

Prof. Dr. Mahasin Faisal A. Alias

Classification of the elements

Inorganic Chemistry

1st lecture

Prof. Dr. Mahasin Faisal A. Alias

2023-2024

PERIODIC TABLE OF THE ELEMENTS

<http://www.periodni.com>

PERIOD	GROUP	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
		IA	IIA	IIIB	IVB	VB	VIB	VIB	VIB	VIB	VIB	VIB	VIB	IIIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1	1.0079 H HYDROGEN																		4.0026 He HELIUM
2	2	6.941 Li LITHIUM	9.0122 Be BERYLLIUM																18.998 F FLUORINE	20.180 Ne NEON
3	3	22.990 Na SODIUM	24.305 Mg MAGNESIUM																35.453 Cl CHLORINE	39.948 Ar ARGON
4	4	39.098 K POTASSIUM	40.078 Ca CALCIUM	44.956 Sc SCANDIUM	47.867 Ti TITANIUM	50.942 V VANADIUM	51.996 Cr CHROMIUM	54.938 Mn MANGANESE	55.845 Fe IRON	58.933 Co COBALT	58.693 Ni NICKEL	63.546 Cu COPPER	65.38 Zn ZINC	69.723 Ga GALLIUM	72.64 Ge GERMANIUM	74.922 As ARSENIC	78.96 Se SELENIUM	79.904 Br BROMINE	83.798 Kr KRYPTON	
5	5	85.468 Rb RUBIDIUM	87.62 Sr STRONTIUM	88.906 Y YTTORIUM	91.224 Zr ZIRCONIUM	92.906 Nb NIObIUM	95.96 Mo MOLYBDENUM	101.07 Tc TECHNETIUM	102.91 Ru RUTHENIUM	102.91 Rh RHODIUM	106.42 Pd PALLADIUM	107.87 Ag SILVER	112.41 Cd CADMIUM	118.71 In INDIUM	121.76 Sb ANTIMONY	127.60 Te TELLURIUM	126.90 I IODINE	126.90 Xe XENON		
6	6	132.91 Cs CAESIUM	137.33 Ba BARIUM	138.91 La-Lu Lanthanide	178.49 Hf HAFNIUM	180.95 Ta TANTALUM	183.84 W WOLFRAM	186.21 Re RHENIUM	187.08 Os OSMIUM	193.22 Ir IRIDIUM	195.08 Pt PLATINUM	196.97 Au GOLD	200.59 Hg MERCURY	207.2 Pb LEAD	208.98 Bi BISMUTH	209 Po POLONIUM	210 At ASTATINE	222 Rn RADON		
7	7	223 Fr FRANCIUM	226 Ra RADIUM	227 Ac-Lr Actinide	267 Rf RUFERFORIUM	268 Db DUBNIUM	268 Sg SEABORGIUM	268 Bh BOHRIIUM	268 Hs HASSIUM	268 Mt MEITNERIUM	268 Ds DARMSTADTIUM	268 Rg ROSGENTIIUM	268 Cn COPERNICIUM	267 Fl FLEROVIUM	267 Uup UNUNPENTIUM	267 Lv LIVERMORIUM	267 Uus UNUNSEPTIUM	267 Uuo UNUNOCTIUM		

Legend for element classification:

- Metal (Blue)
- Semimetal (Green)
- Nonmetal (Yellow)
- Alkali metal (Light Blue)
- Alkaline earth metal (Light Green)
- Transition metals (Dark Blue)
- Lanthanide (Pink)
- Actinide (Light Pink)
- Chalcogens element (Light Green)
- Halogens element (Light Yellow)
- Noble gas (Light Blue)

STANDARD STATE (25 °C; 101 kPa)

- Ne - gas
- Hg - liquid
- Fe - solid
- Tc - synthetic

LANTHANIDE

57	138.91	La	LANTHANUM
58	140.12	Ce	CERIUM
59	140.91	Pr	PRASEODYMIUM
60	144.24	Nd	NEODYMIUM
61	145	Pm	PROMETHIUM
62	150.36	Sm	SAMARIUM
63	151.96	Eu	EUROPIUM
64	157.25	Gd	GADOLINIUM
65	158.93	Tb	DYSPROSIUM
66	162.50	Dy	DIYSPROSIUM
67	164.93	Ho	HOLMIUM
68	167.26	Er	ERBIUM
69	168.93	Tm	THULIUM
70	173.05	Yb	YTTERIUM
71	174.97	Lu	LUTETIUM

ACTINIDE

89	227	Ac	ACTINIUM
90	232.04	Th	THORIUM
91	231.04	Pa	PROTACTINIUM
92	238.03	U	URANIUM
93	237	Np	NEPTUNIUM
94	244	Pu	PLUTONIUM
95	243	Am	AMERICIUM
96	247	Cm	CURIUM
97	247	Bk	BERKELIUM
98	251	Cf	CALIFORNIUM
99	252	Es	EINSTEINIUM
100	257	Fm	FERMIUM
101	258	Md	MENDELEVIUM
102	259	No	NOBELIUM
103	262	Lr	LAWRENCIUM

(1) Pure Appl. Chem., 81, No. 11, 2131-2156 (2009)
 Relative atomic masses are expressed with five significant figures. For elements that have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element. However three such elements (Th, Pa and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Electronic structure and Periodic Law

Types of elements: According to the electronic configurations, the elements may be divided into four types. The four types of elements are:

1. The Inert Gases (Elements of **0** group).
2. The Representative elements (**s** and **p** block elements).
3. The Transition Elements (**d** block elements).
4. The Inner Transition Elements (**f** block elements).

The Inert Gases: The zero group elements have been placed at the end of each period in the periodic table. It appears that these elements having s^2p^6 electronic arrangements in the outermost level are very stable. Helium has $1s^2$ table arrangement and all other inert gases have s^2p^6 outer configurations. These elements are colorless gases.

The Representative Elements (s and p block elements): These elements generally belongs to a **A** sub-group of the Periodic Table. These elements have the outer most energy level in complete just after the complete or stable groupings of s^2p^6 .

The chemical behavior of these elements depends up on the valence electrons and these are both metals and nonmetals. The alkali metals (**Group IA**) and alkaline earth metals (**Group IIA**) are **s** block elements. The valence electrons of all the elements from boron to halogens (**Group IIIA to VIIA vertically**) occupy **p** orbitals. Hence these elements are called **p** block elements. They generally form colorless compounds.

The Transition Elements (d block elements): These elements are generally heavy metals of sub-group **B** and contains two incomplete energy levels because of the building up of the inner **d** electrons. The chemical properties of these elements depend up on the electrons from the two outermost levels (**s** and **d** electrons). These elements generally form coloured compounds. These elements have normally the same number of electrons in the outermost level but have a progressively greater number of electrons in an inner level (such as **d** level) and hence they are called as “Transition Elements”.

The Inner Transition Elements (f block elements): These elements have three incomplete outer levels. The orbital in which the electron is added on increasing the atomic number is an **f** orbital. The inner transition elements (lanthanides and actinides) are all metals and show variable oxidation states. Their compounds are highly colored.

The properties of Transition Elements (d block elements)

The properties of transition elements are summarized in the following points:

1. All the elements are of high melting points, electropositive and heavy metals.
2. These metals have almost the same atomic and ionic sizes. There is only slight increase in the ionization energy of the formation of M^{+2} ions.
3. All these elements show positive oxidation states of **+2** and **+3** generally and form mostly ionic compounds. Higher oxidation states are also exhibited in some cases.
4. As a general rule, the transition elements form colored compounds.
5. These elements are also effective catalytic agents.
6. All these form quite a large number of complex compounds.

These properties are due to the influence of the incomplete inner **d** orbitals in the transition elements.

Variation of Properties within Periods and Groups

1. **Variation of Metallic Character of the elements:** Generally, it may be noticed that in the periodic table the metallic character of the elements decreases from left to right progressing in the series but increase in moving vertically from top to bottom in the groups. The term “metallic character “is a rough and combination of a number of specific properties, such as electrical and thermal conductivities, metallic lustre, reducing properties...etc. Except the transition elements, the trend in the variation of metallic character of elements follows the above generalization. For instance, the most non-metallic elements, fluorine, chlorine, oxygen, sulphur, nitrogen are found at

the upper right of the periodic table where as the most basic metals, the alkali and alkaline earth metals are at the lower left of the table.

- 2. Variation in atomic size:** The atomic size in each succeeding element in a period decreases. When the succeeding electrons go in to the same energy levels they are subject to greater attraction by the increased nuclear charge and hence the elements in a series show gradual decrease in the atomic size. Vertically in the groups the succeeding elements increasing atomic radii. This is due to the fact that the additional electron occupies a new sub-level with a quantum number higher than those of already filled energy levels.
- 3. Variation in Ionic Radii:** It is obvious that the size of a positive ion will be less than that of atom from which it is formed. There is considerable decrease in size due to the loss of the outer most electron particularly in the case of alkali metals. Thus in the series, the decrease in the ionic sizes of Na^+ , Mg^{+2} , Al^{+3} and Si^{+4} appear to be considerable as compared to the atomic sizes of the parents atoms. It will also be seen that the greater the nuclear charge, the smaller is the ionic radius in series. In a given group of the periodic table positive ions of succeeding elements have larger ionic radii.

A simple negative ion formed by the addition of one or more electrons to the outer most energy levels of an atom, is expected to be much larger than the parent atom. In a given group the negative ions will have larger radii due to larger number of electron levels. The ionic sizes in a series also follow the same trend as in case of positive ions , i.e., the sizes decrease gradually from element to element.

- 4. Variation in the ionization potential:** Ionization potential is defined as the energy required to remove the outermost electron from an atom. In general, the greater the nuclear charge of atoms having the same number of electron orbit, the greater the ionization potential. Thus the ionization potential increases in a series and shows decreasing tendency with a group in the periodic classification.
- 5. Variation in Electronegativities:** The power of attraction that an atom shows for electron in a covalent bond (electronegativity) also shows periodic variations. The most electronegative elements are found towards the end of

the periods. Metal having low electronegativities are found at the beginning of the periods. Thus the alkali metals show gradually decreasing electronegativity values within the group. The halogens are most electronegative elements and the values decrease from fluorine to iodine.

- 6. Variation in the Oxidizing and Reducing Power:** Oxidizing substances have tendency to accept electrons and are converted in to lower oxidation states. The non-metals at the extreme right of the periodic table tend to act as oxidizing agents in chemical reactions with other substances. Similarly, reducing substances give up electrons and are converted in to higher oxidation state during chemical reaction. The reducing power is the highest with the metals at the beginning of the periods. Thus alkali metals have the greatest reducing power. In general, the reducing power of the elements is progressively lower as we pass across the periods and higher, as we go down the groups.

Usefulness of the Periodic Table

1. Classification of the elements.
2. Prediction of undiscovered elements.
3. Correction of atomic weight.
4. Periodic table in industrial research.

Limitation of the periodic Table

- 1. Position of hydrogen:** The position of hydrogen in the periodic table is left undecided. It has similarities in properties with both the alkali metals and halogens. According to the atomic number or atomic weight, hydrogen should occupy apposition just before helium. Hydrogen is a gas like fluorine and chlorine and forms compounds like **CH₄**, **SiH₄** which are like **CCl₄** and **SiCl₄** respectively. Even Solid hydrogen is a non-metal resembling iodine. The hydrogen molecule is diatomic like halogen. On the other hand, hydrogen resembles lithium and other alkali metals in having one electron $1s^1$ which can be lost in forming the hydrogen ion. Again, sodium hydride and sodium fluoride are both crystalline ionic solids, a point which shows similarity of

hydrogen with fluorine. But in most cases it assumes a +1 oxidation state. For this reason, hydrogen is usually included in group **IA** of the table.

2. Position of lanthanides (Rare Earths) and Actinides: The rare earths are also known as lanthanides. Lanthanide series are metals. On the other hand, the elements of actinide series are trans-uranium elements. The lanthanides elements have two outer most energy levels identically occupied by electrons which give them great similarities in properties. Similarly, the electronic configurations of the elements of actinides series have been found to very similar to that of lanthanides. Both of these groups of elements contain **f** energy levels which are being systematically filled. Thus, in lanthanide series, cerium to lutccium contains $4f^2$ to $4f^{14}$ and the actinide series of the $5f^2$ to $5f^{14}$ is being completed at lawrencium (**103**). Their compounds are very closely related to one another which involves tremendous difficulties in their separation. It may be assumed that these elements form a sort of bridge between the preceding and following elements. Thus, for the same reason, lanthanide and actinide series are generally omitted from the main table and placed at the bottom of the periodic table.

Diagonal relationships: Lithium of group **IA** resembles magnesium of group **IIA** in many respects contrary to its group properties. Similar relationship exists between the some other elements. Beryllium of group **IIA** shows similarity with aluminum of group **IIIA**. Boron of group **IIIA** shows likeness with silicon of group **IVA**. Thus the light elements of one group shows similarity in properties with the second elements of the following groups. This similarity is generally referred to as diagonal relationship in the periodic table as shown below:

Group	I	II	III	IV	V	VI	VII	0
Element	Li	Be	B	C	N	O	F	Ne
		↘	↘	↘	↘	↘	↘	↘
Element	Na	Mg	Al	Si	P	S	Cl	Ar

The diagonal relationship between the elements may be explained in terms of the:

1. Electropositive character of the elements. Although an element present in a given group is more electropositive than the corresponding element of the next higher group, the elements more electropositive in passing down the group. Thus, **Li** in group **IA** is more electropositive than **Be** in group **IIA**, but **Mg** is also more electropositive than **Be**. Thus, both **Li** and **Mg** are more electropositive than **Be** and less electropositive than **Na**. The other explanation is based on the
2. Sizes of the ions formed by the removal of valence electron. Thus, **Li⁺** ion is almost of the same size as **Mg⁺²** ion. Similarly, **Be⁺²** and **Al⁺³** ions have approximately the same ionic size. **B⁺³** and **Si⁺⁴** also present the same situation. Compounds having similar properties of the elements showing diagonal relationship are formed due to the effect of ionic sizes.

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Periodic trends in atomic, electronic configuration & Shielding

Inorganic Chemistry

2nd lecture

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2023-2024

PERIODIC TABLE OF THE ELEMENTS

<http://www.pertodni.com>

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7	7	223 Fr FRANCIUM	226 Ra RADIUM	227 Ac ACTINIUM	232.04 Th THORIUM	238.03 Pa PROTACTINIUM	244 Pu PLUTONIUM	244 Am AMERICIUM	243 Eu EUROPIUM	151.96 Gd GADOLINIUM	157.25 Tb TERBIUM	162.50 Dy DYSPROSIUM	164.93 Ho HOLMIUM	173.05 Yb YTERBIUM	174.97 Lu LUTETIUM	223 Fr FRANCIUM	226 Ra RADIUM	227 Ac ACTINIUM	232.04 Th THORIUM	238.03 Pa PROTACTINIUM	244 Pu PLUTONIUM	244 Am AMERICIUM	243 Eu EUROPIUM	151.96 Gd GADOLINIUM	157.25 Tb TERBIUM	162.50 Dy DYSPROSIUM	164.93 Ho HOLMIUM	173.05 Yb YTERBIUM	174.97 Lu LUTETIUM	

RELATIVE ATOMIC MASS (1)

GROUP IUPAC

GROUP CAS

ATOMIC NUMBER

SYMBOL

ELEMENT NAME

STANDARD STATE (25 °C; 101 kPa)

Ne - gas
Hg - liquid
Fe - solid
Ts - synthetic

Legend:

- Metal
- Semimetal
- Nonmetal
- Alkali metal
- Alkaline earth metal
- Transition metals
- Lanthanide
- Actinide
- Chalcogens element
- Halogens element
- Noble gas

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Modern periodic list:

The modern periodic list relies on two characteristics for arranging the elements:

- 1- Similar characteristics in the elements in the same column (family characteristics).
- 2- The elements in a row or line are arranged according to atomic number and not according to atomic weight, from smallest to largest.
- 3- All elements written in **black** are solids at room temperature.
- 4- All elements written in **red** are liquid elements/substances at room temperature.
- 5- All elements written in **blue** are gaseous elements/substances at room temperature.
- 6- All items written in **blank font (white)** are manufactured items.

1- الصفات المتشابهة في العناصر المتواجدة في العمود الواحد (صفات العائلة). وتمثل (المجموعة أو الزمرة).

2- العناصر في الدور او السطر الواحد ترتب حسب العدد الذري وليس حسب الوزن الذري من الأصغر الى الأكبر. وتمثل (الدورة).

3- كل العناصر المكتوبة باللون الاسود هي عناصر/مواد صلبة في درجة حرارة الغرفة.

4- كل العناصر المكتوبة باللون الأحمر هي عناصر/مواد سائلة في درجة حرارة الغرفة.

5- كل العناصر المكتوبة باللون الأزرق هي عناصر/مواد غازية في درجة حرارة الغرفة.

6- كل العناصر المكتوبة بالخط المفرغ (اللون الأبيض) هي عناصر مصنعة.

Periodic trends in atomic & electronic configuration

General introduction

Inorganic chemistry is concerned with studying the properties of more than a hundred elements in their different states within the periodic table (the number of which has **reached 118** so far) and their compounds and complexes, as well as their applications in various fields that are in direct contact with human life and daily activities. Many attempts have been made to classify elements in different ways, but the most common and widely used is what the scientist Mendeleev arrived at in 1869, according to which he demonstrated that the general properties of elements are related to their electronic configuration and atomic weights.

Mendeleev arranged the elements into vertical groups, in which the elements **have the same number of electrons in their outermost energy orbitals, and into horizontal rotations, in which the elements have the same principal quantum number (n).**

Electronic Structure and Periodic Table

The periodic table consists of eight main numerical groups (groups, columns) and seven horizontal periods (periods).

1- Short Periods

a- First short periods (n=1)

This period consists of only **two** elements **He₂, H₁** and this period is filled with only two electrons.

b- Second short periods (n=2)

This period consists of **eight** elements and is filled with only eight electrons.

2 nd period = Li(3) → Ne (10).

c- Third short period (n=3)

This period is filled with only **8** electrons, which means that it consists of eight elements.

3 nd period = Na(3) → Ar (18).

2- Long periods

a- first long period or fourth period

This period consists of **18** components.

4 th period = K(19) → Kr (36).

b- Second long period or fifth period

This period consists of **18** components.

5th period = Rb(37) → Xe (54).

c- Third long period or sixth period

This period consists of **36** components.

6th period = Cs(55) → Rn (86).

d- Forth long period or 7th period

This period consists of **32** components.

Fr(87) → Ha (105)

"Main group elements" (group and columns)

The periodic table groups are divided into eight main groups, and at the same time they are divided into two secondary groups or two secondary categories, called group **A** and group **B**. The elements in the periodic table are divided into:

1- Noble gases VIII

These elements are represented by the eighth group (VIII A), also called the zero group elements, as these elements are distinguished by the fact that all their shells are completely filled with electrons and their location is at the far end of the periodic table.

2- Representative elements

These elements have secondary shells that are unsaturated with electrons of the **S** and **P** type, represented by groups, in which the **S** shell is not filled with electrons and these elements behave as metals, while the secondary shell of the **P** type is not filled with electrons for the group elements, some of which behave as nonmetals and the other part as metalloids.

In other words (it has internal energy levels that may be filled with electrons to their maximum capacity and is divided into two groups [Noble gas] nS^{1-2}).

A- Alkali metals (elements)

B- Alkali earth elements

Because the outer shell is not saturated. If electrons are added to the **S** shell, then the first is called the **S-block elements group** (alkaline and alkaline earth). Or a group of pre-transition elements. If the addition to the secondary

shell is **P**, then the other is called a group of P-block elements, or post-transition elements.

Alkali earth elements

As for the **third** group, it begins with the element boron (**B**) and ends with the element thallium (**Th**).

As for the **fourth** group, it begins with carbon (**C**) and ends with lead (**Pb**).

As for the **fifth** group, it begins with the element nitrogen (**N**) and ends with the element bismuth (**Bi**).

3- Main Transition Elements

These elements are divided into:

A- First transition elements series.

B- Second transition elements series.

C- Third transition elements series.

These elements are represented by groups (**IB-VIIIB**) that have an outer secondary shell type (**d**) that is not completely filled with electrons. These elements are placed in the middle of the periodic table, and they are all metals.

Inner Transition Elements

The internal transition elements are called f-block elements, these elements have a secondary shell type and consist of **14** elements and their outer shell contains sublevels of the type f, d, s (ns , $(n-1)d$, $(n-2)f$) and the **f** orbitals are not filled. It consists of two families or classes: the lanthanides and actinides which are placed at the bottom of the periodic table.

How to write an Electronic Configuration

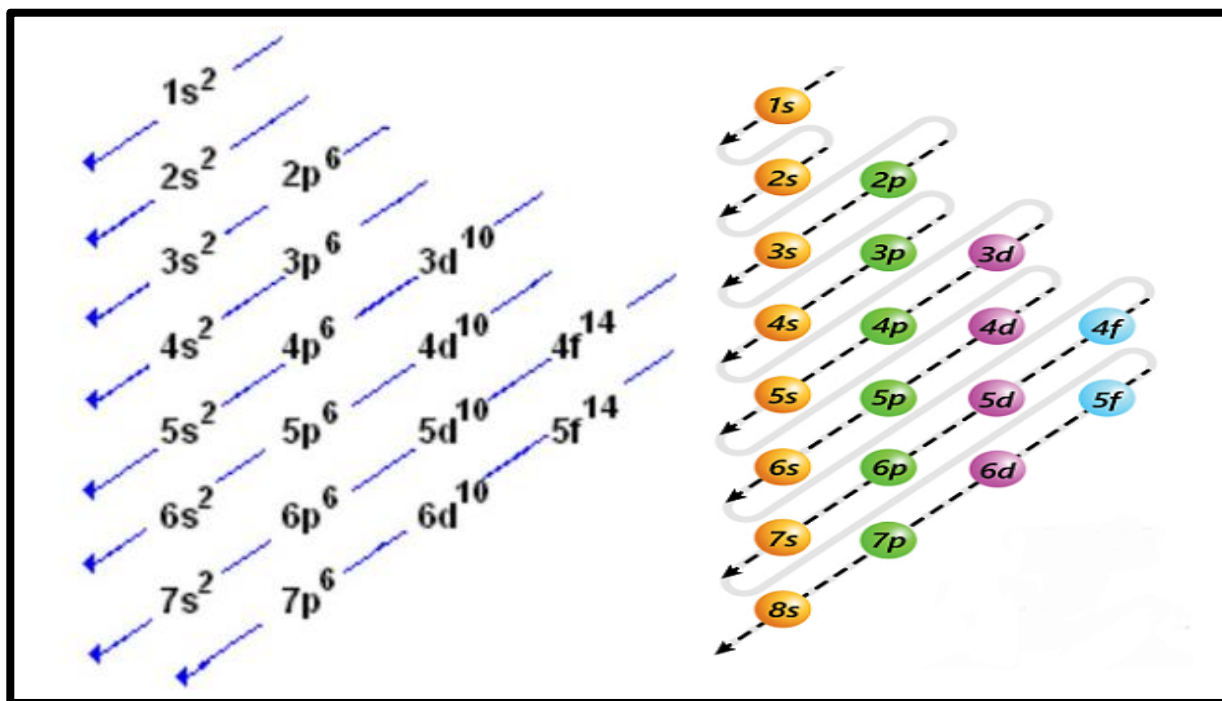
Basically, **three rules** are required to write a correct electron configuration:-

- 1-** The Aufbau Principle.
- 2-** Pauli Exclusion Principle.
- 3-** Hund's Rule.

Firstly: Aufbau Principle or the upward construction principle

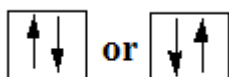
Electrons enter the lower energy sublevels first and then fill the higher ones after that.

Note: The energy of the orbital increases with increasing quantum number. The principal quantum number, often written **n**, represents the energy of the orbital and its distance from the nucleus.

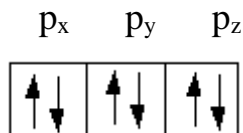


Pauli's Rule: If in the same atom, no two electron can have the same set of quantum numbers

There is only one orbital in the **n=1** quantum shell, from Pauli Exclusion Principle, a maximum of two electrons can be accommodated in it. Using the symbol of **S** orbital with maximum number of electron can be written as **1S²** or **1S^{↑↓}** represented box (or square) and arrow as:



Thus, the three orbitals in a **P** subshell can accommodate six electron, **nP⁶** (**nP_x², nP_y², nP_z²**) or (**nP_x^{↑↓}, nP_y^{↑↓}, nP_z^{↑↓}**) or using the Box and arrow as:



The five and seven orbitals in **d** and **f** subshells can accommodate a total of ten and fourteen electrons respectively:



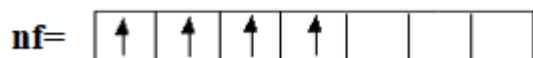
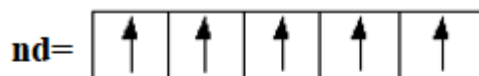
There is one orbital in the quantum shell $n=1$, according to the Pauli Exclusion Principle, the maximum number of electrons that can occupy or inhabit that single orbital is two electrons.

Hund's Rule of Maximum Multiplicity

Hund's rule requires that electrons be distributed unpaired into independent orbitals of equal energy as much as possible.

