Polarization & Polarity

Inorganic Chemistry (2)

3rd lecture

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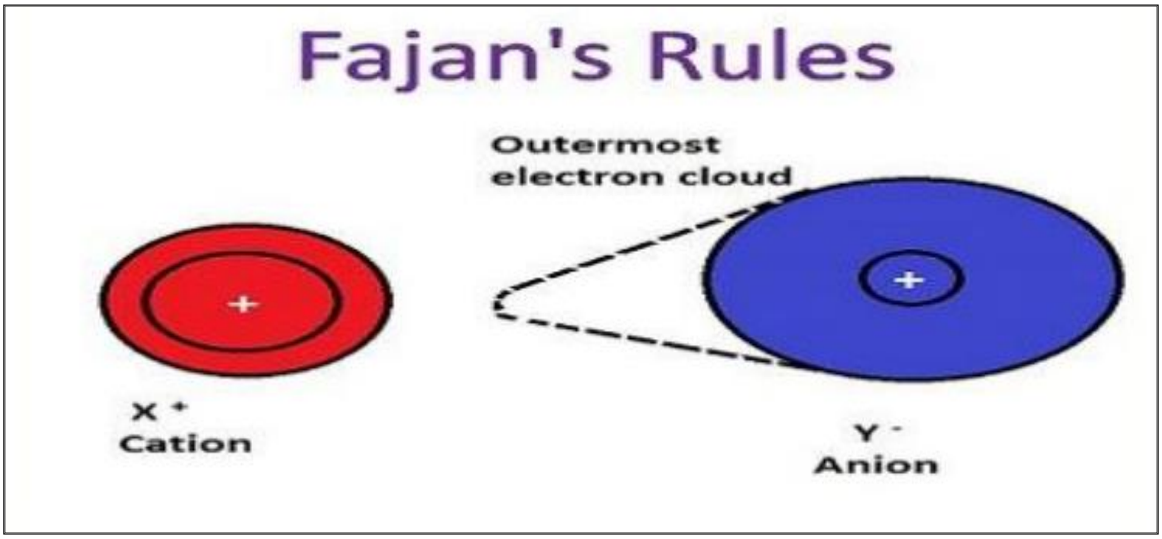
Polarization:

Polarization: is the mutual distortion that occurs to the double ion A^+B^- The scientist Fajan's assumed that the polarization that occurs to the negative ion results from the attraction between the electron cloud in it and the field of the positive ion, as well as from the repulsion of the positive ion with the nucleus of the negative ion. A similar polarization may occur for the positive ion. When the negative ion is large in size, the positive ion is able to polarize more easily, that is, the electronic cloud of both ions interferes with each other, and by increasing this interference to the final limit, the formation of a covalent bond occurs. The more polar the ion, the less polar the molecule.

Polarization can also be defined as the appearance of covalent properties in ionic compounds.

The scientist Fajan's has developed rules to determine the factors affecting polarity:

1. Polarization increases when the charge of the positive or negative ion is high. The repulsion caused by a single-charged negative ion has fewer electrons than a double-charged negative ion. Also, a double-charged or triple-charged positive ion attracts electrons more strongly than a single-charged ion.
2. Polarization increases when the size of the positive ion is small and the size of the negative ion is large due to the concentration of the positive charge on a small area due to the small size of the positive ion. The negative ion has a high polarizability. The larger the size of the negative ion, the greater the polarity, that is, the appearance of the covalent character of the bond increases, and thus the degree of melting decreases, since as the polarity increases in compounds, the degree of melting decreases.



