds can be placed around the triangle.

**Features of triangle:** Three species at the vertices of the triangle are: caesium (metallic), fluorine (covalent) and caesium fluoride (ionic). On the right side (from ionic to covalent), the bottom side (from metallic to covalent) and the left side (from ionic to metallic).

As discussed above ionic bonding is characterized by a large difference in electronegativity. Because a large difference indicates that the average electronegativity must be intermediate in value. The compound CsF, for instance, with Δχ = 3.19 and χ_mean = 2.38, lies at the ‘ionic’ apex of the triangle.
Covalent bonding is characterized by a small difference in electronegativities. Such compounds lie at the base of the triangle. Binary compounds that are predominantly covalently bonded are typically formed between nonmetals, which commonly have high electronegativities. It follows that the covalent region of the triangle is the lower, right-hand corner. This corner of the triangle is occupied by F₂, which has Δχ = 0 and χ_{mean} = 3.98. Metallic bonding is also characterized by a small electronegativity difference, and also lies towards the base of the triangle. In metallic bonding, however, electronegativities are low, the average values are therefore also low, and consequently metallic bonding occupies the lower, left-hand corner of the triangle. The outer corner is occupied by Cs, which has Δχ = 0 and χ_{mean} = 0.79. The advantage of using a Ketelaar triangle over simple electronegativity difference is that it allows us to distinguish between covalent and metallic bonding, which are both indicated by a small electronegativity difference.

(c) **Acidic and basic character of XOH** (X = Metal or non-metal) molecule in aqueous solution.

This prediction can be made by considering the ionisation of XOH molecule in aqueous solution as follows.
If $|\chi_O-\chi_H| > |\chi_O-\chi_X|$ O-H bond will be more polar than O-X bond and hence the ionization of XOH molecule in aqueous solution will take place at O-H bond and H$_2$O$^+$ ions will be produced as shown below:

$$
\begin{align*}
X-O-H & \rightarrow XO^- + H^+ \\
H^+ + H_2O & \rightarrow H_3O^+
\end{align*}
$$

X-O-H + H$_2$O $\rightarrow$ XO$^-$ + H$_3$O$^+$

The production of H$_2$O$^+$ ions confirms that XOH molecule will behave as an acid in its aqueous solution.

On the other hand $|\chi_O-\chi_H| < |\chi_O-\chi_X|$, now the O-H bond is less polar than O-X bond. Therefore it is clear that now the X-O bond is more polar than O-H bond, hence the ionization of XOH molecule in aqueous solution will take place at O-X bond OH$^-$ ion will be produced as shown.

$$
\begin{align*}
X-O-H & \rightarrow X^+ + OH^- \\
X^+ + H_2O & \rightarrow [X\leftrightarrow OH_2]^+
\end{align*}
$$

X-O-H + H$_2$O $\rightarrow$ [X$\leftrightarrow OH_2$]$^+$ + OH$^-$

Production of OH$^-$ ion confirms that the XOH behave as base in its aqueous solution.

e.g. Predict which of the following hydroxy compounds is acidic and which is basic in aqueous solution? NaOH, ClOH (given $\chi_N$ = 0.9 $\chi_O$ = 3.5 $\chi_H$ = 2.1 $\chi_C$ = 3.0)

Pauling electronegativity values of individual elements of those molecules and difference as follows

$$
\begin{array}{ccc}
\Delta \chi & 2.6 & 1.4 \\
X_{atom} & 0.9 & 3.5 & 2.1 \end{array}
\begin{array}{ccc}
\Delta \chi & 0.5 & 1.4 \\
X_{atom} & 3.0 & 3.5 & 2.1
\end{array}
$$

Na-O bond is more polar hence in solution O-H bond is more polar hence in solution NaOH gives OH$^-$ and behave as basic solution ClOH gives H$^+$ and behave as acidic solution

(d) **Cause of diagonal relationship.** We discussed the digonal relationship of some 2nd period elements with 3rd period, due to almost same radii. Apart from radii their electronegativity values also as comparable and behave as similar chemical properties.

(e) **Bond angle.** This concept explains the variation of bond angle in a molecule. For example. Consider a molecule AB$_n$ (A is the central atom, B are the atoms attached with atom A and n is the number of B atoms). The bond angle of AB$_n$ changed on the degree of electronegativity of central atom.