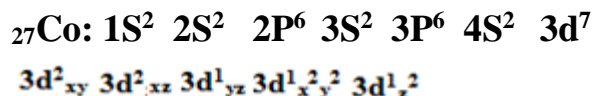
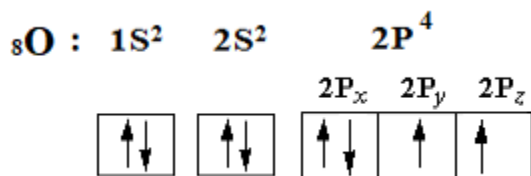
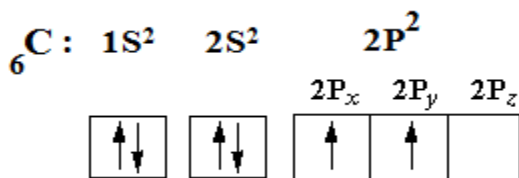
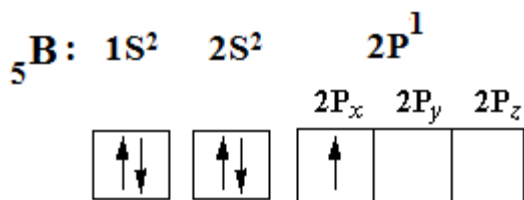
The reasons that led to the formulation of this rule can be understood by understanding the force of electrostatic repulsion that exists between negatively charged electrons. The repulsion between electrons that occupy different regions of space (or orbitals separated from each other) weakens or decreases, while the electrostatic repulsion between paired electrons that occupy the same space or region of space (i.e., they occupy the same orbital) strengthens or increases.

Electron configuration according to Hund's rule:-



The decrease in electrostatic repulsion between electrons results in a reduction in the energy content of the atom.

Examples of Pauli's Rule & Hund's rule



Since the electrons are distributed individually, then the sixth electron is paired, and then the seventh electron is in the **d** orbital.

Covalent electrons

They are the electrons in the outer orbit that participate in the bonding process. If the **outer orbit is saturated**, the atom is stable and chemically inert, as in the inert elements such as **helium** and **neon**.

If the **outermost orbital of the electrons is not saturated**, the atom is **unstable** though being **electrically neutral**, it tends to **reach a state of stability** by **granting or gaining**.

Neighboring atoms share valence electrons to reach a saturated state and thus bond atoms with each other.

For **S** section, then the period number = n for the outer shell **S**.

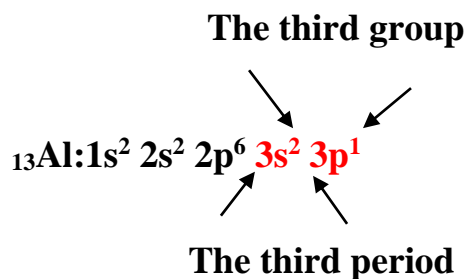
For the **P** section, the period number = n for the outer shell **P** and outer **S**.

For the **S** section, the group number = the number of outer **ns** electrons

For the **p** section, the group number = the number of outer **ns** electrons + the number of outer **np** electrons.

Examples:

The third group results from the collection of **3s**, **3p** electrons.



Group=2+1 the total number of electrons in **S** and **P=3**.

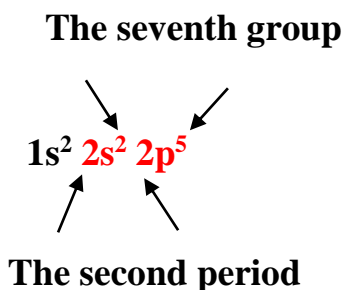
- The **p** section because it ends with the outer p envelope

Examples for determining period and group

- Various examples of identifying the period, group, and section of an element:

Determine the period, group, and section or period of the element whose atomic number is **F₉**.

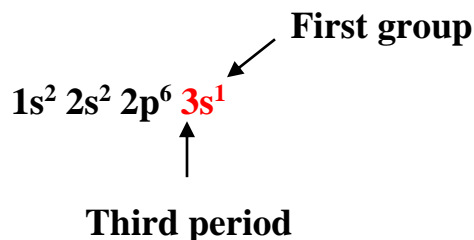
- The seventh group results from the addition of valence electrons 5+2.



This element is in the second period because it ends with the principal quantum number **2**. It also falls within the seventh group (A VII A) due to the presence of seven electrons in the shell parity it is also located in the **P** section, where the element's valence electrons are located in addition to it ended with section **F**.

Determine the period, group, and sector of the element whose atomic number (**Z**) is:

- **11 Electronic arrangement:**
- **The first group and third period**



This element is located in the **third period** because it ends with a principal quantum number **3**.

It also occurs in the first group (IA): due to the presence of one electron in **3s**. The **S** section is where the valence electron of the element is located where the valence electron is located for the element as well ended with orbital **s**.

Shielding or Screening

If Bohr's laws were reviewed in calculating the speed of the electron.

$$mvr = \frac{nh}{2\pi}$$

$$v = \frac{nh}{2\pi mr}$$

(The energy of the electron in the orbit) $E_n = \frac{2\pi^2 me^4 z^2}{n^2 h^2}$

$$\Delta E = \frac{2\pi^2 me^4 z^2}{h^2} (1/n_1^2 - 1/n_2^2)$$

$$n_2 > n_1$$

But if we assume that the electron completely left the atom, then $n_2 = \infty$ and ΔE in this case corresponds to the ionization energy.

Ionization energy: It is the least energy required to completely displace or remove an electron from an atom and convert it into a positive ion. This energy is measured in energy units K J mole^{-1} , K cal mole^{-1} .

$$1\text{eV} = 23.6 \text{ K cal.mole}^{-1} = 96.49 \text{ K J mole}^{-1}$$

In the hydrogen atom, the value of $n = 1$, and thus the numerical value of the ionization potential of the hydrogen atom can be found according to the same law.

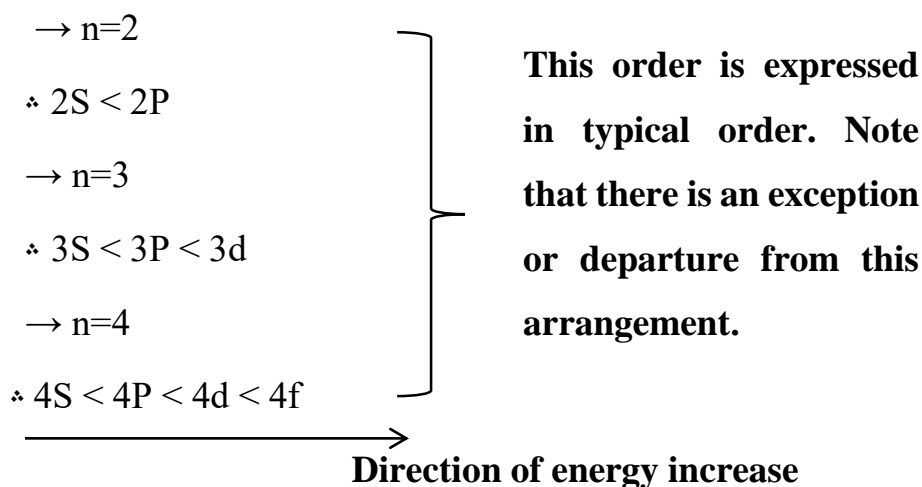


$$\text{IpH} = 13.6 \text{ eV}$$

$$\text{IpLi} = \text{IpH} \times Z^{*2} / n^2$$

$$\text{IP} = \frac{2 \pi^2 (1.6 \times 10^{-19})^4 \times 9.11 \times 10^{-31} (1)^2}{(1)^2 (6.626 \times 10^{-34})^2}$$

Shielding: The reduction of true nuclear charge (Z) by inner electron or orbitals to the effective nuclear charge (Z^*) that experiences by outer electrons or orbitals is called **Shielding** or **Screening**. For a given principle quantum number (n), S orbital is least screened or shielded and has the lowest energy; P, d, and f orbitals have successively higher energy.



It was stated above indicates the diversity of the energies of the secondary shells of a particular primary shell in the multi-electron atom [Such as ${}_6\text{C}$, ${}_7\text{N}$, ${}_8\text{O}$]. There is no variation in the energies of the secondary shells of excited atoms and hydrogen ions due to the complete lack of blocking in single-electron systems.

Shielding Constant (S)

In general, the ionization potential of the second atom is higher than the ionization potential of the first atom, and the ionization potential of the third atom is higher than the ionization potential of the second atom, but it has been found in practice that the ionization potential of **Li** is **5.7 eV**, i.e. much lower than the ionization potential of hydrogen, and it is the correct value for the following reasons:

- 1- That the last electron of lithium is located in the **2S** orbital or **n = 2**, and this means that it is farther from the nucleus than the electrons located in the **1S** orbital or **n = 1**, which are closest to the nucleus, so the attraction of the nucleus on the ions of the outer shell located in **2S** is weaker than the attraction of the hydrogen atom. For the outer electron located in **1S**, that is, the energy required to lift the electron is less than the energy required to remove an electron in the hydrogen atom.
- 2- The nucleus of the lithium atom, which is **Z=3**, is surrounded by two **1S²** electrons revolving around the nucleus, which leads to blocking the charge of the nucleus from the third electron located in **2S¹**, meaning that the effect of the charge of the nucleus on the last electron is less than it is with **2S¹** electrons, so the nucleus' attraction to this electron is less. The energy required to remove the electron becomes low, and S orbital electrons are generally considered to be the most sensitive to the charge of the nucleus, or in other words more capable of blocking the charge of the nucleus than the rest of the other electrons. Also, the blocking of **1S** electrons is higher than the blocking of **2S** electrons.

←————— **Increase of shielding**
S > P > d >

- 1- Increase of sensitivity towards nuclear charge (**Z***).
- 2- Increase of attraction toward nuclear charge.
- 3- Increase of shielding or screening (**S**).

This means that what affects the electrons as their atomic number increases is not the total charge of the nucleus (**Z**), which represents the atomic number, but rather the amount of this charge that reaches the electron and is called the effective charge. We call it Effective nuclear charge, which is the

charge that reaches. The electron after some or a percentage of it is blocked by the electrons in the inner shells, that is, after blocking. The effective charge can be calculated from the scientist Slater's equation:

$$Z^* = Z - S$$

Where :

$$Z^* = Z - S.$$

Z^* = effective nuclear charge.

Z = Total nuclear charge (atomic no.)

S = Shielding or Screening constant.

The Effective Nuclear Charge (Z^)*

H is the actual nuclear charge that a particular electron experiences. Effective nuclear charge depends on the numerical values of (n) and (ℓ) of the electron of interest, because electrons in different shells and subshells approach the nucleus to different extents. The effective nuclear charge is sometimes expressed in terms of the true nuclear charge (Z) and an empirical shielding constant ;by the writing:

$$Z^* = Z - S$$

Note that the experimental blocking constant varies depending on the secondary shell or the type of orbital.

$$\begin{array}{c} \text{Shielding increases} \\ \leftarrow \\ S > P > d > f \\ \rightarrow \\ \text{Shielding decrease} \end{array}$$

It can be said that the closer the electron is to the nucleus, the relatively high the effective or actual nuclear charge it senses. The reason for this is due to the diversity of the distances between the various electrons and the nucleus, as well as to blocking by the electrons themselves.

For the purpose of understanding many topics related to the blocking constant, such as atomic size, electronegativity, and ionization energy, the scientist Slater developed a set of preliminary rules to estimate the extent of the approximate blocking of electrons. These rules can be summarized in the following points:

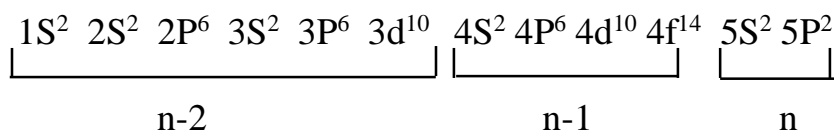
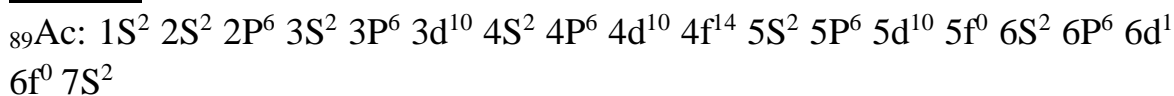
To calculate the blocking constant **S** for an electron located in the **ns** or **np** secondary level, we follow the following steps:

1. The electron configuration of the element is written from left to right according to the following order. This order is called the **Slatter order**.
 2. If the electrons that belong to any group are located to the right of the electron for which the blocking constant is to be calculated, they do not contribute to the value of the blocking constant, or in other words, the value of the blocking constant has = **zero**.
 3. The electron belongs to the same main shell of the **ns** or **np** type to block the electron for which the blocking constant is to be calculated as **0.35**.
 4. Every electron belonging to the **n-1** main shell blocks the electron for which the blocking constant is to be calculated, with an amount of **0.85**.
 5. Every electron belonging to the main shell of type **n-2** or less is completely blocked, that is, by an amount = **1**.
- a- To calculate the blocking constant for an electron located in the secondary level of the **nd** or **nf** type, all electrons that are located to its left are completely blocked, that is, by one amount, and that are located within the same level. The level is blocked by **0.35**, or in other words, to calculate the blocking constant for an electron located in the secondary level of the **nd** or **nf** type, we use all the previous points except points **4.5**, which become as follows:

All electrons located in the groups to the left of the **nd** or **nf** group block the orbital with its blocking constant by an amount equal to **1**, that is, they are completely blocked.

Example: Calculate the effective nuclear charge for the nuclear charge for the electron no. 64 for the Ac element.

Solution

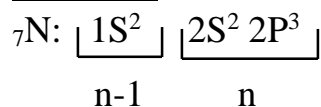


$$S = 3 \times 0.35 + 32 \times 0.85 + 28 \times 1 = 44.35$$

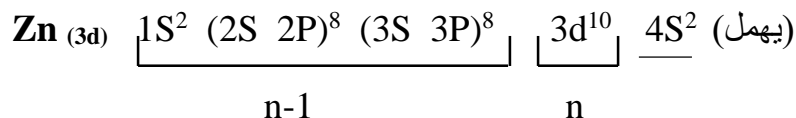
$$Z^* = 89 - 44.35 = 44.65.$$

Example: Find the effective nuclear charge on the last electron in the following elements and ions, ${}^7\text{N}$, ${}^{30}\text{Zn}$, ${}^{51}\text{Sb}$, ${}^{26}\text{Fe}^{+2}$, ${}^{22}\text{Ti}^{+2}$, ${}^{29}\text{Cu}$.

Solution:

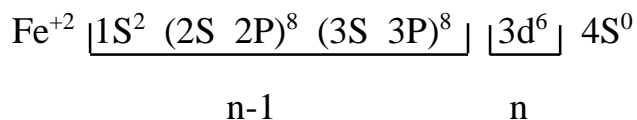
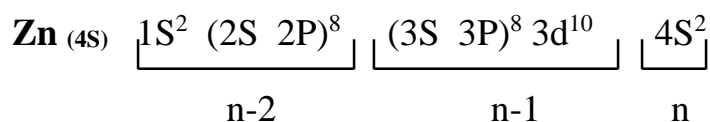


$$S = 4 \times 0.35 + 2 \times 0.85$$

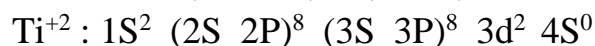


$$Z^* = Z - S$$

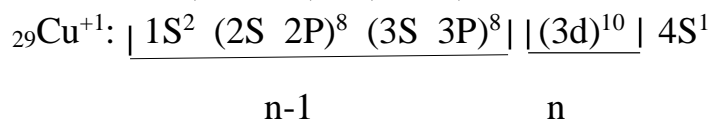
$$Z^* = 30 - 21.15 = 8.85$$



$$S = (5 \times 0.35) + (18 \times 1)$$



$$S = (1 \times 0.35) + (18 \times 1)$$



$$S = (0 \times 0.35) + (18 \times 0.85) + (10 \times 1)$$

✚ Which of the following pairs has the highest Ip and why?

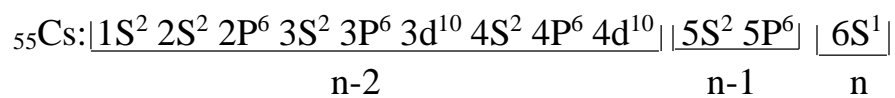
a- Li or Cs

Solution:

$${}^3\text{Li}: 1\text{S}^2 2\text{S}^1 \quad S = 0 \times 0.35 + 2 \times 0.85 = 1.7$$

$$Z^* = Z - S = 3 - 1.7 = 1.3$$

$$\begin{aligned} I_{p\text{Li}} &= I_{p\text{H}} \times (Z^*)^2 / n^2 = 13.6 \times (1.3)^2 / (2)^2 \\ &= 5.7118 \text{ eV.} \end{aligned}$$



$$S = 0 \times 0.35 + 8 \times 0.85 + 46 \times 1 = 52.3$$

$$Z^* = Z - S = 55 - 52.3 = 2.7$$

$$\begin{aligned} \text{Ip}_{\text{Cs}} &= \text{Ip}_{\text{H}} \times (Z^*)^2 / n^2 = 13.6 \times (2.7)^2 / (6)^2 \\ &= 2.754 \text{ eV.} \end{aligned}$$

b- Li or F }
c- Cs or F } **Home work**

Prof. Dr. Mahasin Faisal A. Alias

Periodic trends in atomic, electronic configuration & Shielding

Inorganic Chemistry

3rd lecture

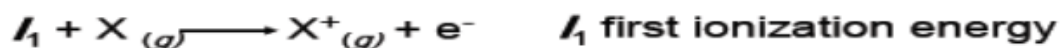
Prof. Dr. Mahasin Faisal A. Alias

2023-2024

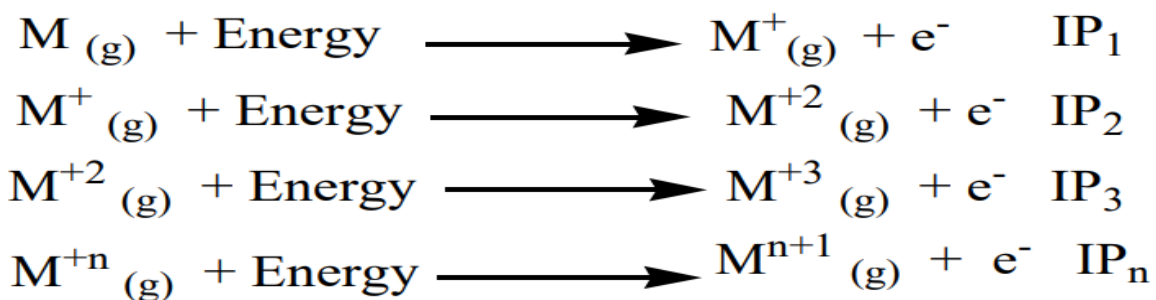
General and periodic properties of the main elements

- **Potential ionization (IP):** It is defined as the lowest energy It is necessary to remove an electron from an atom in the gaseous state. The voltage value increases Ionization, in cycles, by increasing the atomic number due to the decrease in the diameter of the atom, the attractive forces between the nucleus and the valence electrons increase due to the constant quantum number. The main one is to increase the charge of the acting nucleus.
- In the group, the value of the ionization potential decreases with increasing atomic number due to the increase in half diameter, increasing the number of levels, i.e. increasing the principal quantum number and thus reducing the attraction between the nucleus and the outer electrons or valence electrons.
- **Ionization energy:** the minimum energy required to remove an electron from an atom in gas state.
- As for the saturated element, it is very stable, so that the resulting repulsive energy. The amount of pairing of electrons is less than the energy required to dislodge an electron from the valence shell.
- **When comparison (مقارنة) the ionization potential of nitrogen (N) and oxygen (O),** we notice a decrease the value of the ionization potential for oxygen compared to nitrogen due to energy the repulsion that occurs between the extra electron and the half electrons Saturated (couple energy) leads to reduced stability and thus Losing the fourth electron in orbital **P** is easy, according to... Oxygen, while nitrogen, is half saturated, so it is stable for this reason its ionization energy is high, and the same is the case with beryllium and boron also.

Ionization potential sequence



The ionization energy required to remove one electron from a gaseous atom is called the first ionization energy (IP₁). Ionization required to extract the second electron with the second ionization energy (IP₂) and so on.



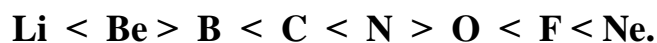
It has been observed that the ionization energy increases according to the following order:

$$\text{IP}_1 < \text{IP}_2 < \text{IP}_3 < \text{IP}_4 \dots\dots\dots \text{IP}_n$$

The value of ionization energy depends on the following factors:

- The amount of effective nuclear charge, which in turn depends on the extent of blocking of other electrons.
- The distance between the electron and the nucleus, or in other words, the length of the most probable radius for this electron.
- The extent of permeability of the electron to the electron cloud to other electrons, as the permeability of electrons decreases in this direction:
S > p > d > f.
- The amount of charge of the positive ion, as the ionization energy increases with the increase in charge of the positive ion.

The following figure gives a simplified explanation that the ionization potential decreases in a single group with an increase in the atomic number, while the ionization potential in a single cycle increases as the atomic number increases as a result of the contraction of the sizes of atoms in a single cycle as a result of the increase in the effective nuclear charge. **with the exception of elements that contain saturated shells or half saturated.**



Determination of Ionization energy

$$E_n = -2\pi^2 m e^4 z^2 / n^2 h^2 \dots \text{ H, He}^+, \text{Li}^{+2}$$

$$E_n = -2\pi^2 m e^4 z^2 / h^2 \dots \text{when } n=1$$

when $z \& n=1$

$$E_n = -2\pi^2 m e^4 / h^2$$

$$\Delta E = IP = 2\pi^2 m e^4 z^2 / n^2 h^2$$

Ionization Energy

- Example.
- Calculate the ionization energy of B^{+4} .
- Ionization energy = 1310 KJ/mol (Z_{eff}^2/n^2)
- So we can measure Z_{eff} .
- The ionization energy for a 1S electron from sodium is.
- 1.39×10^5 KJ/mol.
- The ionization energy for a 3S electron from sodium is.
- 4.95×10^2 KJ/mol.

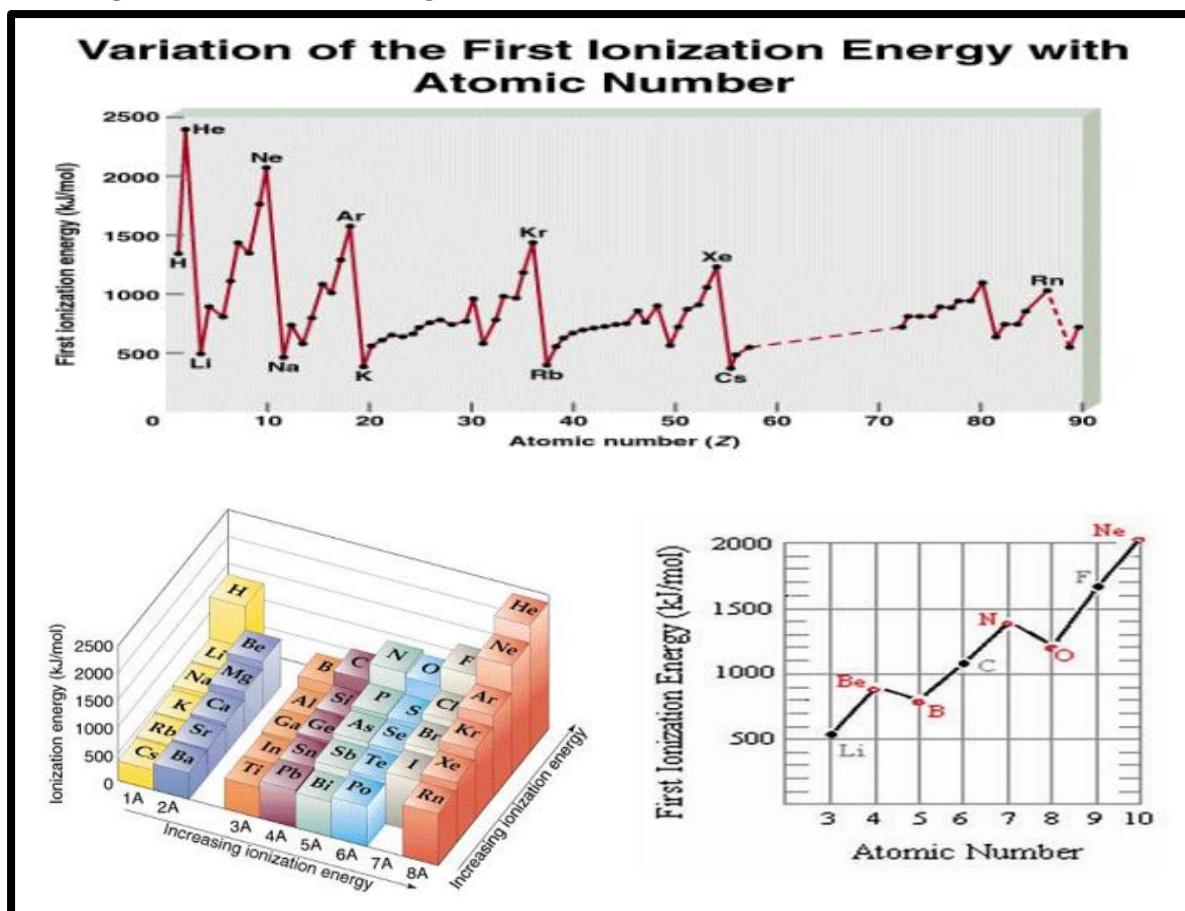
Computed and calculated values of Ground-state, 1st and 2nd ionization energies

Element	Computed values			Experimental values [4]	
	Ground State	1st Ionization energy	2nd Ionization energy	1st Ionization energy	2nd Ionization energy
Hydrogen	-8.4	8.4		13.6	
Helium	-77.64	31.4	46.2	24.6	54.4
Lithium	-183.66	3.4	86.7	5.4	75.6
Beryllium	-388.38	10.9	12.6	9.3	18.2
Boron	-654.16	10.8	25.9	8.3	25.2
Carbon	-1006.82	13.0	16.4	11.3	24.4
Nitrogen	-1455.46	15.9	23.6	14.5	29.6
Oxygen	-2008.56	16.1	31.4	13.6	35.1
Fluorine	-2676.80	23.2	40.0	17.4	34.9
Neon	-3470.44	31.1	49.2	21.6	40.9

Computed and calculated effective nuclear charge of the first ten elements of the periodic table

Element	Atomic number, Z	Effective nuclear charge Z^* (Computed)	Effective nuclear charge [5]
Hydrogen	1	0.849	1
Helium	2	1.844	1.6875
Lithium	3	2.937	2.9606
Beryllium	4	3.538	3.6848
Boron	5	4.39	4.6795
Carbon	6	5.135	5.6727
Nitrogen	7	5.877	6.6651
Oxygen	8	6.614	7.6579
Fluorine	9	7.351	8.6501
Neon	10	8.084	9.6421

The first ionization potential varies with atomic numbers:



Electron Affinity (EA)

It is defined as the change in energy as a result of the atom (in the gaseous state) gaining an electron to form an ion this energy is equal to the ionization energy of the resulting negative ion.