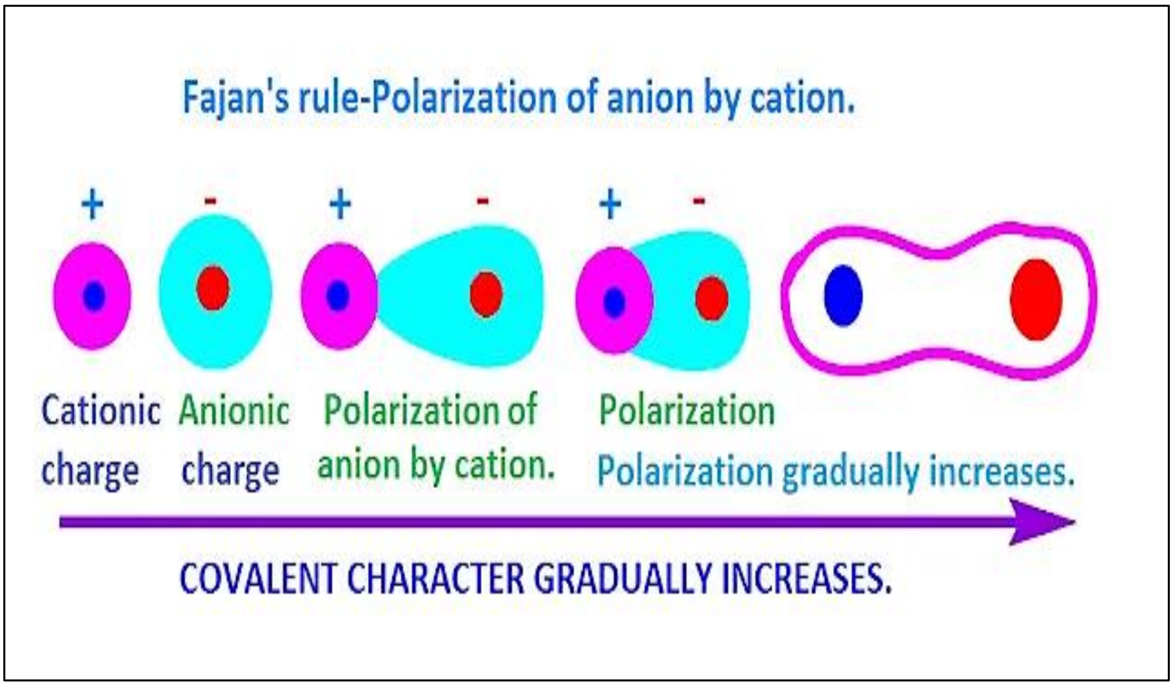


Table: Shows the decrease in melting points with Increase the Polarization of the negative ion.

Compound.	Negative ion	Melting point (Kelvin)
CaF_2	F^-	1665
$CaCl_2$	Cl^-	1009
$CaBr_2$	Br^-	1003
CaI_2	I^-	848

Table: Shows the decrease in melting point with increase Polarization is the result of an increase in positive charge.

Compound.	Positive ion	radius	Melting point (Kelvin)
NaCl	**Na^{+1}**	**102**	**1073**
$MgCl_2$	**Mg^{+2}**	**72**	**985**
$AlCl_3$	**Al^{+3}**	**53**	**453**

Whereas **F< Cl < Br < I** are from one group, which is the group of halogens, the most polarized of which is iodine **I**, while the least polarized is fluorine **F**. The polarity increases for the following compounds:-

CaF < CaCl < CaBr < CaI

$\longrightarrow$

Polarization increases

We note that the positive ion is itself calcium, while the negative ion represents the group of halogens, where it represents the compound

CaF is a compound with **low polarity**, meaning it has an ionic character and a high melting point.

CaI is a **highly polar** compound, that is, it has a covalent nature and a low melting point.

In one group, the polarization of the positive ions increases from bottom to top (that is, as the radius decreases and the charge of the nucleus increases).

Ba < Sr < Mg < Be

$\longrightarrow$

Polarization increases

The beryllium ion **Be** is the smallest in size (less radius), meaning it is more polarized.

As for the barium ion **Ba** it is the largest in size (largest radius), meaning it is less polarized.

So-:

Be-Cl > Mg-Cl > Sr-Cl > Ba-Cl

$\longleftarrow$

Beryllium chloride is more covalent than the rest of its group members, while barium chloride is less covalent than the rest of its group members, according to the following table, where we notice that the melting points decrease as the covalent character increases.

Table: Shows Melting points of chloride compounds the second group

Compound.	Positive ion	Melting point (Kelvin)
$BeCl_2$	Be^{+2}	678
$MgCl_2$	Mg^{+2}	985
$SrCl_2$	Sr^{+2}	1145
$BaCl_2$	Ba^{+2}	1233

3. The polarization increases when the electronic arrangement of the positive ion is different from that of the noble gases.

Example:

AuCl, AgCl, CuCl.