*The decrease of the electronegativity of the central atom (A), the B-A-B bond angle also decreases.*

For example the bond angle (H-E-H) in group 15 hydrides EH$_3$ (E= N, P, As, Sb) decreases down the group as the electronegativity of the central atom decreases from N to Sb. Upon decrease of electronegativity of central atom, the E-H bonding electron pairs in EH$_3$ molecules are drawn farther
away from the central atom (E) but nearer to H-atom. The effect of this shifting of the bonding electron pairs towards H-atom is that the repulsion between the bonding electron pair (bp) and lone pair (lp) on the central atom [(bp-lp) repulsion] increases. The increase in (bp-lp) repulsion results in that bonding electron pairs come still close to each other and hence the bond angle progressively decreases from NH$_3$ to SbH$_3$ (see the table).

<table>
<thead>
<tr>
<th>Hydrides, EH$_3$</th>
<th>$\chi_{central \ atom \ (E)}$</th>
<th>$\angle E-H-E \ bond \ angle \ (^\circ)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>3.0</td>
<td>107.5</td>
</tr>
<tr>
<td>PH$_3$</td>
<td>2.1</td>
<td>93.3</td>
</tr>
<tr>
<td>AsH$_3$</td>
<td>2.0</td>
<td>91.8</td>
</tr>
<tr>
<td>SbH$_3$</td>
<td>1.9</td>
<td>91.3</td>
</tr>
</tbody>
</table>

Vice verse the B-A-B bond angle increases with decrease of electronegativity of terminal atom (B). For example consider PX$_3$ (X = Cl, Br, I) and their increase moving from Cl to I. Upon decrease of electronegativity of terminal atom (X), the P-X bonding electron pairs in PX$_3$ molecules are drawn farther away from the terminal atom (X) but nearer to central atom (P). The effect of this shifting of the bonding electron pairs towards P-atom is that the repulsion between the bonding electron pair (bp) and lone pair (lp) on the central atom [(bp-lp) repulsion] decreases. The decrease in (bp-lp) repulsion results in that the bonding electron pairs get farther away from each other, i.e. the X-P-X bond angle increases (See the table).

<table>
<thead>
<tr>
<th>Hydrides, PX$_3$</th>
<th>X_{terminal \ atom \ (X)}</th>
<th>$\angle X-P-X \ bond \ angle \ (^\circ)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCl$_3$</td>
<td>3.0</td>
<td>100.0</td>
</tr>
<tr>
<td>PBr$_3$</td>
<td>2.8</td>
<td>101.5</td>
</tr>
<tr>
<td>PI$_3$</td>
<td>2.5</td>
<td>102.0</td>
</tr>
</tbody>
</table>

(f) **Mechanism of hydrolysis.** When a molecule dissolve in to water, positive component of the molecule react with OH$^-$ of water and produce the corresponding product. Vice-verse negative component of the molecule react with H$^+$ of water and produce the corresponding products. For example consider hydrolysis of BCl$_3$ and Cl$_2$O (BCl$_3$ and Cl$_2$O dissolve in to water)

(g) **Nomenclature of binary compounds.** Generally, binary compounds are regarded as derivatives of more electronegative elements. E.g. ICl named as iodine monochloride not as chlorine monoiiodide. Because the electronegativity of chlorine is higher than iodine. Similarly OF$_2$ given oxygendifluoride

(h) **Calculation of bond length.** Refer application of Pauling’s electronegativity scale.
THE INERT-PAIR EFFECT:

The reluctance of the s-electron pair to take part in the bond formation is known as inert pair effect. This observation is very common in heavier elements of p-block series.

The elements that immediately follow the 4d and 5d transition series are considerably less reactive than their group properties might have predicted and they also prefer oxidation states that are two lower than the usual group valence. Consider, for example, the Group 3 elements. The lighter elements, B, Al, and Ga take only the 3+ oxidation state predicted by their group valence. However, the heavier elements, In and Tl, take both the 3+ and 1+ oxidation states. The same trend observed for the Group 4 elements. Again, the lighter elements C, Si, and Ge take the 4+ valence predicted by their period. However, Sn and Pb can exist in either the 4+ or the 2+ oxidation states. The relative stability of the lower oxidation states for the fifth and sixth series post-transition elements has attributed to the higher-than-expected ionization energies. Consequently, it costs these elements relatively more energy to achieve a higher oxidation state than their lighter group congeners.

The larger-than-expected ionization energies for the post-transition series Group 3 elements result from the fact that the valence s electrons are not shielded from the nucleus very effectively by the intervening d electrons. As the two s electrons are held tighter by the nucleus in the post-transition series elements, the ionization energies for these two electrons are unusually large. The result is that these elements prefer oxidation states that are two lower than their typical group valence.

Summary: History of periodic table development discussed briefly. Some physio-chemical properties and their periodicity (periodic change) discussed.