- i-** Its value increases in one cycle from left to right, and the reason is that electrons are easily attracted towards nucleation means an increase in the effective charge of the nucleus due to the tendency of atoms to fill their orbitals with electrons.
- ii-** The electronic affinity values in each group (group) decrease from top to bottom because electrons the outermost orbitals are less connected because the acting nucleus charge is less due to the increase in number Envelopes, i.e. the principal quantum number.
- iii-** Halogens have the highest value of electronic affinity, and the reason is that they lack one electron to reach to place inert elements, as their effective charge is high and their volume is small.
- The electron affinity energy (E_A) for the nitrogen group is also small because it has a half shell it is saturated, which leads to repulsion between the gained electron and the electrons in the **P** shell.

In one period ${}_9\text{F} > {}_8\text{O} > {}_7\text{N} > {}_6\text{C} > {}_5\text{B}$
←
Electron affinity increased

In one group ${}_3\text{Li} > {}_{11}\text{Na} > {}_{19}\text{K} > {}_{37}\text{Rb}$
←
Electron affinity increased

Always the energy of familiarity first E_A Negative sign: any emitter of heat other than elements Noble elements and elements of the second group **IIA** due to the saturation of their outer shell.

The second and third electron affinities are positive in sign, i.e. endothermic because of the repulsion that occurs between the added electron and the negative ion.

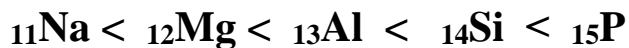


- The value of electron affinity is always less than the value of electronegativity for the element itself because adding an electron to a neutral atom frees up less energy than that added to the positive ion.
- The electronic affinity of the nitrogen ${}_7\text{N}$ group elements low because they have semi-saturated shells, which leads to repulsion the gained electron and the electrons in the shell **np** single.

Electronegativity

- **Electronegativity EN: It is a measure of the tendency of an atom in a molecule to attract electrons towards it in the chemical bond.**
- Electronegativity increases in spins, with increasing atomic number, due to decreasing radius the atom, the increase in the acting nucleus charge, and the forces of attraction as a result of the principal quantum number being constant and increasing number of electrons. Electronegativity decreases in the group due to the increase in atomic number, as a result to increase the radius of the atom, and reduce the forces of attraction between the nucleus and electrons the highest electronegativity is the group of halogens, specifically fluorine **F**. The tendency of the element increases gaining electrons, especially halogens, to saturate their outer shell, while the negativity decreases electronegativity of alkaline and alkaline earth elements because they tend to lose electrons to reach the saturated ranking.

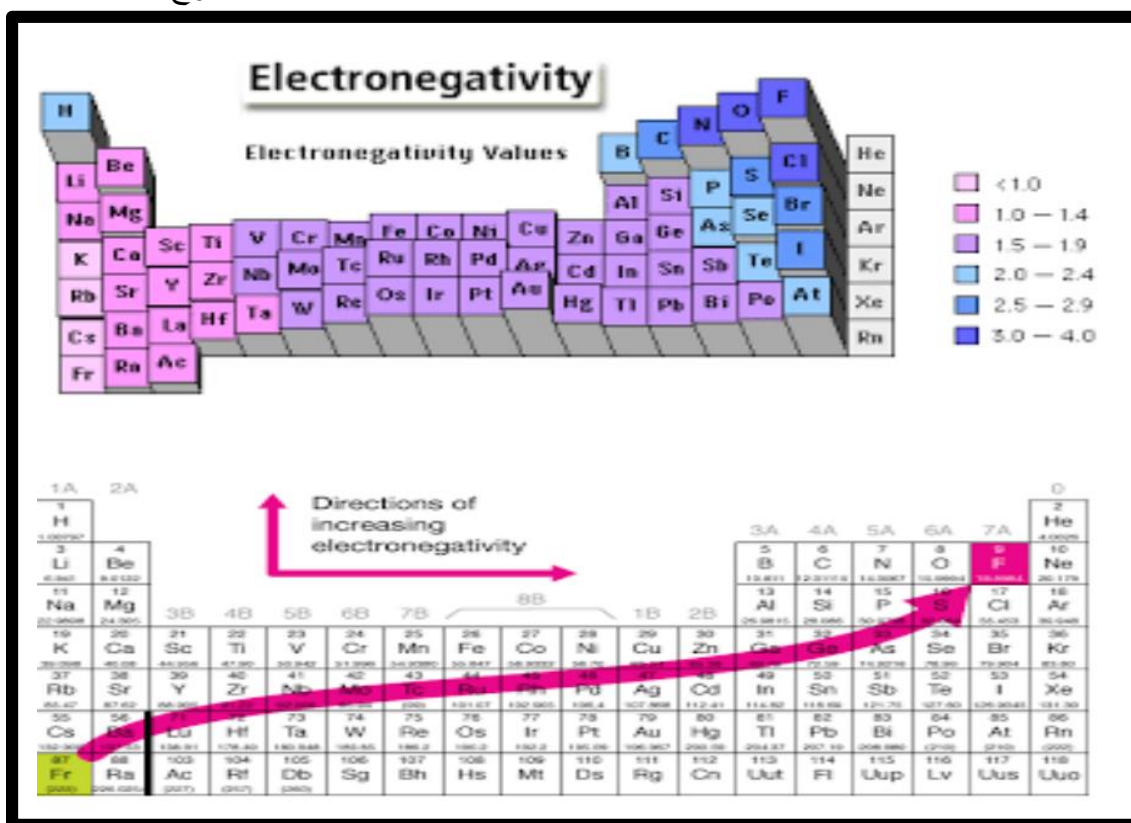
- **Note:** The least electronegative element in the periodic table is cesium Cs.



→
Increased of Electronegativity

E_N : depend on

1. نق ذ (الحجم) عكسي
2. Z^* طردي
3. شحنة الأيون $Z +$ عكسي
4. طبيعة وعدد الذرات
 $\text{PCl}_5 > \text{PCl}_3$
 $\text{FeCl}_3 > \text{FeCl}_2$
5. نوع التهجين



If the difference in electronegativity between the two bonded atoms in a molecule is large, then the bond formed between them has an ionic character, and if the difference is small in electronegativity, the bond formed between them is covalent.

How to calculate electronegativity

1- Mulliken Method.

- It is considered the oldest method of calculating electronegativity, which is based on the idea The electronegativity **EN** of an element is the average of two energies (Ionization energy (IP) and electron affinity energy (EA) according to the following relationship:

$$EN = 1/2(IP + EA) \quad \text{حفظ}$$

Where **EA**, **IP** and **EN** represent the atom in its valence state and not in its valence state the single. Since the valence state of the atom varies with different molecules in which the atom is included, the electronegativity values of the atom in question the calculation by Mulliken's method varies from one molecule to another.

Ex: The I.E. of Be is more than that of B though the nuclear charge of boron atom ($Z=5$) is greater than that of beryllium atom ($Z=4$). This can be explained as follows:

Boron atom ($Z=5$, $1S^2 2S^2 2P_x^1 2P_y^0 2P_z^0$) is having one unpaired electron in the 2p-subshell. **Be-atom** ($Z=4$, $1S^2 2S^2$) is having paired electrons in the 2s-subshell.

As the fully filled 2s-subshell in **Be-atom** is more stable than **B-atom** due to symmetry. More energy would be needed to remove an electron from **Be-atom**. Hence. **Be** has high I.E.

2- Pauling method

- This method is the most widely applied because it relies on the energy of covalent bonds between two combined atoms **A-B**. The bond energy is represented by the symbol **D_{AB}**, which is higher than the energy of the joint calculated on the basis of the arithmetic average or the geometric mean of the bonds **B-B**, **A-A**, which are symbolized by **D_{AA}**, **D_{BB}**.
- If we use the arithmetic average, the axis energy equation **D_{AB}** can be written

As follows:

$$D_{AB} = 1/2[D_{AA} + D_{BB}] + \Delta_{AB} \quad \text{حفظ}$$

- Where Δ_{AB} represents the ionic resonance energy, as Pauling called it, and it increases the greater the difference in electronegativity between the two atoms involved in bond formation.
- By studying a large number of diatomic molecules, Pauling showed that it is possible to calculate the energy Δ_{AB} from the following equation:

$$\Delta_{AB} = 23.06(EN_A - EN_B)^2 \quad \text{by eV unit.} \quad \text{حفظ}$$

It can be written as:

$$EN_A - EN_B = 0.208 \sqrt{\Delta_{AB}} \quad \text{حفظ}$$

Where EN_A is the electronegativity of atom A
 EN_B Electronegativity of the atom B.

There is a relationship between the EN values of the elements measured by Pauling's method EN_P It is measured by Mulliken's EN_M method:

$$EN_P = 0.336 (EN_M - 0.615) \quad \text{رابط العلاقة بين الطرفين (حفظ)}$$

The following example shows how to calculate Δ_{AB} in a molecule ClF using the mean method.

$$D_{Cl-Cl} = 57.3 \text{ kcal.mol}^{-1}$$

$$D_{F-F} = 37.0 \text{ kcal.mol}^{-1}$$

$$D_{Cl-F} = 47.2 \text{ kcal.mol}^{-1} \quad \text{theoretically}$$

$$D_{Cl-F} = 59.5 \text{ kcal.mol}^{-1} \quad \text{practically}$$

By application as follows:

$$D_{AB} = 1/2 [D_{AA} + D_{BB}] + \Delta_{AB}$$

$$D_{Cl-F} = 1/2 [D_{Cl-Cl} + D_{F-F}] + \Delta_{Cl-F}$$

$$59.5 = 1/2 [57.3 + 37.0] + \Delta_{Cl-F}$$

$$\Delta_{Cl-F} = 12.3 \text{ kcal.mol}^{-1}$$

Radii

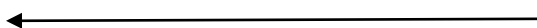
A- Atomic radii

Atomic radius (n): is the distance between the centers of the nucleus the last outer shell of the atom and can be designated as the atom by X-ray diffraction and spectroscopic methods. it was found that many physical properties, such as density, boiling point, and melting point, are related to the sizes of atoms, and since it is not possible to isolate atoms as single atoms, the atomic radius was measured indirectly by measuring the distance between the nuclei of two atoms bonded together in gas molecules or between the nuclei of two ions in gas molecules. Solid state (crystal).

It has been observed that the atomic radius increases with the increase in the atomic number of the elements of one group as we move from top to bottom due to the increase in the number of secondary shells, while the atomic radius in one group decreases with the increase in the atomic number, that is, as we move from left to right due to the increase in the nuclear charge affecting the molecules. In which the number of secondary shells remains constant.

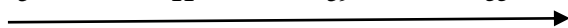
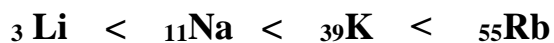
And the elements of the periodic table.

- 1- The radius of the elements of one period decreases as the atomic number increases because of the steady increase in Z^* while the value of n is constant.



The radius increases

- 2- The n of elements in one group increases with increasing atomic number this is because the number of shells increases, meaning the main quantum number increases the nucleus's attraction to electrons decreases, and the size increases.

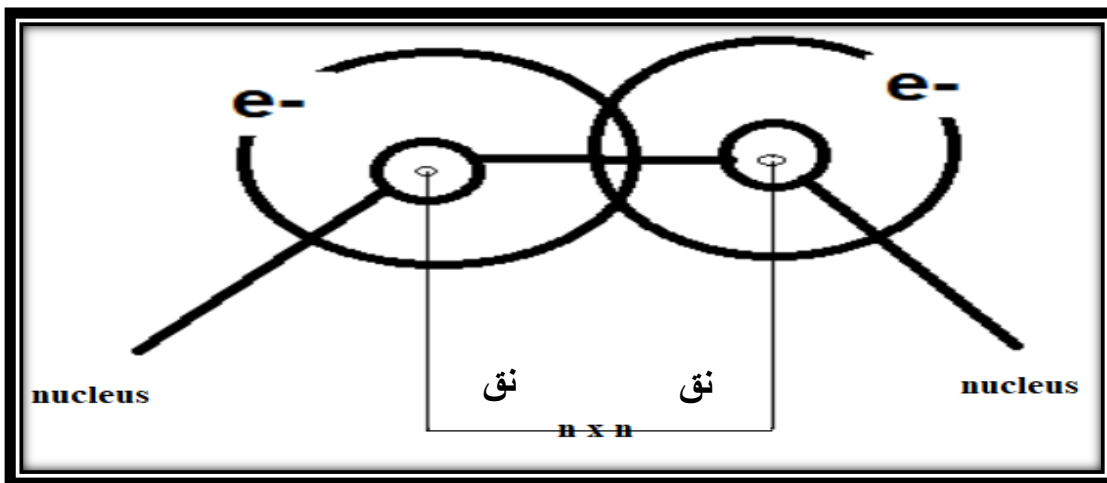


The radius increases

- 3- A sudden increase in atomic purity occurs whenever a new cycle begins Periodic table because a new period means n increases by 1.

B-Covalent radii

Covalent radius: It is half the distance between the nuclei of two atoms they are similar to each other by a single covalent bond.



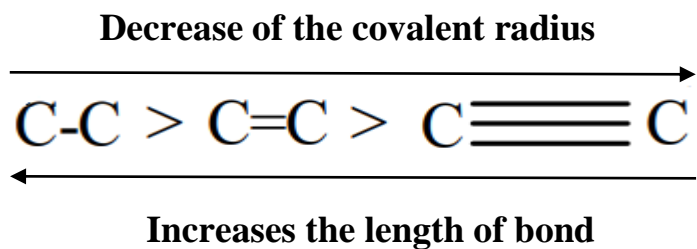
This means that the first atom's electron contributes the same amount as it contributes an electron to the second atom to form the covalent bond, i.e. the effect of the two nuclei is a mutual and equal effect on the two electrons. The covalent radius is measured by X-ray diffraction Spectroscopic methods have shown these studies.

1- The covalent radius of an element remains constant throughout compounds.

Example: The C-C bond has a constant length in all compounds and is equal

1.5 \AA , so the covalent radii equals to $(0.77) \text{ \AA}$. Such as $\text{CH}_3\text{-CH}_3$.

The covalent radius (r) decreases with increasing bond order between two similar atoms.



Ionic radius

In ionic compounds, the radius is measured by diffraction X-rays and the ionic bond is the distance between the two nuclei two ions in contact, one positively charged and the other negatively charged.

$$r_0 = r_a + r_c$$

r_a = anion radii

r_c = cation radii

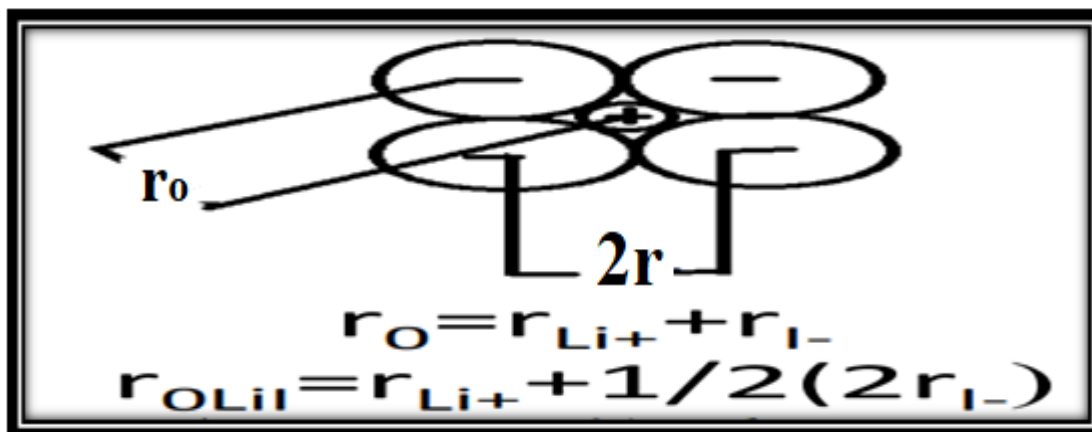
Methods for calculating ionic radius

- 1- Landy method
- 2- Braque's method

Landy method

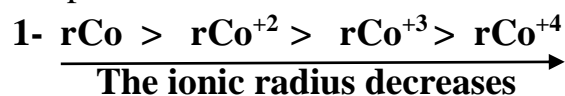
- The scientist has studied lithium halide LiX, where X= F, Cl, Br, and I.

Considering that the positive lithium ion is the smallest ion the positive size is such that it does not prevent contact with the negative halide ions the large charge can therefore be considered half the distance between an examples is the iodide ion nucleus. It is equal to the nucleotide ion Iodide. Using this method, Landy found that the radii for negative iodide ion is 2.13 \AA .

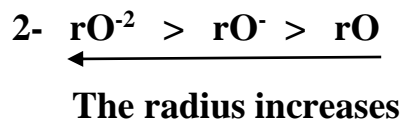


After calculating the radius of I^- ion, Landy was able to calculate $r^- r^+$, for ions Fluorine, chlorine, bromine, sodium, potassium and rubidium.

- Ionic radius increases with increasing atomic number in group or in once group due to increased shielding resulting from the increased number of main shells and dimensions of the effect of nuclear charge on electrons.
- The ionic radius decreases as the oxidation number increases, i.e. as the number increases electrons lost due to increased positive charge density and increased the effective charge of the nucleus, which increases the attraction of the nucleus to the electrons and thus decreases the radius of the positive ion.



The radius of a negative ion is larger than the radius of an atom neutral.



In ions with similar electronic configuration (isoelectronic), it is reduced by half the diameter increases as the atomic number of the ion or atom increases.



Each of them has the same electronic configuration.

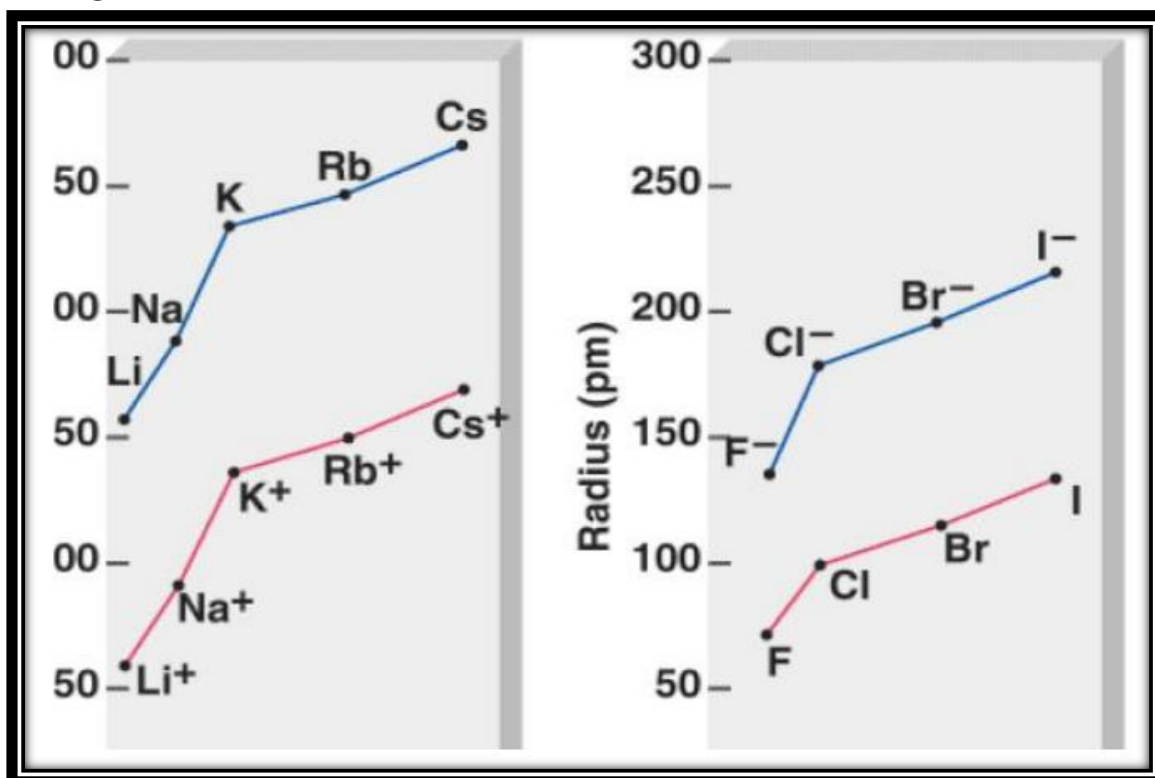


This can be explained by return to the relationship $*Z = Z - S$

Where **S** is the shielding constant and is equal for all ions and atoms above, because it contains the same number of electrons, and the variable remains the same Atomic number **Z**: As the atomic number increases, the effective charge of the nucleus increases and decreases Radius (**r**).

Note: The radius decreases with the increase in the charge of the nucleus acting with fixed of shielding constant.

Comparison between the atomic and ionic radii:



a- Homonuclear Diatomic Molecules *جزيئات ثنائية الذرة متجانسة النواة*

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:

When: d= distance bond length

$$d(A-A) = r(A) + r(A)$$

$$d(A-A) = 2 \times r(A)$$

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

The above equation shows that in the case of homonuclear diatomic molecules of A₂ type. The covalent radius of an atom A, r(A) is equal to one half of the internuclear distance, d(A-A). Therefore, the covalent radius of an atom in a homonuclear diatomic molecules can be obtained by divided the internuclear distance by tow.

Examples:

1. Cl₂ molecules

The value of Cl-Cl bond distance as found experimentally is 1.98 Å°. Thus:

$$r(\text{Cl}) = \frac{d(\text{Cl}-\text{Cl})}{2} = \frac{1.98}{2} = 0.99 \text{ Å}^\circ$$

2. Diamond

The value of d(C-C) distance as found experimentally in a variety of structured hydrocarbons is 1.54 Å°. Thus:

$$r(\text{C}) = \frac{d(\text{C}-\text{C})}{2} = \frac{1.54}{2} = 0.77 \text{ Å}^\circ$$

b- Heteronuclear Diatomic Molecules

جزيئات ثنائية الذرة غير متجانسة النواة

In case of heteronuclear diatomic molecules of **AB** type. bond length, d (A-B) is given by:

$$d (\text{A-B}) = r(\text{A}) + r(\text{B})$$

r(A) and r(B) are the covalent radii of **A** and **B** atoms.

Examples:

1. CCl₄ molecules

The experimentally value of d(C-Cl) is 1.76 Å°. Thus:

$$\begin{aligned}d (\text{C-Cl}) &= r(\text{C}) + r(\text{Cl}) \\r (\text{C}) &= d(\text{C-Cl}) - r(\text{Cl}) \\&= 1.76 - r(\text{Cl})\end{aligned}$$

Thus the covalent radius of carbon atom can be calculated by subtracting the covalent radius of **Cl** atom from **d(C-Cl)** bond length. The covalent radius of **Cl** atom can also be obtained. Provided that covalent radius of **C** atom is known (**r_c**).

2. SiC

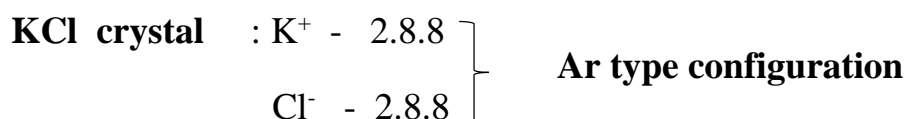
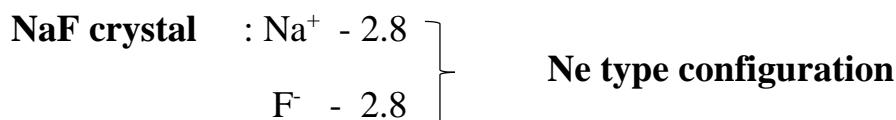
The experimentally value of $d(\text{Si-C})$ is 1.93 \AA . Thus:

$$d(\text{Si-C}) = r(\text{Si}) + r(\text{C})$$

Calculation of ionic radii

Pauling's method

Pauling has calculated the radii of the ions on the basis of the observed internuclear distance in four crystals namely **NaF**, **KCl**, **RbBr** and **CsI**. In each ionic crystal the cations and anions are isoelectronic with inert gas configuration.



Further the following two assumptions are made to assign the ionic radii.

- i. The cations and anions of an ionic crystal are assumed to be in contact with each other and hence the sum of their radii will be equal to the internuclear distance between them.

$$r(\text{C}^+) + r(\text{A}^-) = d(\text{C}^+\text{-A}^-) \quad \text{----- (1)}$$

Where:

$r(\text{C}^+)$ - radius of cation C^+

$r(\text{A}^-)$ - radius of anion A^-

$d(\text{C}^+\text{-A}^-)$ - internuclear distance between C^+ and A^- ions in C^+A^- ionic crystal.