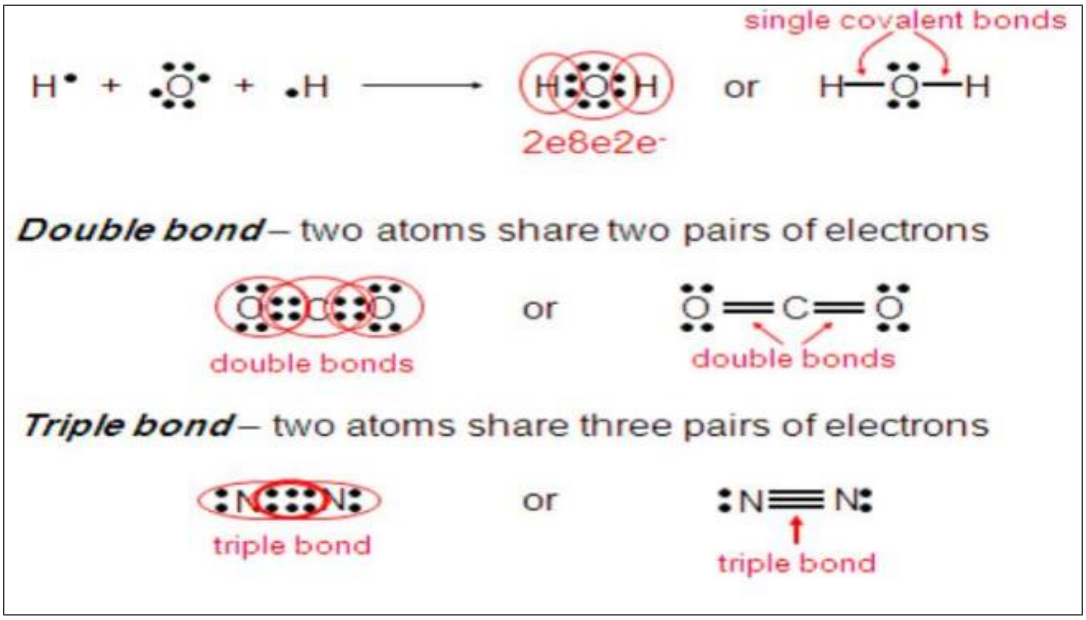
All of them carry a charge of **+1** (they do not have an electronic arrangement for the noble gases) that is, they have a greater polarization than the positive ions that have the arrangement of the noble gases, and that is, they have lower melting points and less solubility. Either **RbCl, NaCl, KCl**, or they all carry a charge of **+1** (have an electronic arrangement similar to the noble gases). That is, it has less polarization and higher melting points than the above ions, in addition to a higher solubility than those that have an electronic arrangement that is not similar to that of the noble gases, according to the table below:

Table: Shows Comparison of the melting points of positive ions that have the noble gas arrangement and ions that do not have the order of the noble gases.

Compound.	Melting point	Water solubility gm/100 ml
NaCl	1073	36
KCl	1044	24
RbCl	995	91
CuCl	965	1.52
AgCl	728	1.5×10^{-4}
AuCl	443	It does not dissolve in water

Covalent Bond

The covalent bond is the bond that is formed as a result of the sharing of two atoms bonded to one or more pairs of electrons, so that each atom contributes half of the number of these bonding electrons.



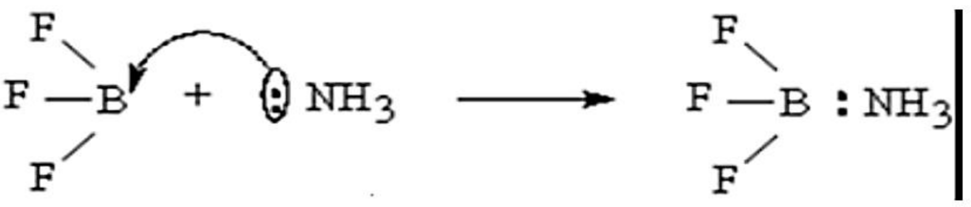
The modern definition of covalent bond

It is the amount of changes that occur or occur in energy when two atoms approach each other, so that the energy of the system becomes the least possible when the distance between the two atoms reaches a distance called the equilibrium distance. The length of the covalent bond is measured using X-ray diffraction.