- ii. For a given noble gas configuration, the radius of ion is inversely proportional to its effective nuclear charge i.e.

$$r(\text{C}^+) \propto 1 / Z^*(\text{C}^+) \quad \text{----- (2)}$$

$$r(\text{A}^-) \propto 1 / Z^*(\text{A}^-) \quad \text{----- (3)}$$

Where:

$Z^*(C^+)$ & $Z^*(A^-)$ are the effective nuclear charge of cation (C^+) and anion (A^-) respectively, on combining (2) & (3).

$$r(C^+) / r(A^-) = Z^*(A^-) / Z^*(C^+) \quad \text{----- (4)}$$

Hence the above two equations (1) & (4) can be used to evaluate the values of $r(C^+)$ and $r(A^-)$ provided that the value of $d(C^+ - A^-)$, $Z^*(C^+)$ & $Z^*(A^-)$ are known.

Example:

Calculate the ionic radii of K^+ and Cl^- ions in KCl crystal. The internuclear distance between K^+ and Cl^- ions are found to be 3.14 \AA .

Solution:

$$r(K^+) + r(Cl^-) = d(K^+ - Cl^-) = 3.14 \text{ \AA}$$

K^+ and Cl^- ions have $Ar(Z=18)$ type configuration. The effective nuclear charge for K^+ and Cl^- can be calculated as follows.

$$K^+ = \begin{matrix} (1s^2) & (2s^2 2p^6) & (3s^2 3p^6) \\ \text{Innershell} & (n-1)^{\text{th}} \text{ shell} & n^{\text{th}} \text{ shell} \end{matrix}$$

$$\begin{aligned} Z^*(K^+) &= Z - S \\ &= 19 - [(0.35 \times 7) + (0.85 \times 8) + (1 \times 2)] \\ &= 19 - 11.25 = 7.75 \end{aligned}$$

$$\begin{aligned} Z^*(Cl^-) &= 17 - [(0.35 \times 7) + (0.85 \times 8) + (1 \times 2)] \\ &= 17 - 11.25 = 5.75 \end{aligned}$$

$$\therefore r(K^+) / r(Cl^-) = Z^*(Cl^-) / Z^*(K^+) = 5.75 / 7.75 = 0.74$$

$$\therefore r(K^+) = 0.74 r(Cl^-)$$

Substitution (2) in (1)

$$0.74 r(Cl^-) + r(Cl^-) = 3.14 \text{ \AA}$$

$$1.74 r(Cl^-) = 3.14 \text{ \AA}$$

$$r(Cl^-) = 3.14 \text{ \AA} / 1.74 = 1.81 \text{ \AA}$$

Prof. Dr. Mahasin Faisal A. Alias

Polarization & Polarity, Covalent and Ionic Bond

Inorganic Chemistry

4th lecture

Prof. Dr. Mahasin Faisal A. Alias

2023-2024

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 polarization:

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 polarization. The larger the size of the negative ion, the greater the polarization, that is, the appearance of the covalent character of the bond increases, and thus the degree of melting decreases, since as the polarization increases in compounds, the degree of melting decreases.

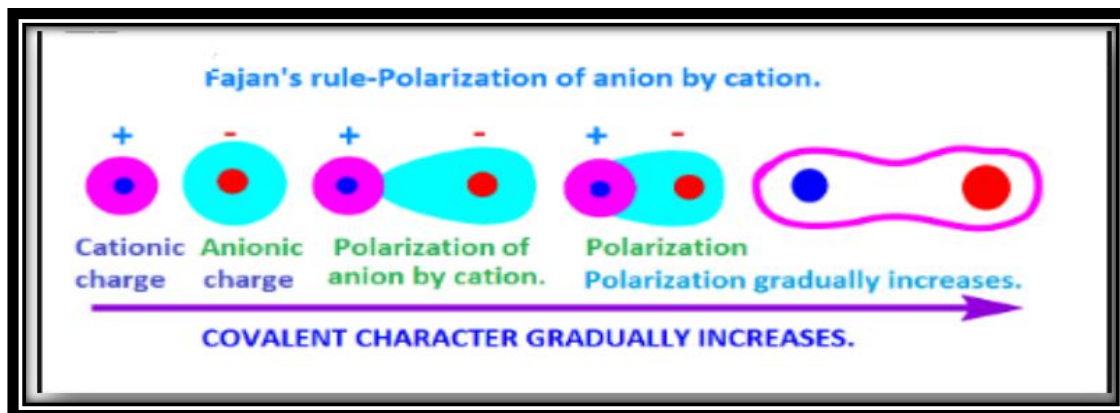


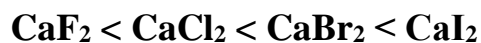
Table: Shows the decrease in melting points with Increase the Polarization of the negative ion.

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:-



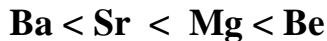
Polarization increases

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

CaF₂ is a compound with **low polarization**, meaning it has an ionic character and a high melting point.

CaI₂ is a **highly polarization** 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).

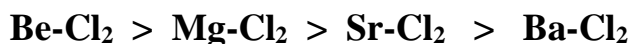


Polarization increases

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-:



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)
BeCl₂	Be⁺²	678
MgCl₂	Mg⁺²	985
SrCl₂	Sr⁺²	1145
BaCl₂	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.

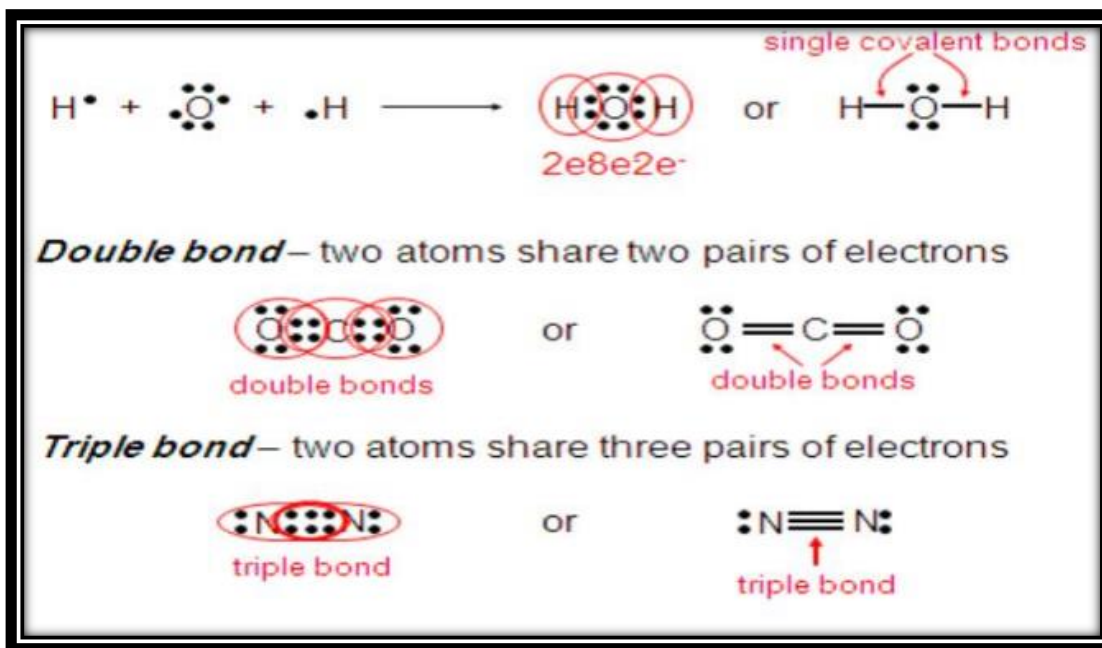
All of them carry a charge of +1 (they do not have an electronic arrangement for the noble gases) that is, they have a greater polarization than the positive ions that have the arrangement of the noble gases, and that is, they have lower melting points and less solubility. Either **RbCl, NaCl, KCl**, 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.



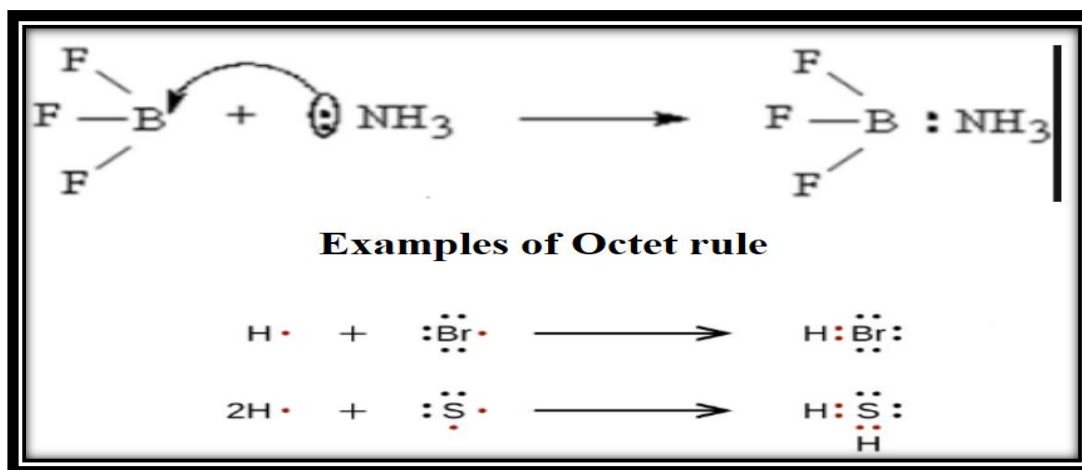
The modern definition of covalent bond

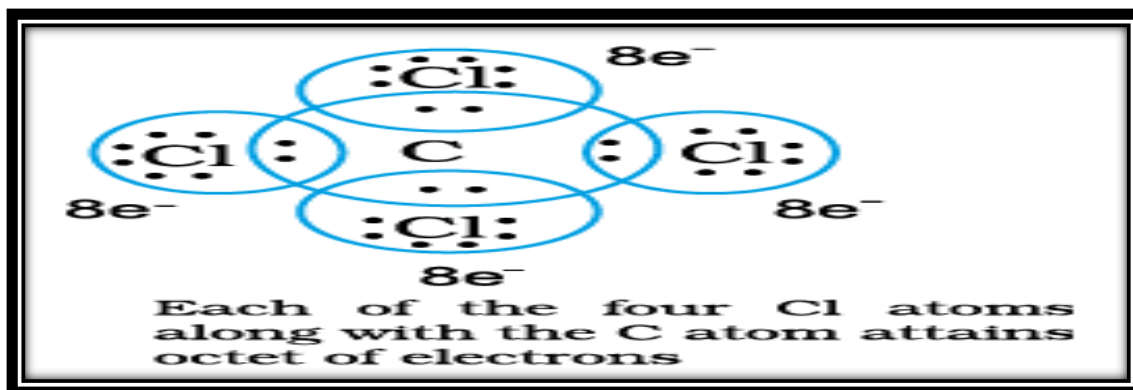
It is the amount of changes that occur or occur in energy when two atoms approach each other, so that the energy of the system becomes the least possible when the distance between the two atoms reaches a distance called the equilibrium distance. The length of the covalent bond is measured using X-ray 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 coupling-spinning of these two electrons when forming the bond in application of the Pauli Exclusion Principle.

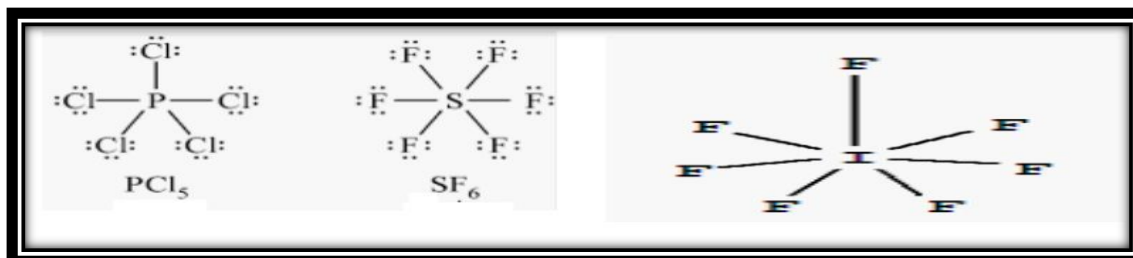
3. The overlap of the orbitals of the two atoms that make up the covalent bond, and this overlap fills the space between the two atoms as a condition for bonding to occur.
4. When covalent bonds are formed between atoms whose orbitals are **S** and **P**, the maximum number of electrons is equal to **8** 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.





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

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-:

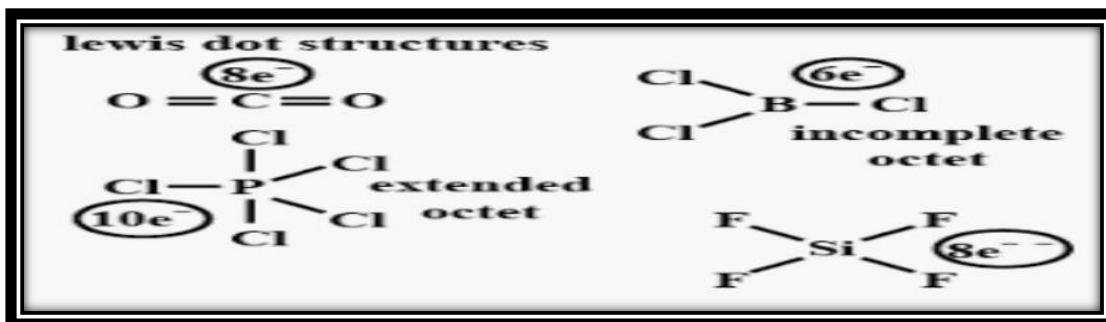


The exceptions to the eight octet rule can be summarized in the points below:

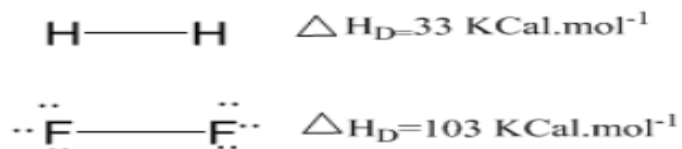
Exceptions to the Octet Rule: (أستثناءات عن القاعدة)

- 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 nonbonding electrons and bonding 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-bonding doublets that repel the bonding 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 ₃ Cl	Polar covalent	-64	61
KBr	ionic	730	1435
Cr ₂ O ₃	ionic	?	4000

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

1. Valence bond theory (VBT).
2. Molecular orbital theory (MOT).
3. Valence Shell Electron Pair Repulsion (VSEPR).

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).

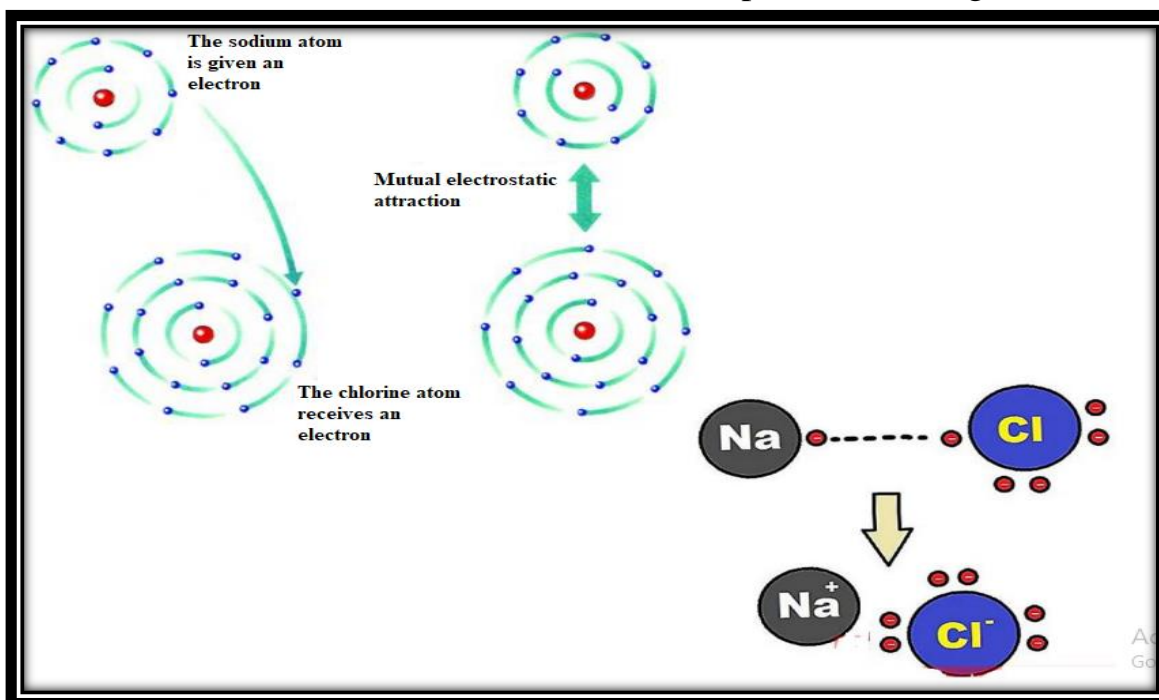
The concept of ionic bonding

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 **Na⁺** which is the positive ion or cation, and the chloride ion **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.

Ionic bonding consists of three steps:

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.



For the formation of an ionic bond, the following conditions must be met:

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.

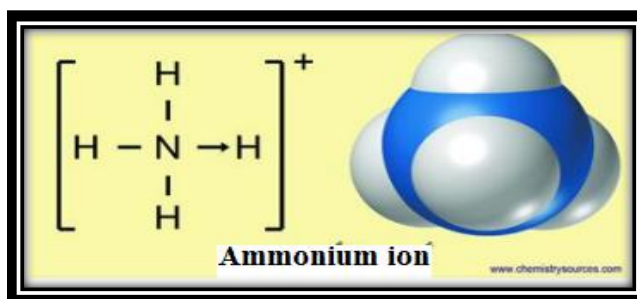
2. That there is an active non-metal capable of gaining one or more electrons without the need for significant energy, i.e. a high electronic affinity for the metal (non-metal). The elements to which the second condition applies are the elements of the seventh and sixth groups.
3. The energy of crystal 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 (2,8,7).

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.

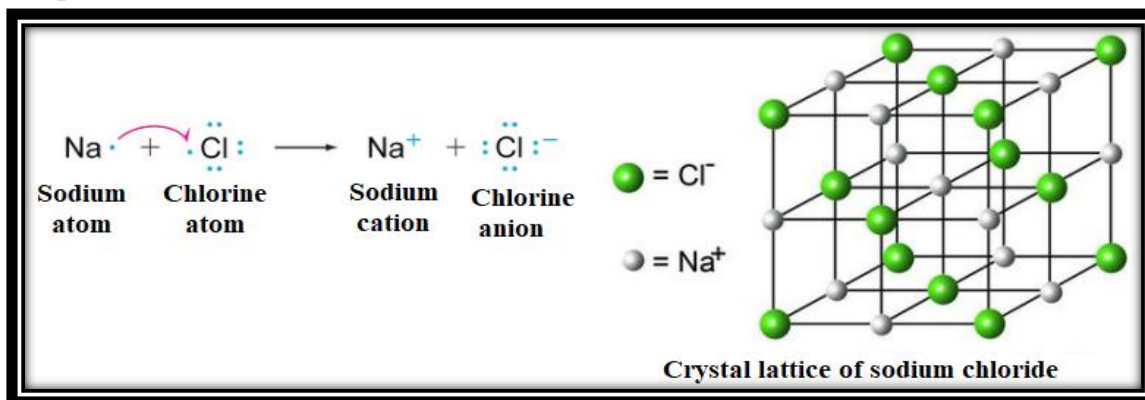
The chlorine ion carries a negative electrical charge because the number of electrons in the orbitals has become eighteen (**18**), while the number of protons in the nucleus is (**17**).

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**).

Note: (electrostatic= ionic bond).

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 ΔEN 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

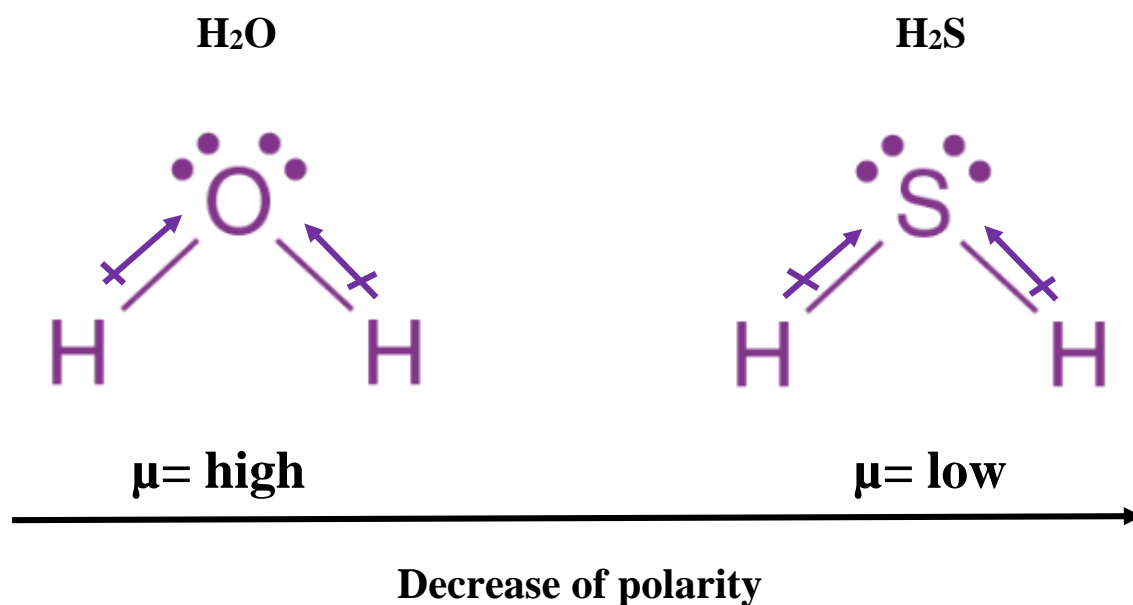
electronegativity. The ionic character increases, as is the case in metallic compounds and alkaline earths. The polarity of the compounds is measured through a dipole moment meter.

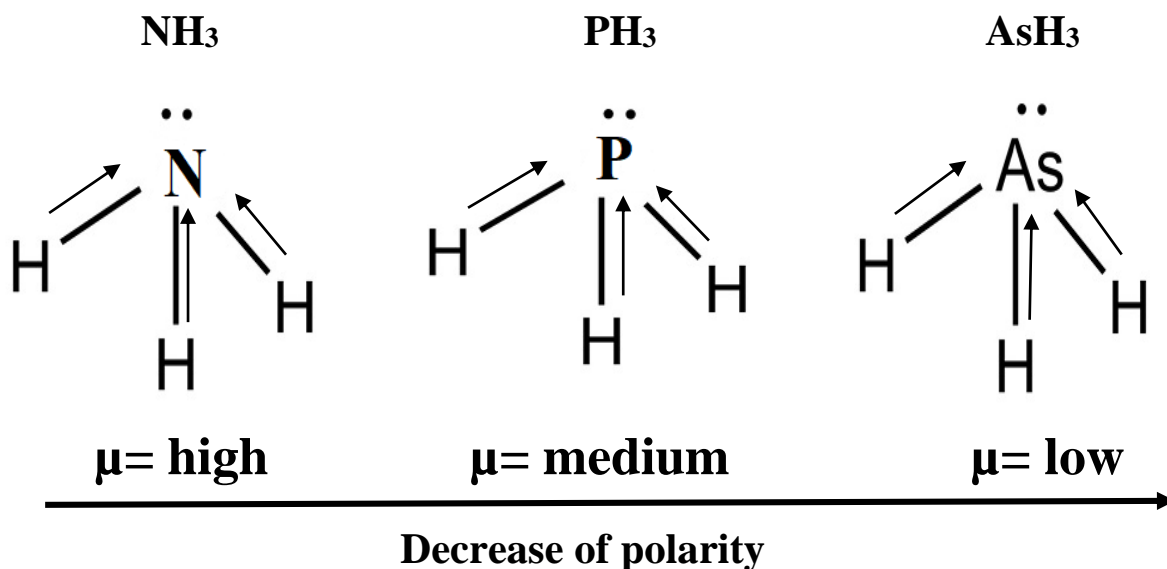
$$\mu = e \times d = e.s.u \times cm = D \text{ (debye)}$$

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.



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





Decrease of μ .

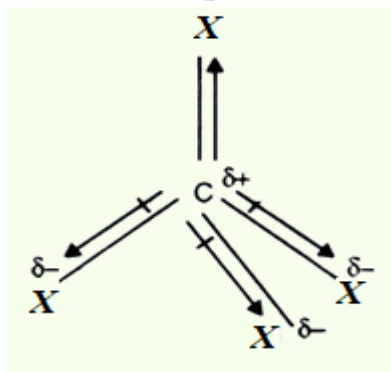
Decrease of electronegativity ΔE_N .

Decrease of polarity.

Decrease of acidity.

Q: Are the following compounds covalent? Cl_4 , CCl_4 , CBr_4 , CF_4 & why?

These compounds is covalent compounds because $\mu=0$.



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

Compare between covalent and ionic compounds:

Covalent compounds	Ionic compounds
1. Gases, liquid, or solids	1. Crystalline solids.
2. Low melting and boiling points.	2. High melting and boiling points.
3. Form molecules in solution	3. Form ions in solution
4. Poor electrical conductors in solution making them nonelectrolytes .	4. Conduct electricity in solution making them electrolytes , but in the solid do not conduct electricity.
5. Many are soluble in non-polar solvents but not in water	5. Many soluble in water but not in nonpolar solvents.
6. Examples: butter, oil, sugar	6. Examples: salt.

Diagonal relationship: The same or similar physical and chemical properties for the elements in the second and third periodic table. Depending on electropositivity and size of elements.

Note:

- ✚ Two types of covalent bond **nonpolar** CCl_4 and **polar** H_2O .
- ✚ Vander Waal radius is **longer** than the covalent radius.

Prof. Dr. Mahasin Faisal A. Alias

Crystal lattice energy, Born Haber process and Solvolysis

Inorganic Chemistry

5th lecture

Prof. Dr. Mahasin Faisal A. Alias

2023-2024

Crystal lattice energy

Its definition is the amount of energy released when one mole of positive ions deposits with one mole of negative ions in the gaseous state in a special geometric arrangement called the crystal lattice to form one mole of a solid ionic compound.



The energy value of the crystal lattice (U) is calculated from the energy of the ionic double M^+X^- each ionization is under the influence of electrostatic attractive forces with the ions opposite to it in charge, so it is called coordination no. The energy released is the energy of attraction and depends on the distance between the two ions in the solid state.

$$-E_{\text{attr.}} = \frac{Z^+Z^-e^2}{4\pi \epsilon_0 r} = \frac{(Z^+e)(Z^-e)}{4\pi \epsilon_0 r}$$

(طاقة التجاذب)

It is the positive and negative charges of the negative and positive ions Z^+ , Z^- , ex. Na^+ , Cl^- .

ϵ_0 = Dielectro constant in air or (space).

r = the distance between negative and positive ion.

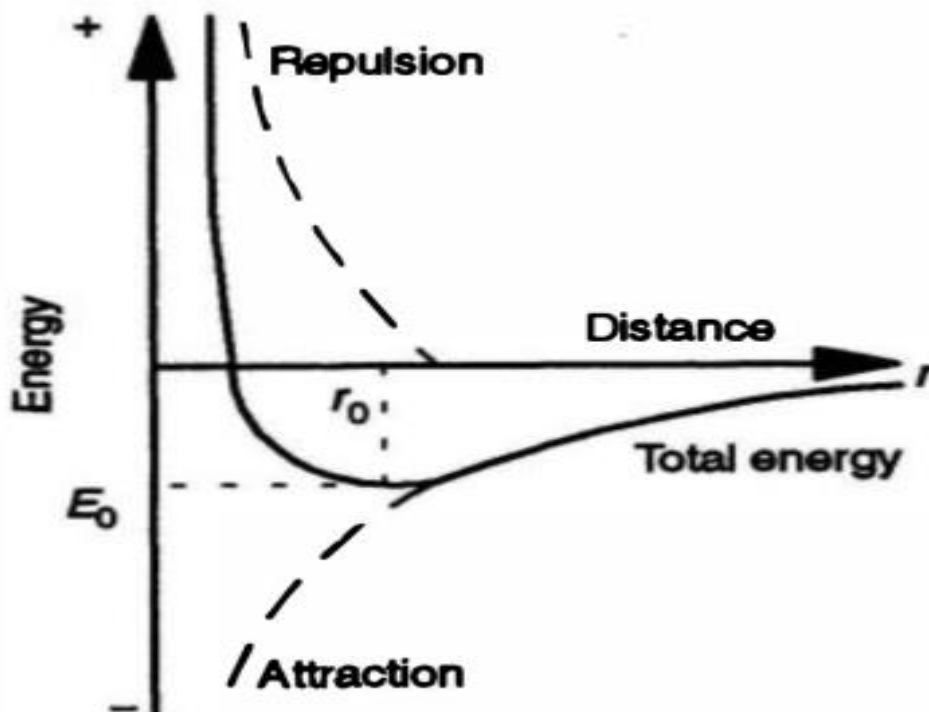
$e = 4.8 \times 10^{-10}$ esu.

$\epsilon_0 = 8.85 \times 10^{-12}$ C²/m.J.

The sign of the attraction energy is **negative**, so its value increases as the distance between the positive and negative ions **decreases**. Therefore, the relationship is inverse and the value of this energy $E_{\text{attr.}}$ becomes **zero** or close to it when the value of r is **infinity**.

$$\frac{du}{dr} = \infty \quad (\text{When } r \text{ value is as little as possible}).$$

$$\frac{du}{dr} = 0 \quad (\text{When } r \text{ value is infinite}).$$



And since the arrangement of the ions in the solid ionic compound determines the coordination numbers in a geometric arrangement that varies from one compound to another and affects the energy of attraction, therefore, a geometric constant is added to this equation that shows the type of crystal lattice of the solid compound, regardless of the charge, size, or type of ions, and this constant is symbolized With the symbol **A**. (**A= Madelung constant**)

$$(-)E_{\text{attr.}} = A \frac{Z^+Z^-e^2}{4\pi \epsilon r}$$

But when the value of **r** decreases to the lowest possible, repulsion forces are generated between the electronic clouds of positive and negative ions. This is done on the basis of calculating the repulsive energy, which is called the **Born** equation.

$$(+)\ E_{\text{rep.}} = \frac{B}{r^n}$$

(طاقة التنافر)

n: Born exponent (Constant).

B: repulsion parameter.

r it is a fixed value that depends on the layer of ions and their ionic distribution or density. The ions are calculated for ions whose electronic distribution matches the distribution of the noble elements. The value of n increases with the increase in the electronic density of the ionic compound, so the total energy can be calculated.

For the ionic compound MX in the crystal lattice from the following relationship:-

$$E_T = E_{\text{attr.}} + E_{\text{rep.}} = \frac{A Z^+ Z^- e^2}{4\pi \epsilon \cdot r} + \frac{B}{r^n}$$

$T = \text{Total energy}$

While E_T for ionic compound:

$$E_T = \frac{NA Z^+ Z^- e^2}{4\pi \epsilon \cdot r} + \frac{NB}{r^n} = U_r$$

N : Avocado No. = 6.022×10^{23}

U° : Crystal lattice energy in Normal conditions.

r_o : the distance between the positive and negative ions.

When a state of balance occurs between the forces of attraction and repulsion, we obtain a state of stability, and here it occurs when the equilibrium distance is reached. In this case, the energy of the crystal lattice represents the stability energy of the ionic compound.

$$U = U_o \quad \& \quad r = r_o \quad \left(\text{When } \frac{du}{dr} = 0 \right).$$

$$\{U_o = \frac{AN Z^+ Z^- e^2}{4\pi \epsilon \cdot r_o} \times \left(1 - \frac{1}{n} \right) \} \dots \text{Born-Landy Equation (حفظ)}$$

معادلة بورن لاندي لحساب طاقة الشبكة البلورية.

This equation is called the **Born-Landy equation** to calculate the energy of the crystal lattice:

$$r_o = r_c + r_a \quad \text{-----(1)}$$

cation anion

$$\frac{Z^*c}{Z^*a} = \frac{r_a}{r_c} \quad \text{-----(2)}$$

$$r_c = \frac{Z^*a r_a}{Z^*c} \quad \text{-----(3)}$$

Substituting into equation 3:-

$$r_o = \frac{Z^+a r_a}{Z^+c} + r_a$$

$$r_o = \left(\frac{Z^+a}{Z^*c} + 1 \right) r_a$$

$$r_a = \frac{r_o}{\frac{Z^+a}{Z^*c} + 1}$$

$$r_c = \frac{Z^*a}{Z^*c + Z^*a} r_o$$

$$r_c = \frac{Z^*c}{Z^*c + Z^*a} r_o$$

Can be calculated r_o by X-ray it is used to calculate the ionic radius of negative and positive ions using the Paulter method based on Z^* for the positive and negative ions.

The values of n must be memorized from the following table:

Electronic Configuration	n value
He	5
Ne	7
Ar, Cu^{+1}	9
Kr, Ag^{+1}	10
Xe, Au^{+1}	12

$$n = \frac{n(\text{positive ion}) + n(\text{negative ion})}{2}$$

✚ For example n value for NaCl:



$$n = 7 + 9 / 2 = 8$$

Born Haber process

The **Born Haber process**, more commonly referred to as the **Born Haber cycle**, is a method that allows us to observe and analyses energies in a reaction. It mainly helps in describing the formation of ionic compounds from different elements. The methodology further enables us to understand the overall reaction process through a series of steps.

The Born Haber cycle was introduced in the year 1919 by German scientists Fritz Haber and Max Born. The Born Haber cycle is mainly used to calculate the lattice energy. It also involves several steps or processes, such as electron affinity, ionization energy, sublimation energy, the heat of formation and dissociation energy.

Considerations

The reaction of electropositive metals with electronegative nonmetals produces ionic solids. Alkali and alkaline earth metals react with halogen family elements to form compounds, which are crystalline ionic solids. Ionic compounds being stabilized by the electrostatic force of attraction between positive and negative charges are expected to have similar physical properties.

But physical properties like stability and the water solubility of these ionic compounds differ much. The difference is attributed to the difference in an enthalpy called 'Lattice energy' between the ionic solids.

Lattice energy is the energy that keeps together the cations and anions of the compound in fixed positions in a crystalline solid state. Lattice energy can be defined as either energy released when gaseous ions form one mole of a solid ionic compound or as the energy required to convert one mole ionic solid into its gaseous ions. There is no way to measure this lattice energy experimentally. Hess's law of heat summation is the only indirect way of estimating the lattice energy.

Application of Hess's law of heat summation to the formation of solid ionic compounds involves enthalpy of all processes that are necessary for the formation of the solid ionic compound from the elemental state of the constituent atoms in a form cycle such that the total energy on summation is **zero**.

What is the Born Haber Cycle?

The Born Haber cycle is a cycle of enthalpy change of process that leads to the formation of a solid crystalline ionic compound from the elemental atoms in their standard state and of the enthalpy of formation of the solid compound such that the net enthalpy becomes zero.

Born Haber Cycle Examples

Example 1: Born Haber cycle of sodium chloride NaCl (or any AB-type Mono-valent ionic solid).

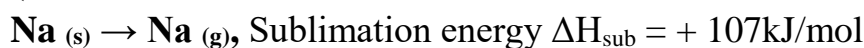
The heat of the formation of sodium chloride (ΔH_f°) from the sodium metal and chlorine gas can be experimentally measured.



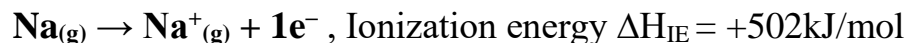
The formation of ionic solid sodium chloride from solid sodium metal and gaseous chlorine is not a single-step process but goes through several processes. Heat changes of all the processes except the lattice energy can be experimentally measured.

The processes or steps in the formation of sodium chloride are as follows:

1. Solid sodium atom sublimates to gaseous atom by absorbing heat energy (ΔH_{sub}).



2. Gaseous sodium atom absorbs the ionization energy to release one electron and forms a gaseous sodium ion.

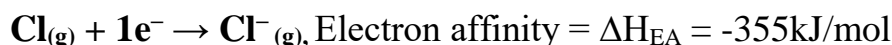


3. Diatomic gaseous chlorine breaks into two individual atoms by absorbing bond energy, such that each chlorine atom absorbs half of the bond energy of the chlorine molecule.

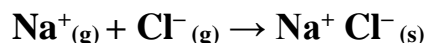


Bond dissociation energy of chlorine = $(1/2)\Delta H_{\text{diss}} = (1/2) 242 = +121\text{kJ/mol}$.

4. Chlorine atom accepts an electron to form a chloride ion and releases energy equivalent to electron affinity.



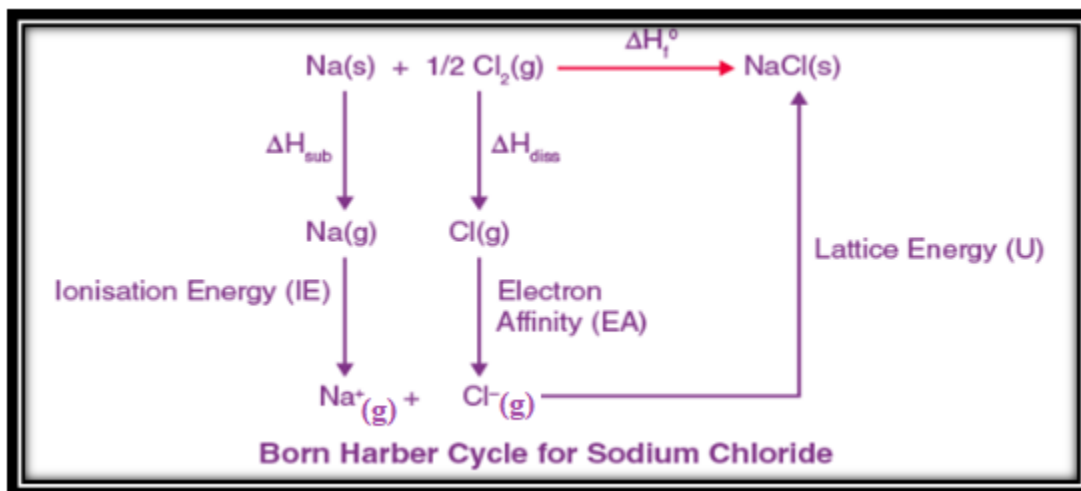
5. Gaseous sodium ion and gaseous chloride ion combine to form a solid sodium chloride molecule and releases energy equivalent to lattice energy.



Lattice energy = $\Delta H_{\text{LE}} = U = ?$

The summation of enthalpy of all the processes (from step 1 to step 5) give the net enthalpy of the formation of solid crystalline sodium chloride from sodium and chlorine in their standard conditions of solid and gas, respectively. This should be equal to the experimentally measured enthalpy of the formation of solid sodium chloride.

The enthalpies are represented as a cycle in the figure.



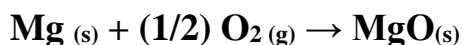
The lattice energy of the sodium chloride solid = $U = \Delta H_f^\circ - (\Delta H_{\text{sub}} + \Delta H_{\text{IE}} + \frac{1}{2} \Delta H_{\text{dis}} + \Delta H_{\text{EA}})$.

$$= -411 -107 -502 -121 +355 = -786 \text{ kJ/mol.}$$

ملاحظة: تزداد استقرارية المركب الأيوني كلما زاد قيمة ΔH_u° $-500 \text{ kJ. mol}^{-1} < -1000 \text{ KJ. mol}^{-1}$

Example 2: Lattice energy of magnesium oxide (or any AB-type Divalent ionic solid).

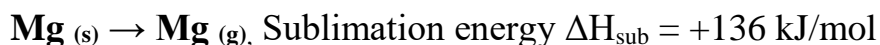
The heat of the formation of magnesium oxide (ΔH_f°) from the magnesium metal and oxygen gas can be experimentally measured.



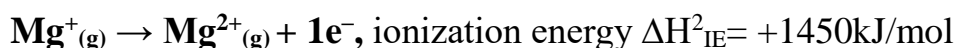
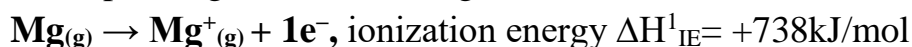
$$\Delta H_f^\circ = -602 \text{ kJ/mol}$$

The processes or steps in the formation of magnesium oxide are as follows:

1. Solid magnesium atom sublimates to a gaseous atom by absorbing heat energy (ΔH_{sub}).

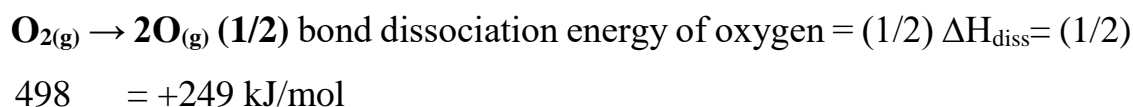


2. Gaseous magnesium atom releases two electrons in two steps with corresponding ionization energies.

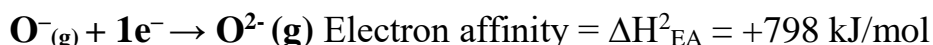


So energy of ionization = $\Delta H_{\text{IE}} = 738 + 1450 = 2188 \text{ kJ/mol.}$

3. Diatomic oxygen breaks into two individual atoms by absorbing bond energy, such that each chlorine atom absorbs half of the bond energy of the chlorine molecule.

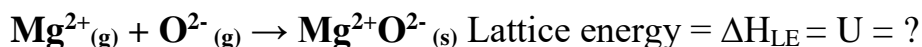


4. Oxygen atom accepts two electrons to form an oxide ion and releases energy equivalent to two-electron affinities.



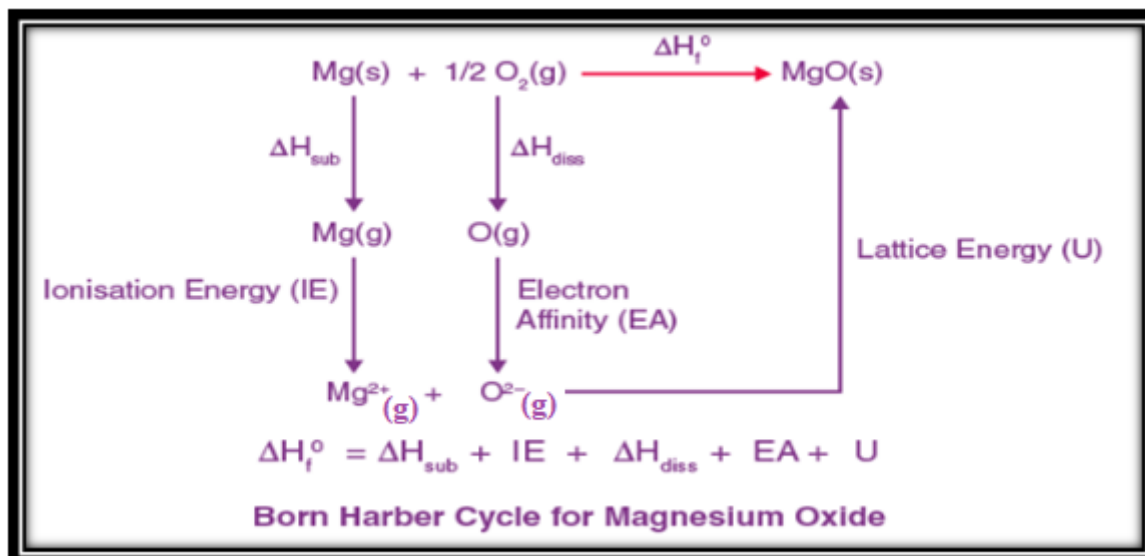
The total energy released as electron affinity by the oxygen atom is = $\Delta H_{\text{EA}} = +656 \text{ kJ/mol}$.

5. Gaseous magnesium ion and gaseous oxide ion combine to form a solid magnesium oxide molecule and releases energy equivalent to lattice energy.



The summation of enthalpy of all the processes from the starting step to the final step gives the net enthalpy of the formation of solid crystalline magnesium oxide from magnesium and oxygen in their standard conditions of solid and gas, respectively. This should be equal to the experimentally measured enthalpy of the formation of solid magnesium oxide.

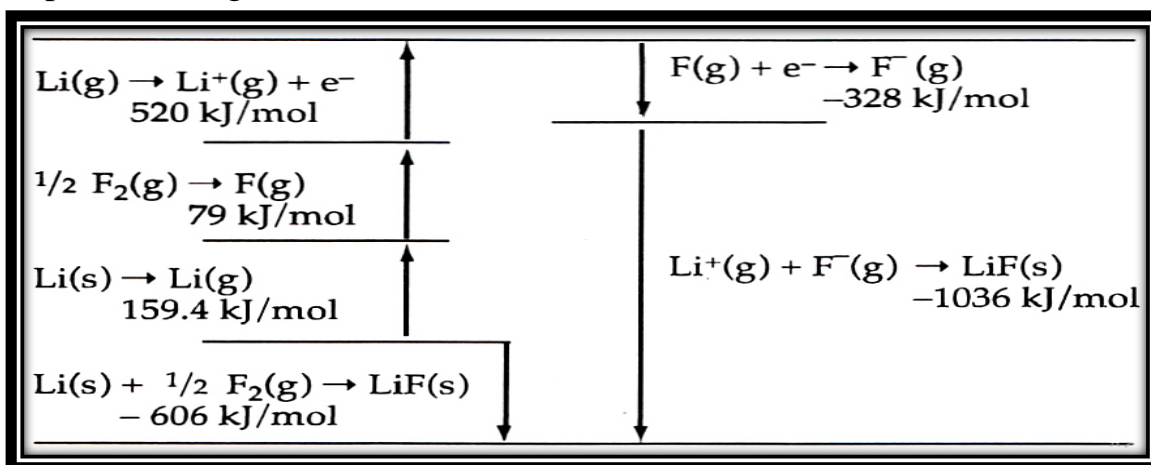
The enthalpies are represented as a cycle in the figure.



The lattice energy of the magnesium oxide solid = $U = \Delta H_f^\circ - (\Delta H_{\text{sub}} + \Delta H_{\text{IE}} + (1/2) \Delta H_{\text{dis}} + \Delta H_{\text{EA}})$.
 $= -602 - 136 - 2188 - 249 - 656 = -3831 \text{ kJ/mol}$.

Formation of LiF

Born–Haber cycle for the standard enthalpy change of formation of lithium fluoride. ΔH_{latt} corresponds to U_L in the text. The downward arrow "electron affinity" shows the negative quantity $-EA_F$, since EA_F is usually defined as positive. The enthalpy of formation of lithium fluoride (LiF) from its elements in their standard states (Li(s) and $F_2(g)$) is modeled in five steps in the diagram:



1. Atomization enthalpy of lithium.
2. Ionization enthalpy of lithium.
3. Atomization enthalpy of fluorine.
4. Electron affinity of fluorine.
5. Lattice enthalpy.

The sum of the energies for each step of the process must equal the enthalpy of formation of lithium fluoride, ΔH_f .

$$\Delta H_f = V + \frac{1}{2}B + IE_M - EA_X + U_L$$

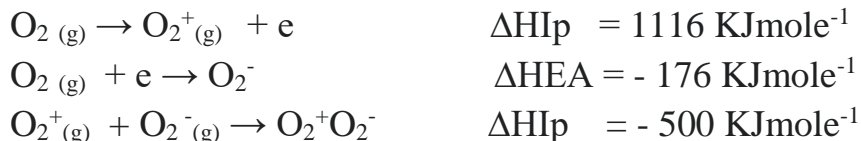
➤ V is the enthalpy of sublimation for metal atoms (lithium).

- B is the bond enthalpy (of F_2). The coefficient $1/2$ is used because the formation reaction is $Li + 1/2 F_2 \rightarrow LiF$.
- Is the ionization of the metal atom:
- Is the electron affinity of non-metal atom X (fluorine).
- Is the lattice enthalpy (define as exothermic here).

The net enthalpy of formation and the first four of the five energies can be determined experimentally, but the lattice enthalpy cannot be measured directly. Instead, the lattice enthalpy is calculated by subtracting the other four energies in the Born–Haber cycle from the net enthalpy of formation. A similar calculation applies for any metal other than lithium and/or any non-metal other than fluorine. The word *cycle* refers to the fact that one can also equate to zero the total enthalpy change for a cyclic process, starting and ending with $LiF(s)$ in the example. This leads to which is equivalent to the previous equation.

$$0 = -\Delta H_f + V + \frac{1}{2}B + IE_M - EA_X + U_L$$

Example: Does this compound exist $O_2^+O_2^-$?



$$\begin{aligned} \Delta H_f &= \Delta H_{Ip} + \Delta H_{EA} + \Delta H_u \\ &= 1116 + (-176) + (-500) \\ &= +488 \end{aligned}$$

∴ The existence of this compound is impossible.

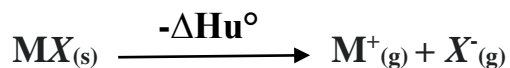
(القيمة موجبة أذن المركب لا يتكون)

Solubility of ionic compounds based on the Born Haber Cycle (enthalpy of solution ΔH_s)

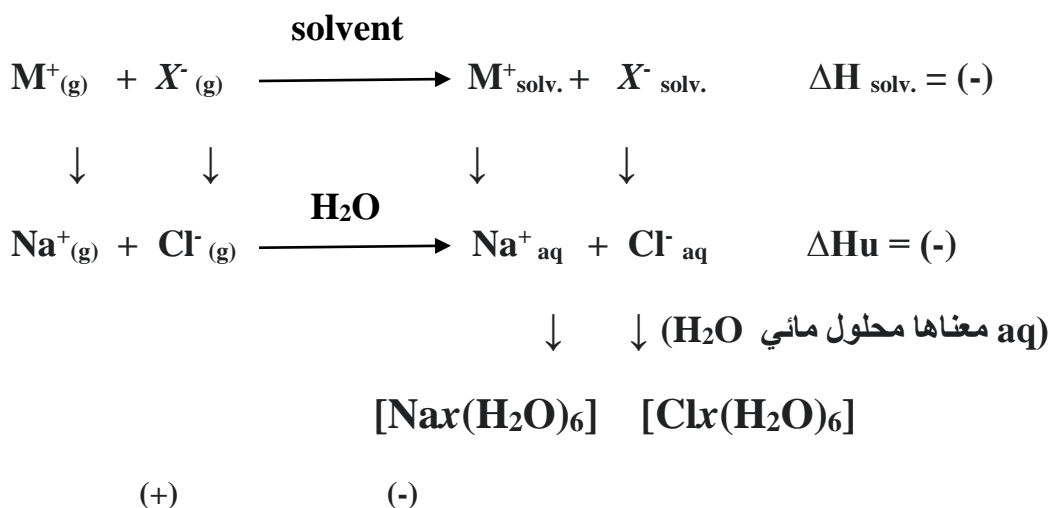
This means calculating the standard molar enthalpy associated with the dissolution of one mole of an ionic compound in one liter of solvent under standard conditions, and this value requires two types of enthalpies.