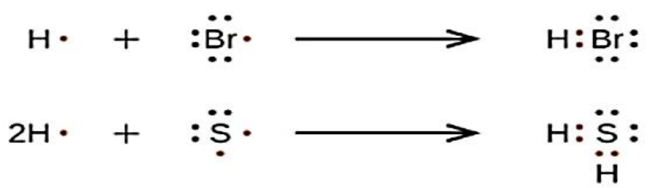
Important rules for forming covalent bonds

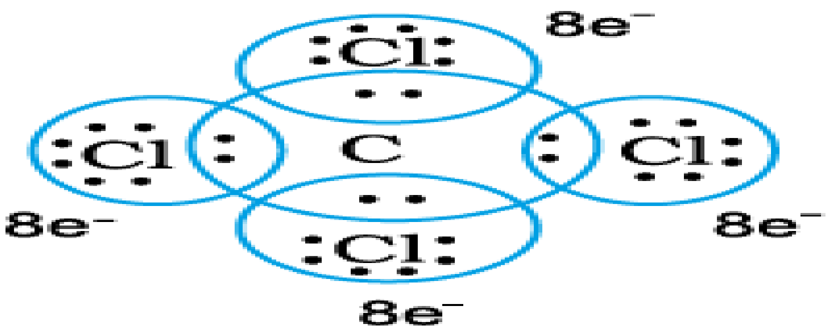
1. In order for a covalent bond to be formed, ionic bonding must not be possible, meaning that the energy of the electron of atom **A** is equal to or close to the energy of the electron of atom **B** for the union of the two atoms and the formation of the covalent bond.
2. The covalent bond results from the sharing of two electrons of close energy, and this means the necessity of double-spinning of these two electrons when forming the bond in application of the Pauli Exclusion Principle.
3. The overlap of the orbitals of the two atoms that make up the covalent bond, and this overlap fills the space between the two atoms as a condition for bonding to occur.

4. When covalent bonds are formed between atoms whose orbitals are **S** and **P**, the maximum number of electrons is equal to **8** in the outer shell of each atom, and it is called the octet rule. This is called the Lewis octet structure, so the total sum of electrons for each atom is = **8** in the outer shell. Lewis theory proves that the formation of a stable compound requires that the atoms reach the noble gas arrangement, such as F_2, NH_3, and CF_4. This is for elements whose number of electrons in the outer shell is not less than four. However, when the number of electrons in its outer shell is less than **4**, the octet rule does not apply to it. For example, in the compound BF_3, the hydrogen atoms need only two electrons to satisfy their S-type outer shell, and the boron atom **(B)** does not have an electronic arrangement that reaches the noble gas because it contains **3** electrons. Only in the outer shell, boron compounds are called electron deficient covalent compounds. Therefore, they can interact with compounds in which an element or central atom has an electron pair that is not covalent.

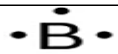
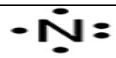
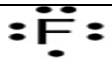


Examples of Octet rule

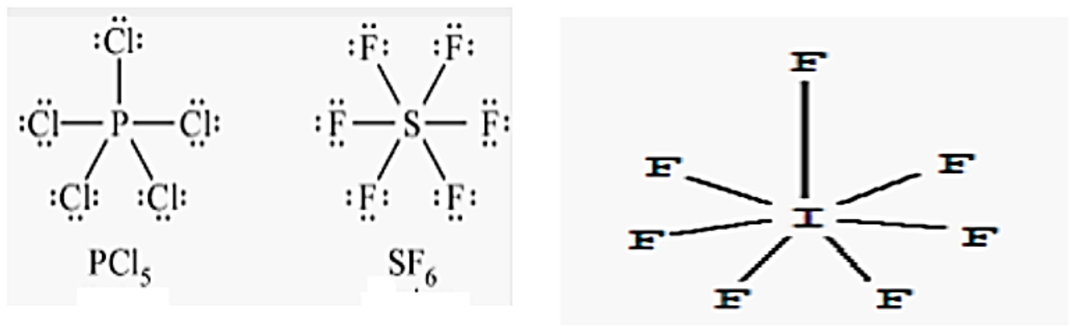




Each of the four Cl atoms along with the C atom attains octet of electrons

Elements	Electron configuration	Electron dot symbol
Li	[He]$2s^1$	
Be	[He]$2s^2$	
B	[He]$2s^2$ $2P^1$	
C	[He]$2s^2$ $2P^2$	
N	[He]$2s^2$ $2P^3$	
O	[He]$2s^2$ $2P^4$	
F	[He]$2s^2$ $2P^5$	
Ne	[He]$2s^2$ $2P^6$	

5. For the elements that have a **d** shell, their valence shell goes beyond the Lewis octet structure, as the third period has many elements with high valence numbers for metals and transition elements, and the number of outer shell electrons is what determines the covalent bonds and can be **5, 6, 7, 8** such as:



The exceptions to the eight octet rule can be summarized in the points below:

<u>Exceptions tp the Octet Rule:</u>

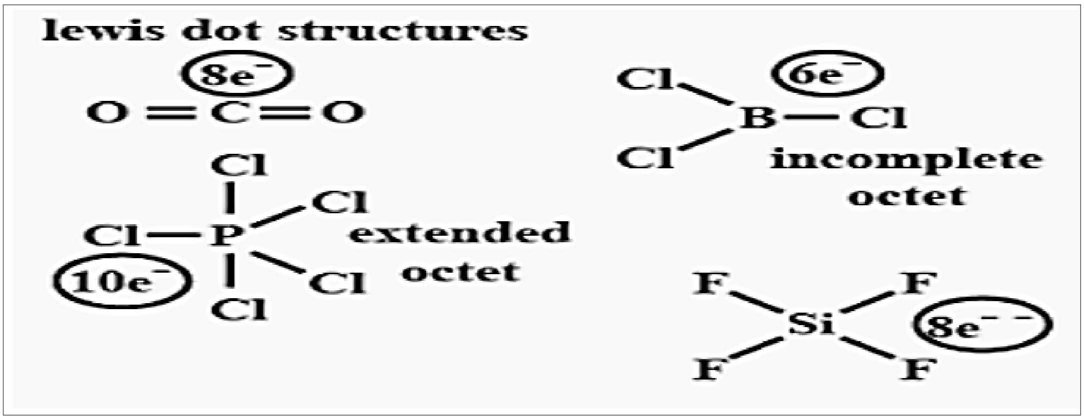
- There are three types of ions or molecules that do not follow the octet rule:

➢ Ions or molecules with an odd number of electrons 1 or 3.

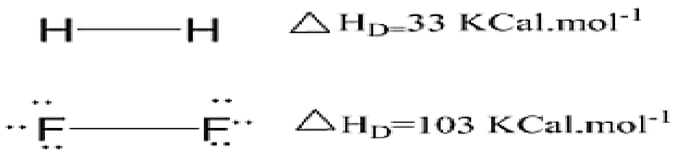
➢ Ions or molecules with less than an octet.

- ➢ Ions or molecules with more than eight valence electrons (an expanded octet).

  Ex: Phosphorus.



6. The repulsion between non-covalent electrons and covalent electrons must be as little as possible. As the number of non-covalent electrons increases, the energy of breaking the covalent bond decreases.



In the F_2 molecule, there are non-allergic doublets that repel the allosteric electrons, causing the atoms to push. As a result, the bond length increases and its breaking energy decreases.

7. Covalent molecules have low melting points because they are electrically neutral, and the most common thing that links them is Van der Waals forces. They are characterized by their poor ability to conduct electrical current due to the lack of electrostatic forces.

Physical properties of some selected compounds			
Compound.	**Type of Bonding**	**Melting temperature °C**	**Boiling temperature °C**
F_2	Nonpolar covalent	-220	-188
CH_4	Nonpolar covalent	-183	-162
NH_3	Polar covalent	-78	33
CH_3Cl	Polar covalent	-64	61
KBr	ionic	730	1435
Cr_2O_3	ionic	2435	4000

There are two theories to explain the formation of the covalent bond:

1. Valance bond theory.
2. Molecular orbital theory.

Ionic bond

An ionic bond is a type of chemical bond in which there is an electrostatic attraction between ions of opposite charge. That is, the positively charged ion forms a bond with the negatively charged ion, and transfers electrons from one atom to another. This type of chemical bond occurs when valence electrons are permanently transferred from one atom to another atom. An atom that loses electrons becomes a cation (positively charged), and an atom that gains electrons becomes an anion (negatively charged).