1- Fracture energy طاقة الكسر (Enthalpy of lattice energy ΔH_u)

This enthalpy is necessary to break the crystal lattice of the solid compound and convert it into its ions in the gaseous state according to the following equation:



2- Positive ions are separated from negative ions using a polar solvent of high dielectric constant, so that each ion is surrounded by a number of solvent molecules, and the resulting heat or enthalpy released is the enthalpy of the solvolysis (ΔH_s).

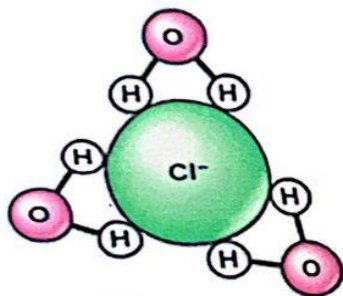


$$\Delta H_s = \Delta H_u^\circ + \Delta H_{\text{solv.}} M^+ X^-$$

$$\Delta H_s = \Delta H_u^\circ + \Delta H_{\text{solv.}} M^+ + \Delta H_{\text{solv.}} X^-$$

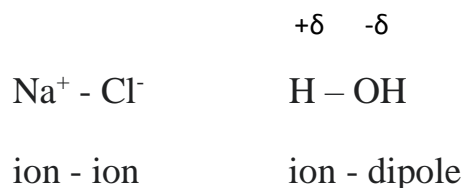
(+)

(-)



The value of the enthalpy of solvolysis is affected by the following factors:

1. The value ΔH_{solv} negativity in ionic compounds increases with the:
 - 1.1. Increase in the electric moment constant and
 - 1.2. The dipole moment of the solvent, and the solute becomes a heat emitter as a result of the ability of the solvent to surround the ions and form (ion-dipole) bonds, which become the strongest (ion-ion) bonds for the solid compound.



If the ion-dipole is stronger than the ion-ion, this means that the value of negative ΔH_{solv} of compound is higher than the value of the positive one, and dissolves the ionic compound **MX**.

إذا كان ion-dipole أقوى من ion-ion

$\Delta H_{\text{u}} < \Delta H_{\text{solv}}$ وبذلك يتمذوب المركب الأيوني **MX**.

2. As the size of the cation decreases and its effective charge increases, the value of the ionic potential increases, which is equal to Z^*/r , and thus its ability to polarize the solvent molecules increases, and thus the value of ΔH_{solv} that negative is increases, or in other words, the bond strength ion-dipole which increases at the expense of the energy value of the crystal lattice or at the expense of the value of the ion-ion.

Note: When the value of ΔH_{s} is negative, the ionic compound dissolves in the solvent. If the value of ΔH_{s} is equal to (1-10 KJmole^{-1}), the compound dissolves, and if the positive value increases to more than 10 KJmol^{-1} , then the compound's solubility gradually decreases.

3. Both change ΔH_{solv} , ΔH_{u} with the radii of the ions, and the difference in the radii separates, that is, as the radii of the positive and negative ions get closer, the solubility of the ionic compound decreases.

4. Ionic compounds of the $M^{+2}X^{-2}$ type will be less soluble than the compound MX because the compounds of the first type will be susceptible to attraction between the positive ion and the negative ion. They will be high because the ionic potential of the positive ion is high due to the increase in the acting charge with the decrease in radius, so that (Z^*/r) is high and thus exerts an attraction. On the negative ion, which is large in size and polarized, the enthalpy of the crystal lattice increases at the expense of the enthalpy of the solute, meaning the ion-ion becomes higher than the enthalpy of the ion-dipole, as in $M^{+1}X^{-1}$ molecules.
5. The ability of the ion to dissolve decreases and the value of the enthalpy of dissolution decreases as the size of the ions increases, especially positive ions. As the size of the positive ion increases, the Z^*/r decreases and its attraction or polarity to the solvent molecules decreases. Therefore, the enthalpy of the crystal lattice favors closeness in sizes, while the enthalpy of dissolution separates the disparity in sizes between positive and negative ions.

Example:

LiF	LiI (أختلاف بالحجم)
Less soluble	More soluble
CsF (أختلاف بالحجم)	CsI
More soluble	Less soluble

6. The dissolution process requires a solvent that is polar and has a high dielectric constant and has the ability to bond with ions and form dissolved species, where ion-dipole bonds are stronger than ion-ion bonds. However, if the solvent is non-polar and has a low dielectric constant, such as CCl_4 or benzene, then the ionic compound will not dissolve and the ion-ion bonds will become stronger than the ion-dipole bonds, so these solvents (CCl_4 and benzene) do not dissolve ionic substances.

Prof. Dr. Mahasin Faisal A. Alias

Covalent Compounds, MOT & VBT

Inorganic Chemistry

6th lecture

Prof. Dr. Mahasin Faisal A. Alias

2023-2024

Covalent Compounds

Lewis's definition of a covalent bond is a bond that results from the sharing of two or more atoms with their electrons in an equal or close contribution (the force that connects the two elements is not an electrostatic force), meaning that the electronic cloud does not move from one atom to another.

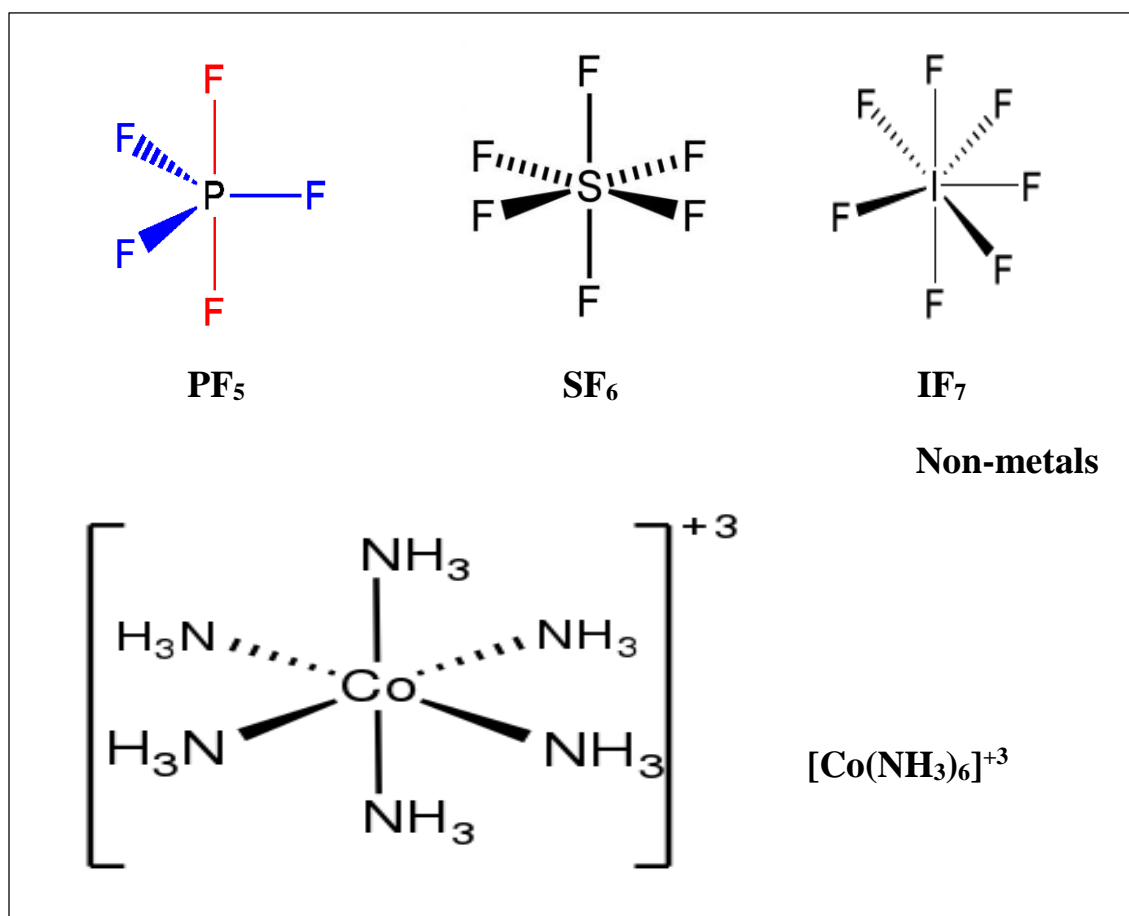
The modern definition of covalent bond is the amount of changes that occur or occur in energy when two atoms approach each other, so that the energy of the system becomes the least possible when the distance between the two atoms reaches a certain amount. This distance is called the equilibrium distance,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

When covalent bond molecules are formed between the **S** and **P** orbital atoms, these molecules have a maximum of electrons equal to eight in their outer shell for each atom, which is called **8** octet rule, making up the molecules, which is called the Lewis octet structure, so the total sum of the outer orbitals = 4 or the sum of total number of electrons.

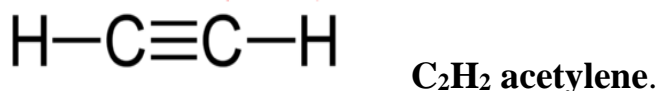
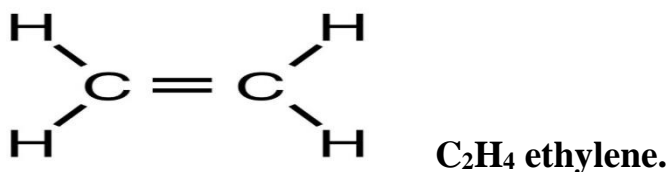
in the outer shell = 8, and the total sum of the pairs of electrons involved in the formation of bonds is also 4, provided that the number of electrons in the outer shell of any atom is not less than four electrons, and Lewis theory proves that the formation of a stable compound requires that the atoms reach the noble gas distribution **CF₄**, **NH₃**, **OF₂**, **F₂**. For example, the fluoride method requires two atoms that have reached the required limits for the envelope (that is, each atom has **8** electrons in its outer shell). As for the elements that contain less than four electrons, the octet Lewis structure does not apply to them, as **H** atoms need only two electrons to complete the envelope of the secondary shell from Type **S**. Also, in their covalent compounds, **B** atoms do not reach the noble gas arrangement because they contain three electrons in the shell. Therefore, boron compounds are called incomplete covalent compounds, for example **BF₃**. Therefore, these compounds can interact with a compound in which an element contains a nonbonding ion pair.

The molecule that has the ability to donate an electron double is called a **Lewis base**. The molecule that accepts the donated pair is called a **Lewis acid**. The compounds that contribute to the electron double are called a **Lewis base**. As for the compounds of boron, they are called **Lewis acids**. Lewis proposed calling the bond resulting from boron a coordination bond to fill the electron deficiency in this atoms.

For elements that contain a **d-type** secondary shell, their valence shell will move further away from the Lewis octet structure. For this type, the third period scale was established, as many elements have high valence numbers for metals and transition elements, and the number of valence shell electrons is determines covalent bonds can be 5,6,7,8.



Double Bonds of Lewis Structures when more than one pair of electrons is used to form a bond between two atoms, the Lewis molecule can also be completed in an ethylene, acetylene, and nitrogen molecule.



The compound NF_5 does not exist because there is no **2d** shell in the **N** atom, but one of the problems that hindered the application of Lewis rules is the structure of the nitrogen oxide molecule $\text{N}=\text{O}$, **NO**.

Molecular Orbital Theory (MOT)

This theory of the two scientists, Hund and Millikan, differs radically from the valence bond theory, as it assumes that the movement of electrons in molecular systems falls under the influence of a group of nuclei returning to the atoms united to form the molecule.

One of the ways to represent this theory is the linear combination of atomic orbitals (L.C.A.O), which assumes the possibility of combining the atomic orbitals of the united atoms that make up the molecule to give the molecular orbitals. That is, the electrons spend most of the time near one of the two controlled nuclei. If the electron is more likely to return to a particular nucleus, the wave function is described as closer to atomic orbital. As for the wave function for a molecular orbital, it is formed by the linear union of the two wave functions of two separate atomic orbitals, so it is formed by the linear union of two molecular orbitals. That is, the number of molecular orbitals resulting or formed from the union of the two atoms is equal to the number of united atomic orbitals, where two types of molecular orbitals are generated, one of which is of low energy and is called bonding molecular orbitals, it is a result of the sum of the atomic orbitals, which can be represented by the equation:-

$$\Psi_b = \Psi_A + \Psi_B$$

Ψ_b = bonding wave function.

Ψ_A = wave function of A atom.

Ψ_B = wave function of B atom.

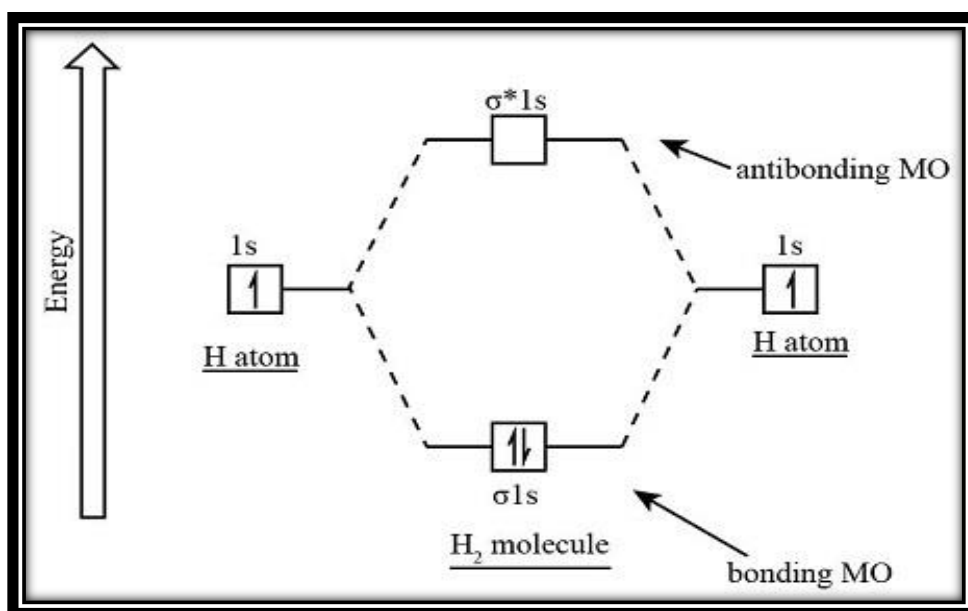
The other molecular orbital with a high energy level is called the antibonding molecular orbital.

$$\Psi_a = \Psi_A - \Psi_B$$

Ψ_a = antibonding wave function.

The molecular orbitals formed are close to the atomic orbitals of the universe b, since the atom possesses atomic orbitals of secondary shells of a type according to the quantum numbers of the atoms or molecules.

The molecule also depends on quantum numbers, and these are called molecular orbitals σ & π .

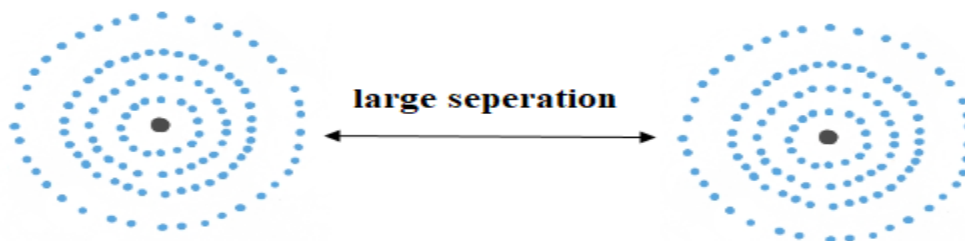


Molecular orbitals are also subject to Pauli's rule of exclusion, and each molecular orbital does not carry more than two electrons. It also follows Hund's rule in distributing electrons, or in other words, the electrons are

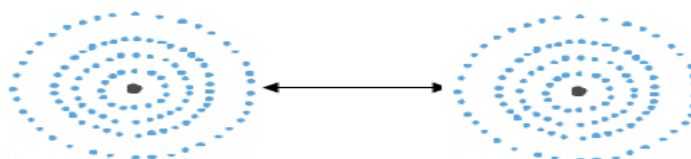
distributed among the orbitals of equal energy individually, and then the pairing process takes place. If one electron is allowed to be inserted into the bonding and allotropic molecular orbital of a molecule or an ion such as H_2^+ , the wave function for the molecule will be as follows:

$$\Psi_{AB} = \psi_b = \psi_A + \psi_B \quad \text{-----(1)}$$

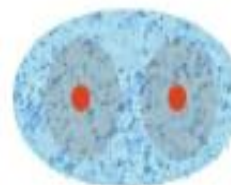
If the H_2^+ molecule contains two electrons, it can be represented starting from their presence at a distance so that they are not affected by the electron cloud of either one of the other, but when approaching each other more, the electronic density between the two nuclei will increase as a result of the interference of the atomic orbitals with each other,



And when the distance between the two atoms decreases further until the state of stability is reached for the two atoms, and the molecular orbital is formed.

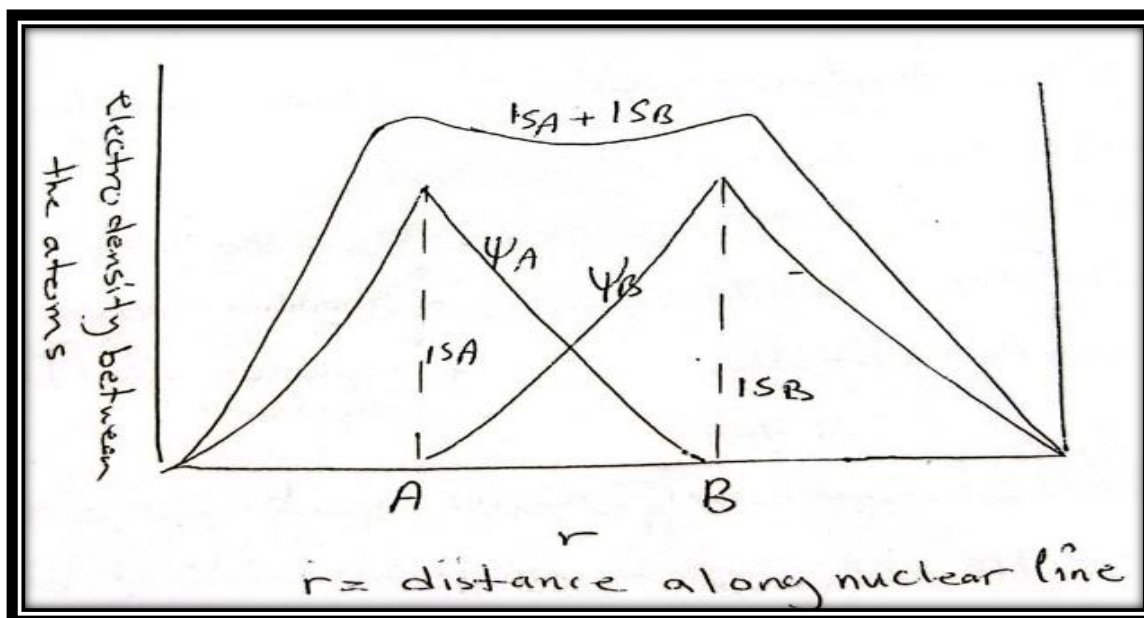


The electronic density is distributed to each of the two atoms, and the maximum density of electrons is between the two atoms. The molecular orbital formed is called the bonding molecular orbital.



This orbital is stable, so that it conserves energy for the system, which increases the stability of the molecule. If the molecular orbital formed is a

linear combination of the orbital functions of two atoms $\mathbf{H}_{A1}, \mathbf{H}_{B2}$, as in the following diagram:



The total wave function is equal to the product of the two functions for each of the two electrons.

$$\Psi_{\text{Molecular}} = \psi_a^A \times \psi_b^B \quad \text{-----(2)}$$

This means that there is no distinction between the two electrons, which leads to:

$$\Psi_{\text{Molecular}} = (\psi_A^1 \psi_B^1) \cdot (\psi_A^2 \psi_B^2) \quad \text{-----(3)}$$

$$\Psi_{\text{Molecular}} = \psi_A^1 \psi_A^2 + \psi_A^1 \psi_B^2 + \psi_B^1 \psi_A^2 + \psi_B^1 \psi_B^2 \quad \text{-----(4)}$$

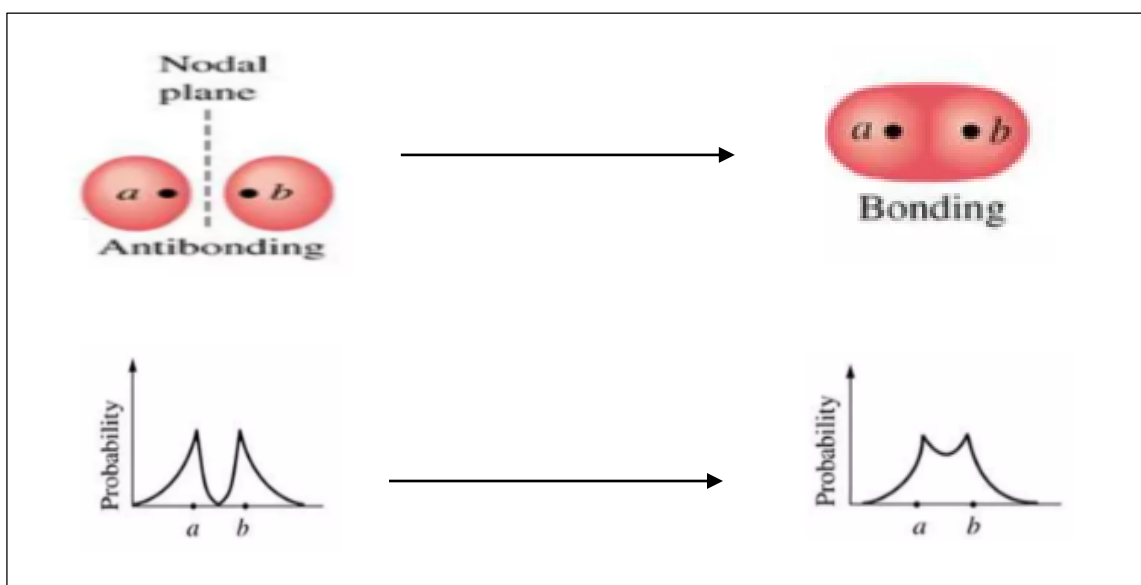
ionic cov. cov. ionic

It is noted from the last equation that there are two terms, one of which is covalent, represented by the two structures $\psi_A^1 \psi_B^2 \psi_B^1 \psi_A^2$, and the other is ionic, represented by the two structures $\psi_A^1 \psi_A^2 \psi_B^1 \psi_B^2$. This confirms the similarity the results of the first theoretical (V.B.T) and the second theoretical (M.O.T).

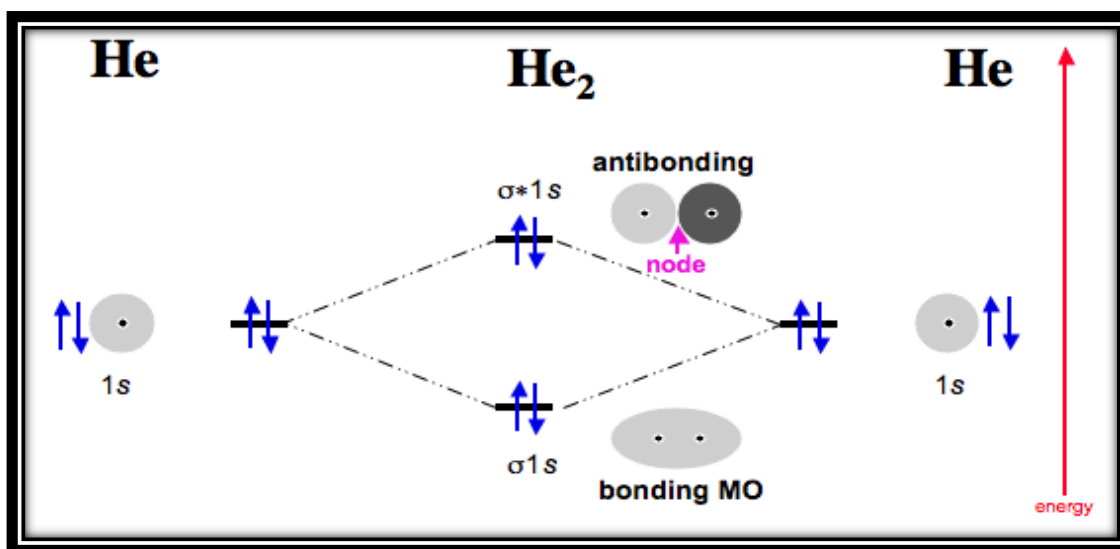
However, it is noted that molecular orbital theory confirm the ionic terms in such a way that it is not equal to the covalent terms because it did not take into account the repulsion that occurs with the electrons. Therefore, the theoretical values of the bond energy and the distance between the two atoms are not consistent or identical with the practical values except after making corrections to equation 4, and these corrections are shown in the following table.

Bond length A°		Bond energy eV	Wave function
0.85	Theoretical value	2.70	$\Psi_b = \psi_A + \psi_B$
0.73		3.49	+* Shielding electron effect
0.741	Experimental value	4.11	+* reputing effect
0.741		4.747	between electrons

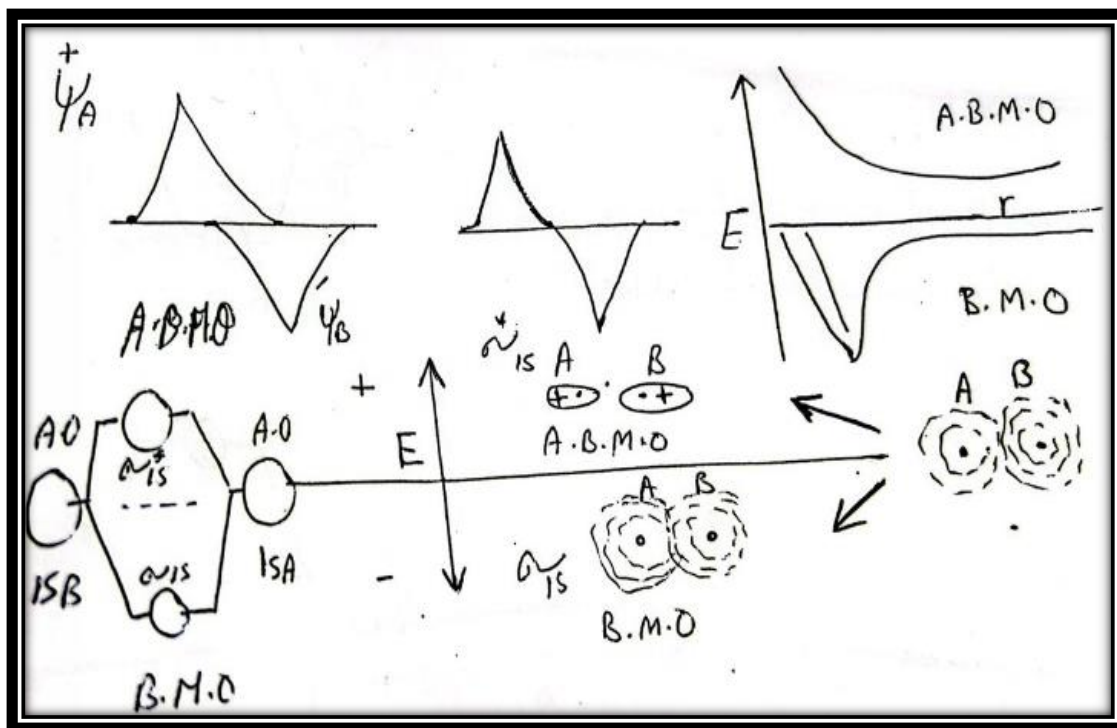
Explaining the hydrogen molecule to the allotropy orbital shows that the electrons spend most of their time in the overlap region between the two atoms H_A & H_B , which makes the attraction between the two electrons and the two nuclei as great as possible, so that the energy level of ψ_b is lower than the energy level of the atomic orbital.



However, if we assume that the molecular orbitals between the two atoms contain more than two electrons, such as the two atoms of helium and He_2 , then two of the electrons occupy the molecular orbital **B.O.M**, giving a molecular orbital of the sigma type σ^b , while the other two electrons occupy the molecular orbital with the anti-bonding type σ^* , and it was later shortened to σ^* which high-energy one shortened σ to σ^b .



Where the electronic density decreases in the overlap region, as the electrons are pushed further from the area between the two nuclei, and the electronic density is as low as possible (so that it reaches zero) in a level called the **nodal level**, which is perpendicular to the line connecting them. As a result, the repulsion between the nuclei of the two atoms increases, and the molecule is made. The first is stable, meaning that the anti-corrosive molecular orbital is less stable and has a higher energy than the atomic orbitals that make it up.



When representing the energy levels between two atoms according to the molecular orbital theory, equivalent orbitals are placed together, taking into account that the most stable levels are in the lower position. If the two atoms are of the same element, then molecules such as He_2 , He_2^+ , H_2^+ , H_2 are formed by linear combination. If the electrons are located in the molecular orbitals of the two atoms, this means that they spend most of their time between the nuclei of the two atoms. However, if they are located in the molecular orbitals of the opposite nature, then they spend most of their time away from the nuclei. In this way, the bond order and the magnetic character of the molecule can be known.

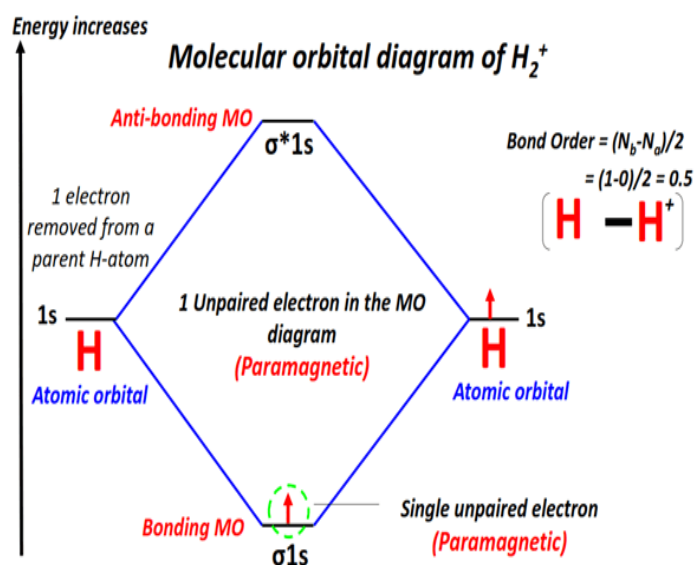
$$\text{Bond order} = \frac{\text{No. of electrons in B.M.O} - \text{No. of electrons in A.B.M.O}}{2}$$

رتبة الأصرة

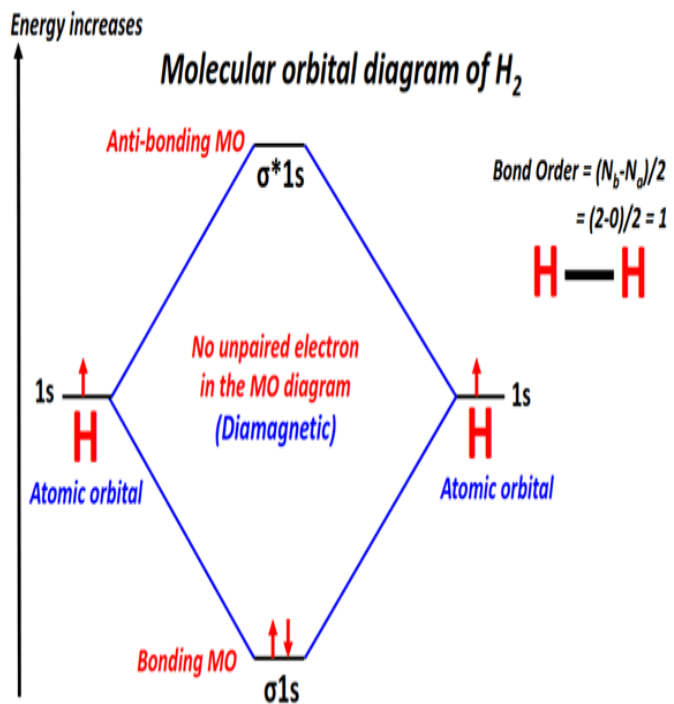
(قانون حفظ)

The first bond that is formed is of the sigma σ type, and the bonds that are formed after it are of the π type. If the bond order is equal to $1/2$, it is also of the sigma type. If the bond order is = 2 , then it is of the sigma σ type, but when it is equal to $1\frac{1}{2}$, it means the presence of one bond sigma σ type and half of bond π type.

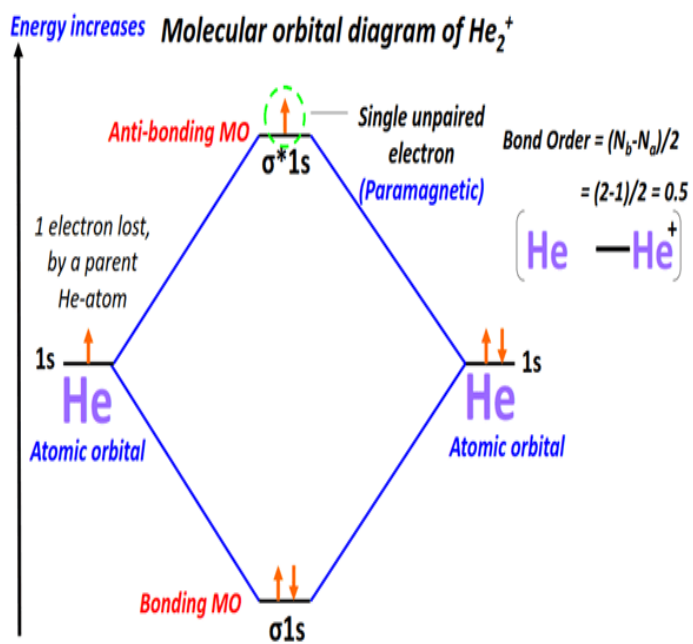
H_2^+ , H_2 , He_2^+ , He_2



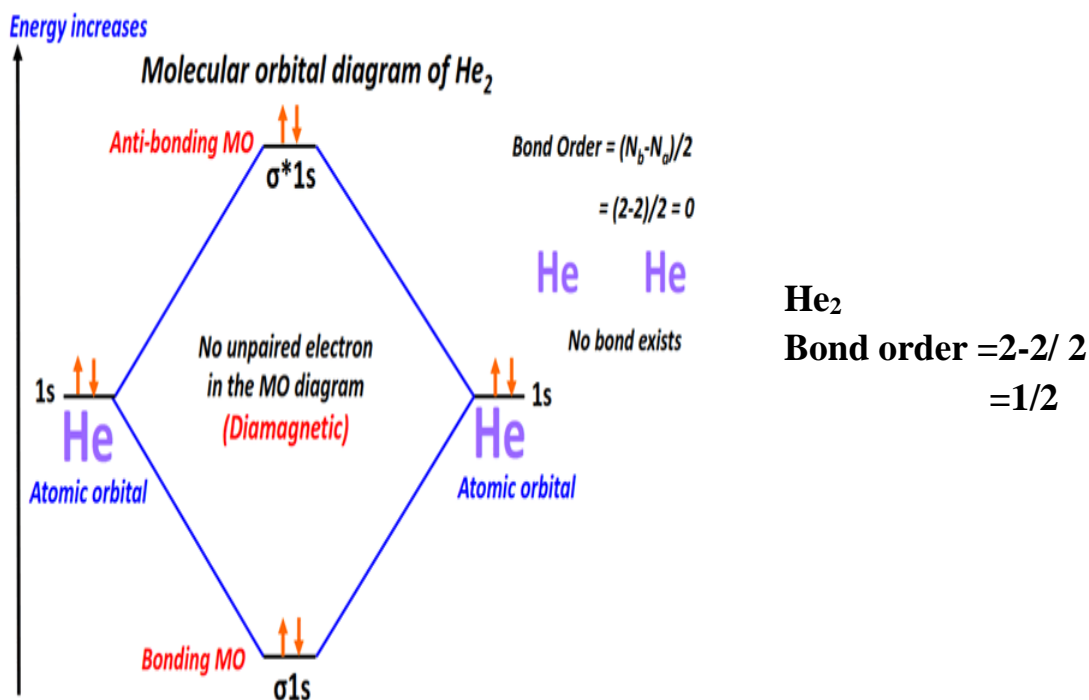
H_2^+
Bond order = $1 - 0 / 2$
 $= 1/2$
Paramagnetic
Type of bond order
 $1/2\sigma$



H₂
Bond order = 1
Diamagnetic



He₂⁺
Bond order = $2 - 1/2$
= 1/2
Paramagnetic



If the molecule contains single electrons, it has paramagnetic properties, but if it contains double electrons, it is repulsed by the magnetic field and is called diamagnetic. Therefore, both of He^{+2} , H_2^+ are paramagnetic, while H_2 the magnetic characteristic have no relation to the stability of the molecule.

The two most important conditions that must be met in the formation of a molecule from the linear interference of atomic orbitals are:

1. The interference between atomic orbitals must be a wave.
2. For effective interference to occur between the orbitals of different atoms, the orbital energies of the two atoms must be approximately equal.

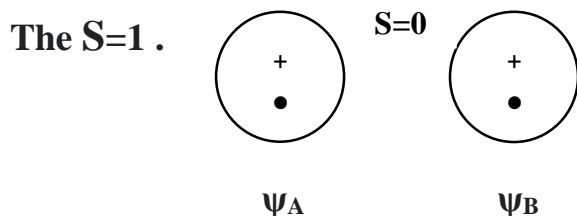
Regarding the first condition, the interference is considered very important, although it is not sufficient to form the bond. The interference is symbolized by the letter **S** and expressed mathematically as follows:

$$(\text{مقدار التداخل}) \quad S = \int \psi_A \psi_B \, dT.$$

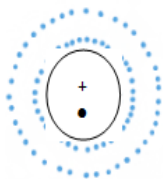
It is a measure of the extent to which the wave function of one of the two atoms overlaps with the wave function of the second atom, and then the distance between the two atoms is infinity, which is a non-bonding case.

- (حفظ) $\left[\begin{array}{l} \text{When } S=0 \text{ non-bonding.} \\ \text{When } S > 0 \text{ Bonding.} \\ \text{When } S < 0 \text{ Antibonding.} \\ S = \text{value of linear overlapping orbital (مقدار التداخل)} \end{array} \right.$

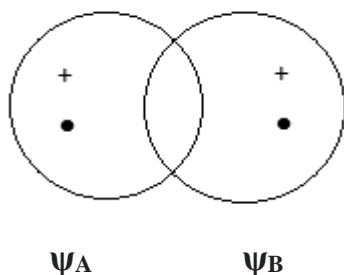
When the distance between two nucleus= 0



$$S = \int \psi_A^2 dT.$$



In this case, both ψ_A and ψ_B correspond to the same wave for one of the two atoms. However, when the distance between the two nuclei is an intermediate between the two values, that is, between zero and infinity, the value of S is positive and an intermediate between **zero** and the integer **1**, we obtain a state of bonding due to the positioning of the two electrons between the two nuclei.



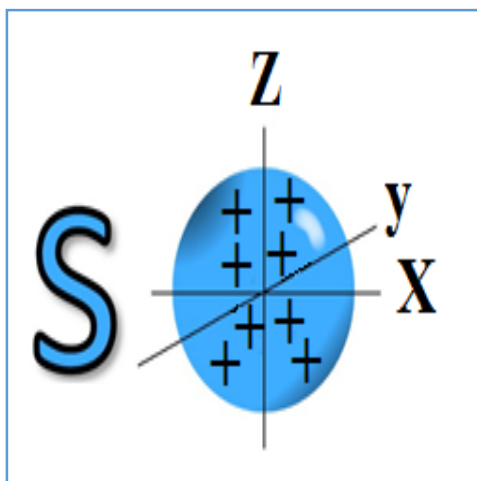
In the case of antibonding, it causes the two electrons to repel and move away from each other and from the nuclei of the two atoms, so the value of **S** is less than **zero**.

It is known that the best way to estimate the strength of the bond is by measuring the energy released when the bond is formed, which is difficult most of the time, but the scientist Pauling invented a method that depends on the interference between the orbitals of the two atoms that make up the bond, whether this interference is positive, negative, or equal to zero, along with knowing the amount of this interference. Between atomic orbitals and this interference depends on:

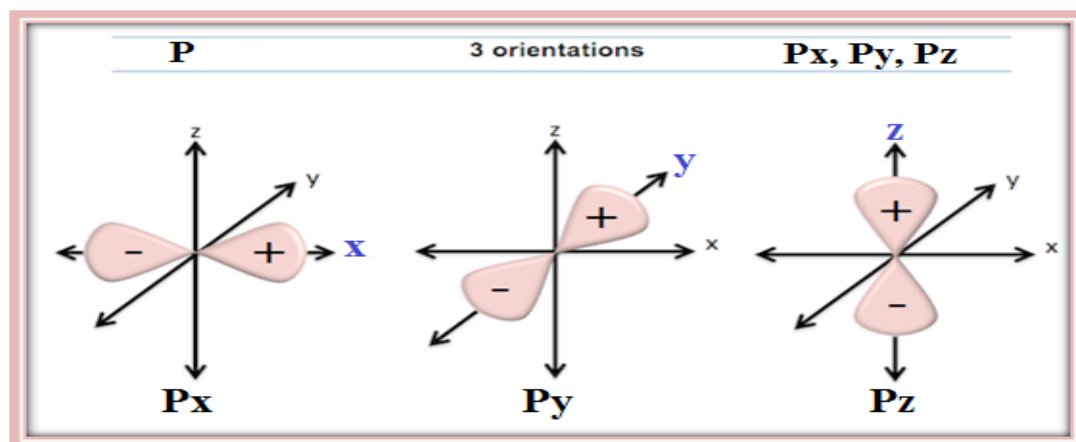
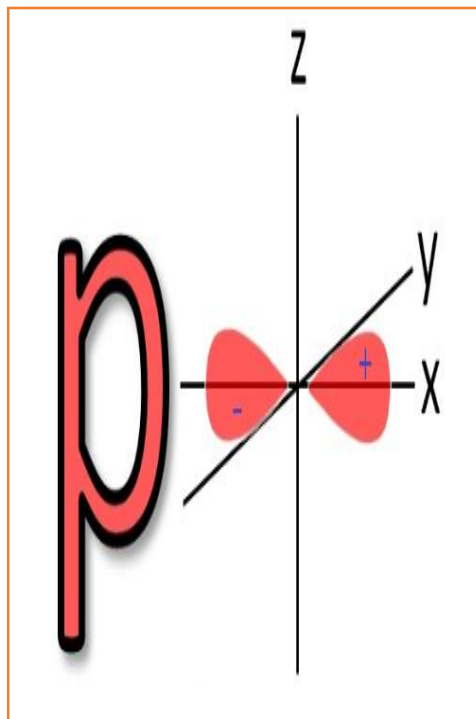
- 1- Energy of overlapping orbital.
- 2- Size of overlapping orbital.
- 3- Distance between two nucleuses.
- 4- Symmetry of overlapping orbital.

Wave function of s, p, d orbitals

If $\ell = 0$, then the number of nodes = 0 and the orbital is of the S type and its shape is spherical or circular, meaning that it has a diagonal function only, and since the resultant of its angular momentum = zero, it is regular symmetric within the three dimensions or axes, and regular symmetry is given the symbol (g) (gerada) and when $\ell = 1$, then the number of nodes = 1.



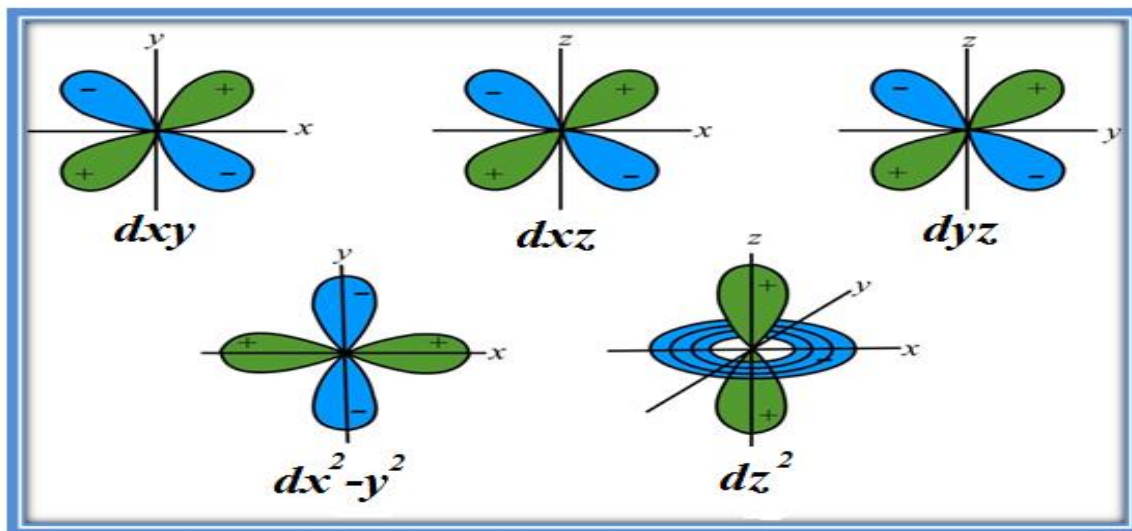
The orbitals of the secondary level are of the p type, and their number is three orbitals called P_z , P_y , P_x , each of which has a node, meaning that the probability of the presence of the electronic density is in the following form, that is, the sign of the wave function changes, and the symmetry is non-spherical, and the probability of the presence of the electronic density and its distribution changes with the change of the angular function and the function. The diagonal is within the Cartesian axes x , y , z for each orbit, and the three (p) orbitals are distributed perpendicular to the three axes:



Orbitals (p) do not have spherical symmetry, but consist of orthogonal lobes of asymmetric sign in the wave function and are symbolized by (u) (ungerada), i.e. the wave function sign changes for each orbital of the p orbitals.

When $\ell = 2$, then the number of orbitals of the secondary level (d), and it has five orbitals, each containing two nodes, that is, for each orbital of the d orbitals, it contains two orthogonal nodes. Opposite to each other, they are symmetrical, that is, the symmetry becomes of the type g, and it is as in the

p orbitals, the wave function changes with $m\ell$, ℓ , r , and the shape of the four d orbitals is identical or similar.



As for the fifth orbital, d_{z^2} , it is located on the z axis. The electronic density, or the presence of the wave function, is as large as possible on the z axis above and below the axis, and the electronic density is less on the Wave $d_{z^2-x^2}$, $d_{z^2-y^2}$. When $\ell = 3$, the number of nodes = 3, meaning that the wave function is unified by the values of ϕ , Θ , r , and the wave function has irregular symmetry (ungerada). Every principal quantum number (n) contains a number of orbitals, which can be known from the following equation:

$$\text{no. of orbital} = n^2, \text{ When } n=1$$

All values of the secondary quantum number ℓ for any primary quantum number n are equal in energy before the magnetic field is applied or if they are empty.

- 1- The secondary quantum number ℓ determines the energy of the electron in the secondary energy level.

$$\text{When } \ell = 0, 1, 2, 3, 4$$

$$s < p < d < f$$

- 2- Each secondary energy level contains a maximum number of electrons depending on the principal quantum number. no. of electron = $2n^2$.

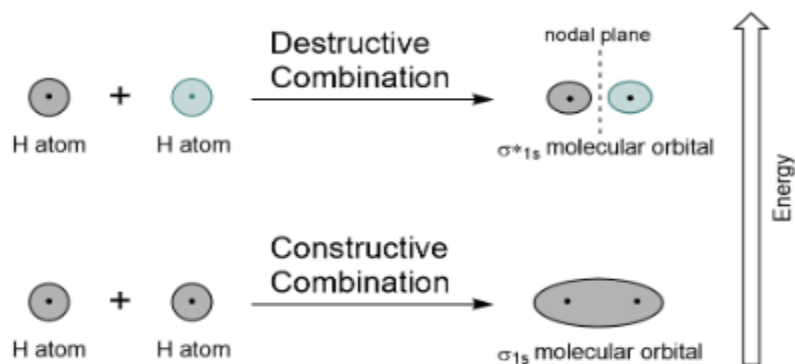
Since each secondary level contains a number of orbitals, which = $2L + 1$, these electrons for each secondary level are distributed among the orbitals so that each orbital does not take more than two electrons.

- 3- Since each principal quantum number n contains a number of secondary levels, the determination of the energy of any electron is based on the principal quantum number n formed by the secondary. Based on the rule that the lowest-energy secondary shell is filled first.

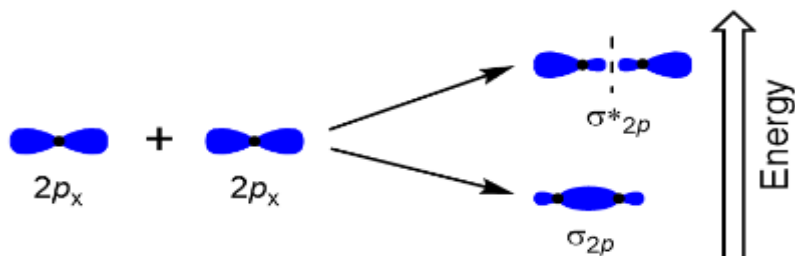
Symmetry of Molecular Orbital and Types of Linear Combination and Overlapping

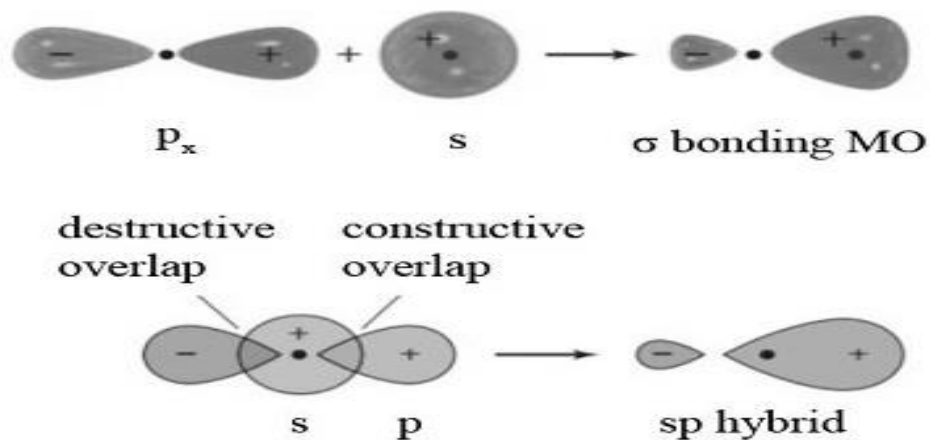
Symmetry of molecular orbitals and types of linear interference:

1. **Sigma σ^*** orbital is a molecular orbital with cylindrical symmetry around the molecular axis between the two nuclei. If the nuclei are two similar atoms of the type **S** and **P** orbitals, then the molecular orbital is formed between the two atoms.