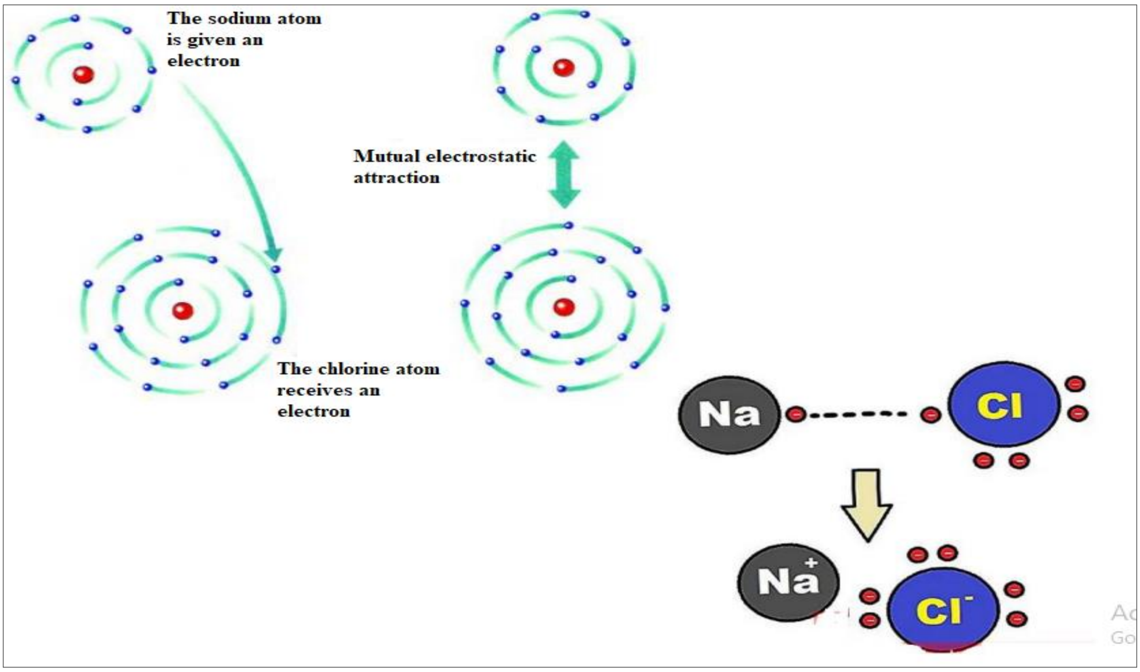
The concept of ionic bonding

An ionic bond is the bond through which electrically charged particles, called ions, interact to form ionic solids and liquids. This bond is the product of electrostatic interactions between hundreds of millions of ions, and is not limited to just a couple; That is, it bypasses the attraction between the positive charges towards the negative charge. Consider, for example, the ionic compound sodium chloride **NaCl**, better known as table salt. In sodium chloride, the ionic bond predominates, so it consists of sodium ions $\mathbf{Na^+}$ which is the positive ion or cation, and the chloride ion $\mathbf{Cl^-}$ which is the negative ion or anion.

Also known as an electrovalent bond or electrovalence, it is a type of bond that results from the electrostatic attraction between ions of opposite charge to each other in a chemical compound. This bond is created when the valence electrons move permanently from one atom to another atom. Atoms that lose electrons become positive ions (cations), while atoms that gain electrons become negative ions (anions). Ionic bonds are found in compounds known as ionic or electrovalent compounds, which can be simplified by the compounds that result from the interaction of nonmetals with alkali or alkaline earth metals. In such compounds, each positive ion is surrounded by negative ions, and each negative ion is surrounded by with positive ions.

***<u>Ionic bonding consists of three steps</u>*:**

1. The active metal (metal) loses the electron furthest from the nucleus, and becomes positively charged.
2. The non-metal (non-metal) gains this electron, and becomes negatively charged.
3. An electrostatic attraction occurs between the positive and negative ions.



<u>For the formation of an ionic bond, the following conditions must be met:</u>

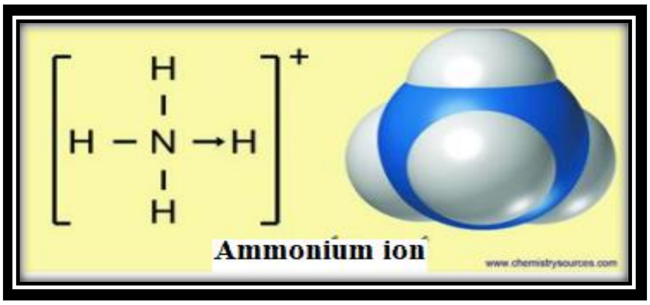
1. There should be an active metal capable of losing one or more electrons with the lowest amount of energy, i.e. the smallest ionization potential of the metal atom (metal), and the elements to which the first condition applies are the first and second groups, which are the alkaline elements and the alkaline-earth elements, respectively.
2. That there is an active non-metal capable of gaining one or more electrons without the need for significant energy, i.e. a high electronic affinity for the metal (non-metal). The elements to which the second condition applies are the elements of the seventh and sixth groups.
3. The energy of crystal bonding and the energy of electrostatic attraction between ions are large.

The ionization energy of metals is low, which makes them tend to lose electrons and form positive ions. Nonmetals are distinguished by their high electrical affinity, and thus their eagerness to gain electrons and form negative ions.

When a non-metal atom approaches a metal atom, it tends to attract the valence electrons of the metal atom, so the positive and negative ions are formed, and as a result, an electrical attraction occurs between them, which leads to the release of a large amount of energy due to this attraction, so the energy of the resulting compound decreases.

The energy resulting from the attraction of negative and positive ions is known as the energy of the crystal lattice and is defined as the amount of energy resulting from the attraction of positive and negative ions to form one mole of crystals of a solid.

An ionic bond can arise between atomic groups such as the negative nitrate group NO_3^- with a positive group ion such as the ammonium group.



Examples of ionic bonds

The element chlorine reacts with the element sodium to form the compound substance sodium chloride (sodium salt).

The atomic number of sodium is **(11)**, so its electronic structure is (2,8,1).

The atomic number of chlorine is **(17)**, and therefore its electronic composition is (2,7,8).

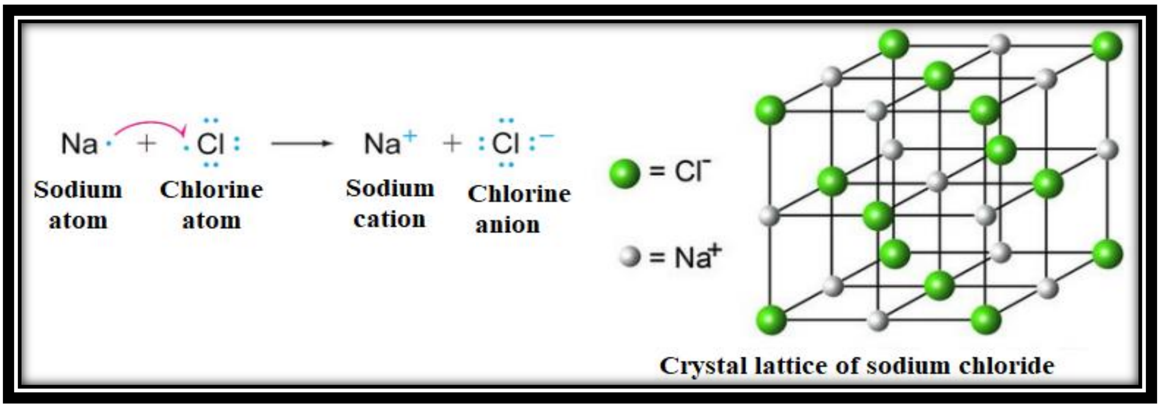
One electron moves from the outer shell of the sodium atom to the outer shell of the chlorine atom, thus forming a chloride ion, whose electronic structure is similar to neon.

The chlorine ion carries a negative electrical charge because the number of electrons in the orbitals has become eighteen **(18)**, while the number of protons in the nucleus is **(17)**.

Sodium ion carries a positive electric charge because the number of electrons in orbitals is **(10)**.

While the number of protons in the nucleus did not change **(11)**.

There is an electrostatic force of attraction between these two ions that keeps them in contact with each other.



Ionic compounds are formed when strongly electropositive atoms and strongly electronegative compounds interact with each other. Ions in a crystal of an ionic substance hold together through attractive forces between opposite charges. An ionic bond is not a bond in the real sense at all, as the ions attract each other just as the poles of a magnet attract each other. When an ionic substance is dissolved in water, the ions separate from each other and are able to move freely in the solution.

General Properties of Ionic Compounds

Ionic compounds are characterized by the following:

1. It is distinguished from other solid materials in that it is brittle and cannot be malleable or ductile. The fragility of these materials is due to the fact that any attempt to compress the crystals leads to severe repulsion and the crystal shatters.
2. Its melts and solutions are characterized by good conduction of electrical current, due to the disintegration into positive and negative ions, and these ions conduct electricity.
3. It is characterized by high melting and boiling points, and the reason is due to the increased forces of attraction between the positive and negative ions, which act as double electrodes with a certain torque that results in the ions coming together.
4. It does not dissolve in organic solvents, but rather it dissolves in polar solvents such as water. The reason for the dissolution of ionic substances in polar solvents is due to the formation of a type of bond between the ion and the polar solvent molecules.

5. The reaction is fast and complete, because the reaction occurs once the ions collide.

Polarity

It is a measure of the ionic character in the covalent bond, and the polarity depends on the difference in electronegativity between the two elements **A** and **B** that make up the bond. As the difference in electronegativity between the two elements **A** and **B** increases, that is Δ**EN** the larger, the polar character increases, and when the difference in electronegativity between **A** and **B** decreases, the covalent character increases. And the meaning of this both nuclei of the elements **A** and **B** contribute the same amount to their influence on the shared electron clouds between them for this bond, in the case of a difference in electronegativity, the element is the most electronegative.

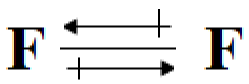
The common electron cloud is concentrated on it more than the less electronegative element, which will suffer from a decrease in electronegativity. The ionic character increases, as is the case in metallic compounds and alkaline earths. The polarity of the compounds is measured through a dipole moment meter.

$$\mu = e \times d = e.s.u \times cm = D \text{ (debey)}$$

μ increases with the increase in the polarity of the bond, which is a vector value between the resultant direction of the electronic clouds, such that it reaches the point of repulsion between the nuclei of the two atoms, and the distance traveled by the electronic cloud increases in the direction of the more negative element.

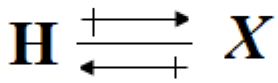
X **= F, Cl, Br, I.**

F_2



μ= 0

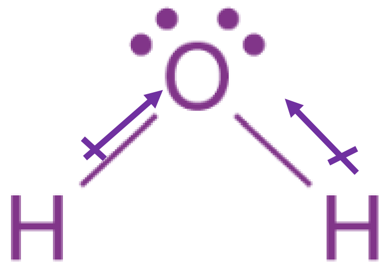
H*x*

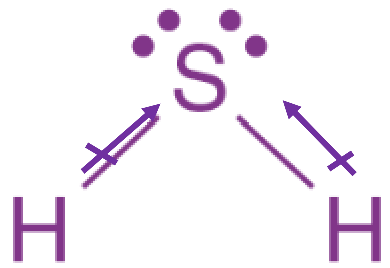


μ ≠ 0

The polarity of the same compounds increases as the difference in electronegativity increases.

H_2O **H_2S**

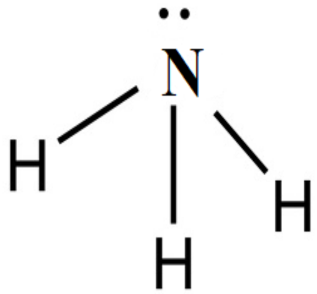


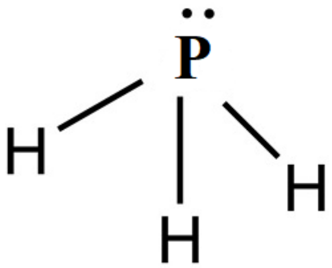


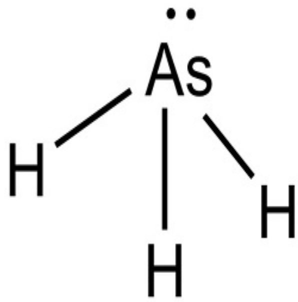
μ= high μ= low

Decrease of polarity

NH_3 PH_3 AsH_3







μ= high μ= medium μ= low

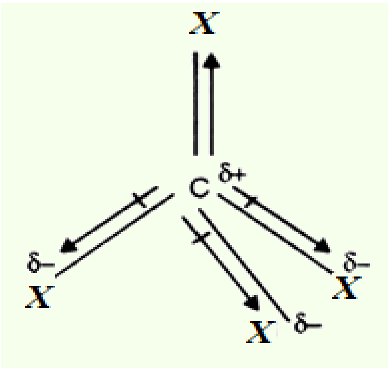
Decrease of polarity

H-F < H-Cl < H-Br < H-I

Decrease of μ.
Decrease of electronegativity ΔEN.
Decrease of polarity.
Decrease of acidity.

Q: Are the following compounds covalent? CI_4, CCl_4, CBr_4, CF_4 & why?

These compounds is **<u>covalent compounds</u>** because **μ=0**.



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||
CCl_4 < C_6H_6 < $(C_2H_5)_2O$ < $CHCl_3$ < $CH_3CH=O$ < CH_3-C- CH_3 < C_2H_5OH < H_2O

Increasing of polarity/ Increasing of μ/ Increasing of dielectric constant