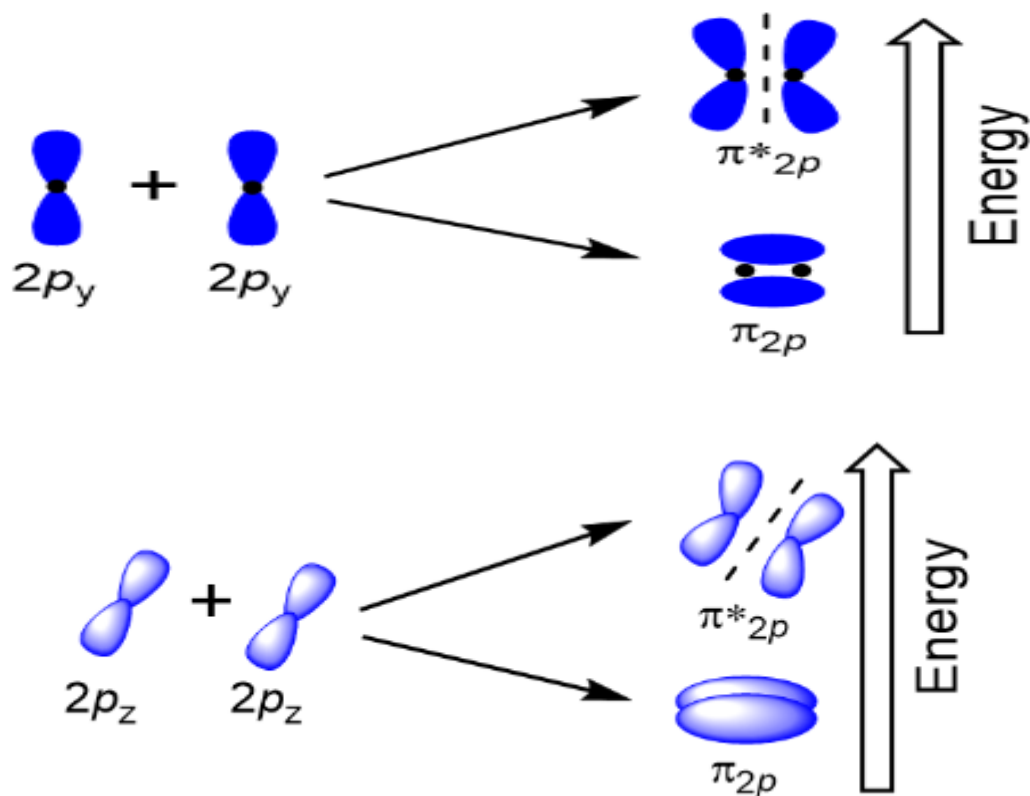
The sigma molecular orbitals also consist of the linear union between the **P_x** orbitals, specifically the **P_x** type, arranged along the x axis between the two nuclei, so they have the same sign. The electronic density is highest possible in the bonding region, but against bonding, the electronic density is reduced and the energy level becomes higher than that of atomic orbitals.

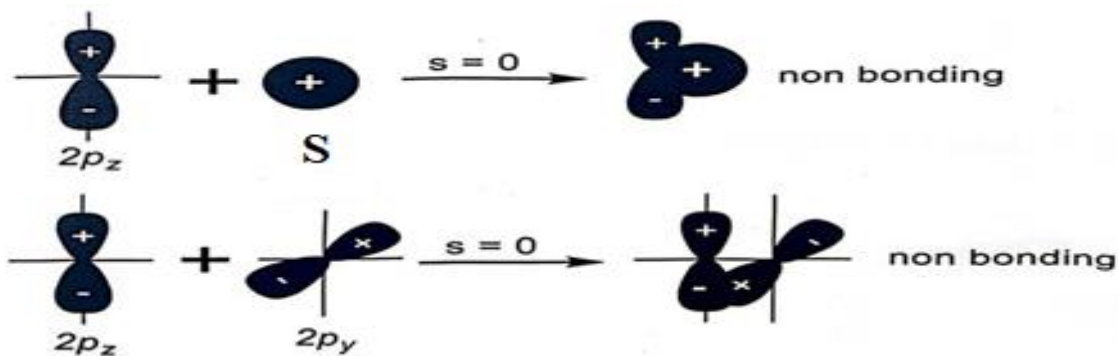




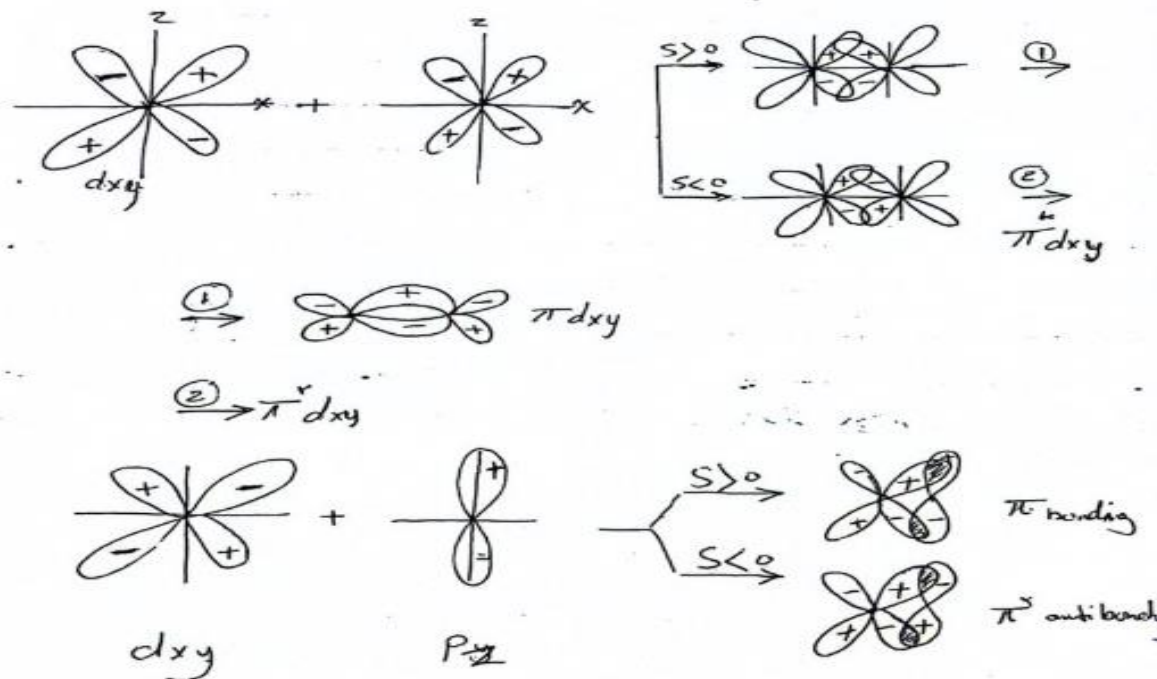
2. π orbital

In atoms containing p orbitals, the union of P_y with P_y orbitals, or P_z with P_z orbitals, that are parallel to each other, leads to interference from the top and bottom of the line connecting the nuclei of the two atoms and the level of the bond (the level of the knot formed by the type of π). The electronic density in the π orbitals is distributed on two opposite sides in a sign and the wave symbol. The electronic density in the π orbitals is distributed on two opposite sides in a sign and the wave symbol.





The molecular orbital is of the πp type (bonding) of the irregular symmetry type (ungarada), similar to a flip around the center of the molecule, while the π^* type is of the regular type d-type orbitals consist of the following form:

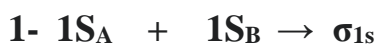


Lateral overlap occurs between two parallel orbits and the type of bond formed is (π).

$$\left. \begin{array}{l} dx^2-y^2 + dxz = \\ dx^2-y^2 + dyz = \\ dx^2-y^2 + dz^2 = \end{array} \right\} S=0 \text{ nonbonding.}$$

$$\left. \begin{array}{l} dx_y + S \\ dy_z + S \end{array} \right\} S=0 \text{ nonbonding}$$

For the sequence of energy levels of similar atom molecules containing **S** and **P** type orbitals.

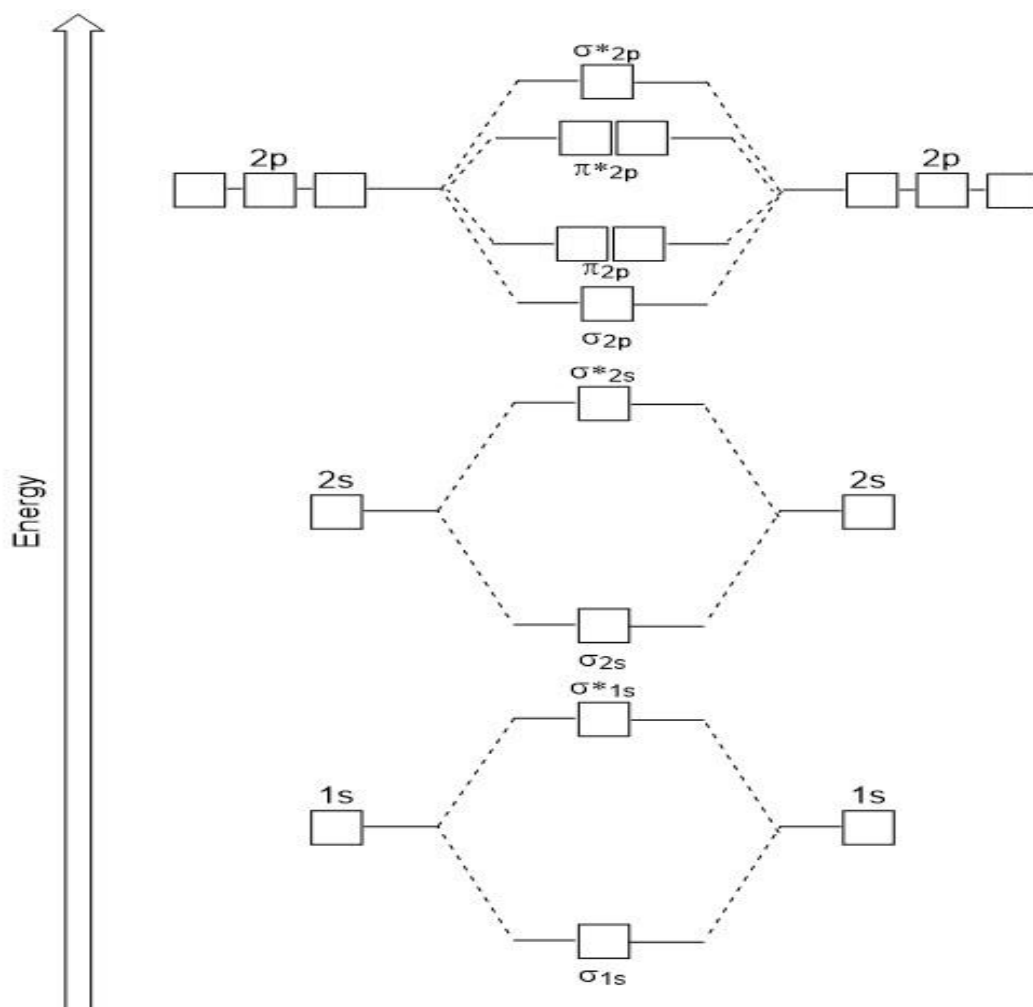


Energy difference

Their energies are equal,
so when filling these two
orbitals we must observe
Hund's rule

Both π_{2Py} & π_{2Pz} exist at the same energy level, as is the case for π^*_{2Py} & π^*_{2Pz} . Therefore, when filling electrons, Hund's rule must be observed. If the atoms are small, the energy level π_{2Pz} & π_{2Py} will be lower than the energy level σ_{2Px} because in small atoms there is a convergence between the **2S** & **2P** energy levels, and the opposite happens in large atoms. Therefore, the distribution of electrons among the molecular orbitals in boron and carbon is as follows:

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi_{2p_y} = \pi_{2p_z} < \sigma_{p_x} < \pi^*_{2p_y} = \pi^*_{2p_z} < \sigma^*_{2p_x}$$



While for N, O and above, the distribution of molecular orbitals is as follows:

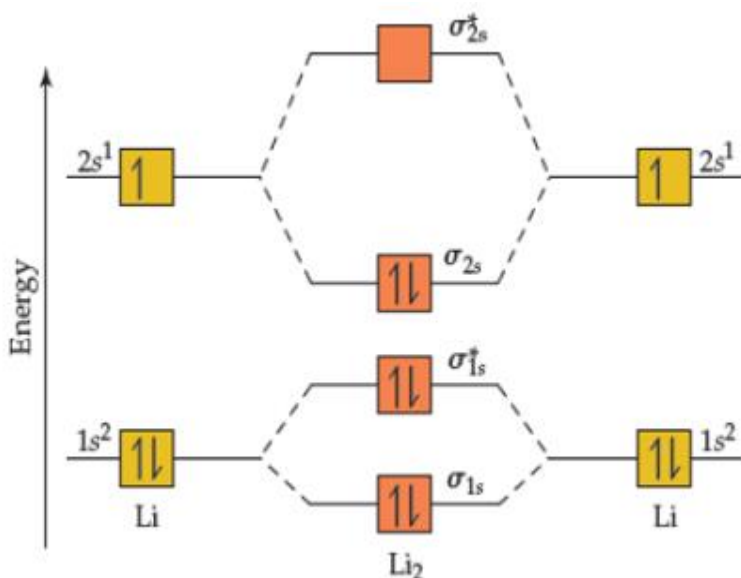
$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2p_x} < \pi_{2p_y} = \pi_{2p_z} < \pi^*_{2p_y} = \pi^*_{2p_z} < \sigma^*_{2p_x}$$

Energy sequence \longrightarrow

(مخطط الطاقة للحفظ)

Example: Do these molecules exist, do these molecules have magnetic properties, and what is their stability if they are present? Li_2 , N_2 , O_2 .

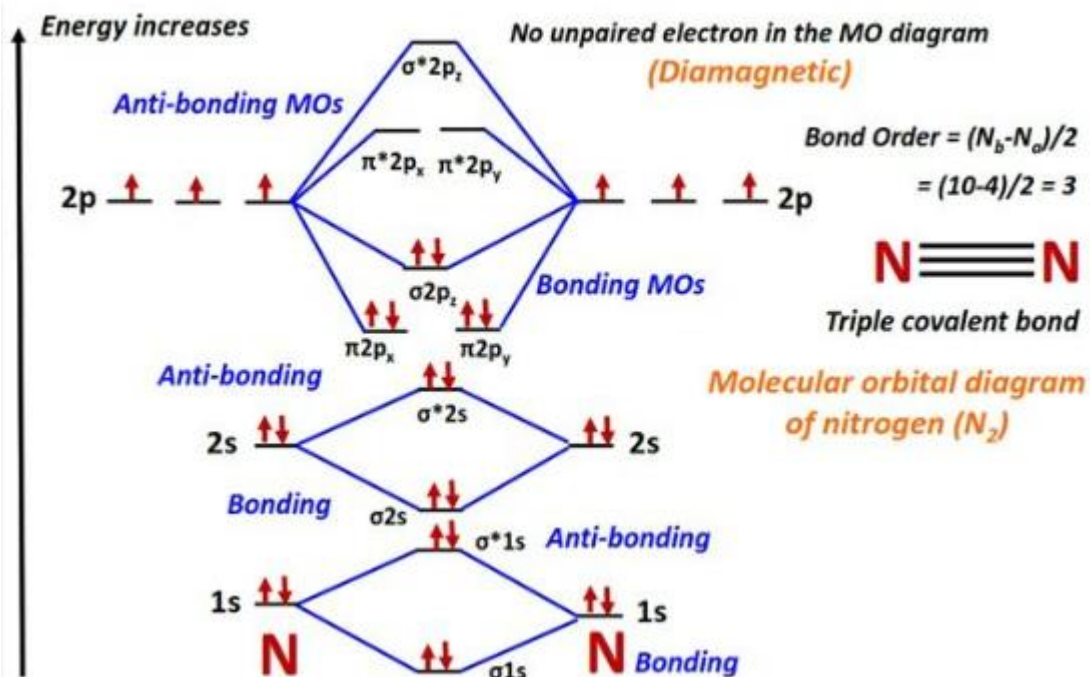
$3\text{Li}: 1s^2 2s^1$

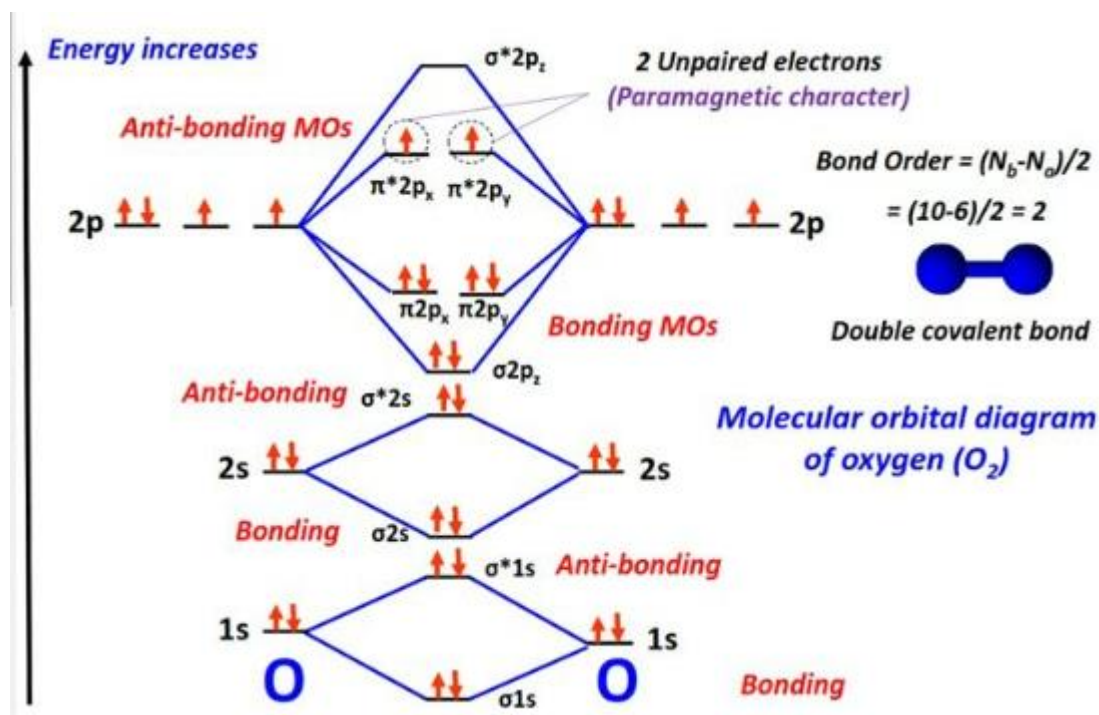


Li_2

$$\text{Bond order} = \frac{4-2}{2} = 1$$

The magnetic character depends on the number of individual electrons. Since the molecule does not contain individual electrons, this molecule has diamagnetic properties.





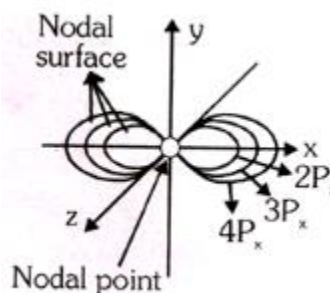
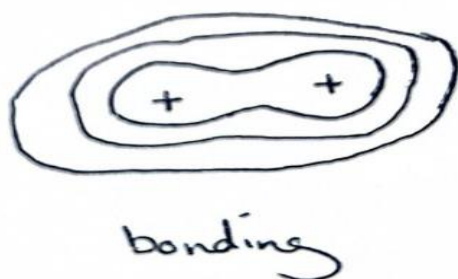
Assignment: Are the following molecules exist or not exist? Then calculate the rank of the bond Ne_2 , F_2 and the magnetic characteristic?

Overlap:

$$\Psi_b = \psi_A + \psi_B \quad \psi: \text{wave function}$$

$$\Psi_a = \psi_A - \psi_B$$

The integral $\int \psi_a \psi_b dt$ is known as the overlap integral S , and is very important in bonding theory. In the bonding orbitals the overlap is positive and the electron density between the nuclei is increased, whereas in the antibonding orbital the electron density between the nuclei is decreased. In the former case, the nuclei are shifted from each other and the attraction of both nuclei for the electrons is enhanced. This results in a lowering of energy of the molecule and is therefore a bonding situation. In the second case, the nuclei are partially barred toward each other and the electrons tend to be in those regions of space in which mutual attraction by both nuclei is severely reduced.



$S > 0$ - bonding

$S < 0$ - antibonding

$S = 0$ - non bonding

The strength of bond will be roughly proportional to the extent of the overlap of the atomic orbitals. This is known as the overlap criterion of bond strength and indicated that bonds will form in such a way as to maximize overlap.

In **S** orbital the sign of the wave function is very were the same (with the exception of small intranodal region for $n > 1$) and so there is no problem with matching the sign of the wave functions to achieve positive ways of arranging the orbitals, some resulting in positive overlap some in negative overlap and some in which the overlap is exactly **Zero**. Bonding can take place only when the overlap is positive.

Bond order: The bond order is defined in MO theory as the number of electron pairs occupying bonding MO's Minus number of electron pairs occupying antibonding MO's, thus the bond orders in **H₂⁺**, **H₂**, **HHe**, **He₂**, **1/2**, **1**, **1/2**, **0** respectively.

The hydrogen molecule is considered more stable than the lithium molecule **Li₂**. Likewise the boron **B₂** molecule is considered more stable than the **Li₂** molecule for the following reasons:

1. The bond of the hydrogen molecule is shorter and stronger than the bond of **Li** because the radius of the **Li** atom is larger than the radius of the **H** atom because the **Li** atom is located in the second period.

Also, the molecular orbital of the H_2 molecule σ_{1s} is closer to the nuclei of the two H_2 atoms relative to the molecular orbital σ_{2s} of the Li atom, where it is. The nuclei of the Li atom are two groups larger than the nuclei of the H_2 atom, so their attraction to the orbital is less than that of the H_2 molecule.

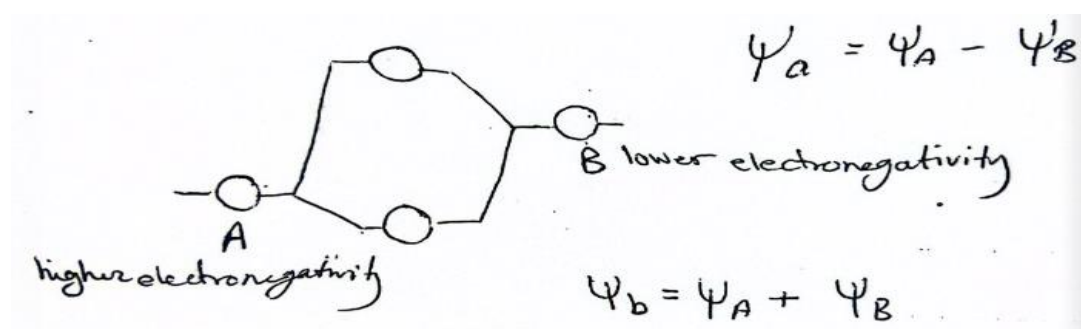
2. The bond energy is higher in the boron molecule than in the lithium molecule, and the bond length in the boron molecule is shorter than the bond length in the lithium molecule because the radius of the boron atom is smaller than the radius of the lithium atom, and this results from an increase in the effective charge Z^* of the boron atom.
3. The length of the bond increases and its energy decreases with the increase in the atomic number within one group, and the length of the bond shortens and its energy increases with the increase in the atomic number within one period.
4. All alkali metal molecules, from Li_2 to Cs_2 , have a bond rank equal to one, and their magnetic properties are of the diamagnetic type, and the same is true for the halogen elements.

General Notes: (ملاحظة هذه المعلومات)

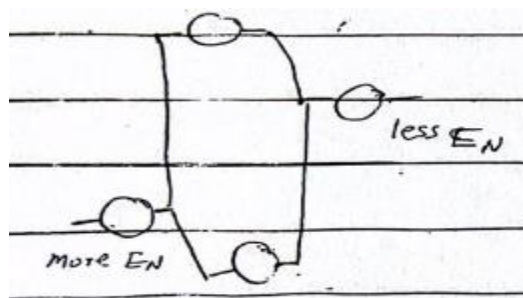
1. When calculating the bond order, the electrons in the (non-bonding orbital) are not included in the calculation, and the energy level of these orbitals is the same as the energy level of their possible atomic orbitals. This results from the fact that these orbitals are not similar in orbital symmetry, so the process does not contribute in bonding process.
2. Heterogeneous molecules that are diatomic of the type (**np, ns**). The bond formed between the atoms of the two different elements means that they are different in their electronegativity values, as well as that they are different in the effective charge, even if the two elements belong to the same cycle, such as **N, O**. This leads to a change in the energy level of one of them is relative to the energy level of the other element. For an element with high electronegativity, the orbital energy level is lower than the atomic orbital energy level for an element with low electronegativity.
3. The contribution of the more electronegative element to the formation of the allosteric molecular orbital is greater than the contribution of the less

electronegative element. This means that the energy level of the allotropic molecular orbital is closer to the energy level of the other, more electronegative element $F \bullet \text{---} \bullet H$.

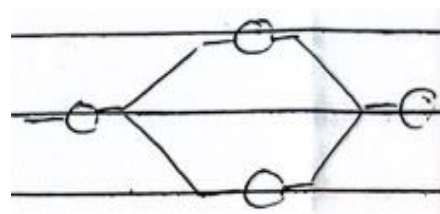
- The contribution of the less electronegative element to the formation of the anti-electronic molecular orbitals is greater than the contribution of the more electronegative element. This means that the energy level of the anti-electronic molecular orbitals is close to the energy level of the less electronegative element, and therefore the electrons of the anti-electronic molecular orbitals spend most of their time near the less electronegative element.



- Non-bonding electrons appear if the two elements are from different spins and maintain the same level.
- As the difference in electronegativity increases, the covalent character decreases, the polarity of the bond increases, and the ionic character gradually appears. For example, CsF and $CsCl$ ionic compounds, that is the energy of the mutual influence of exchange energy, the nuclei of the two atoms on the covalent electrons decreases as a result of the difference in energy levels.



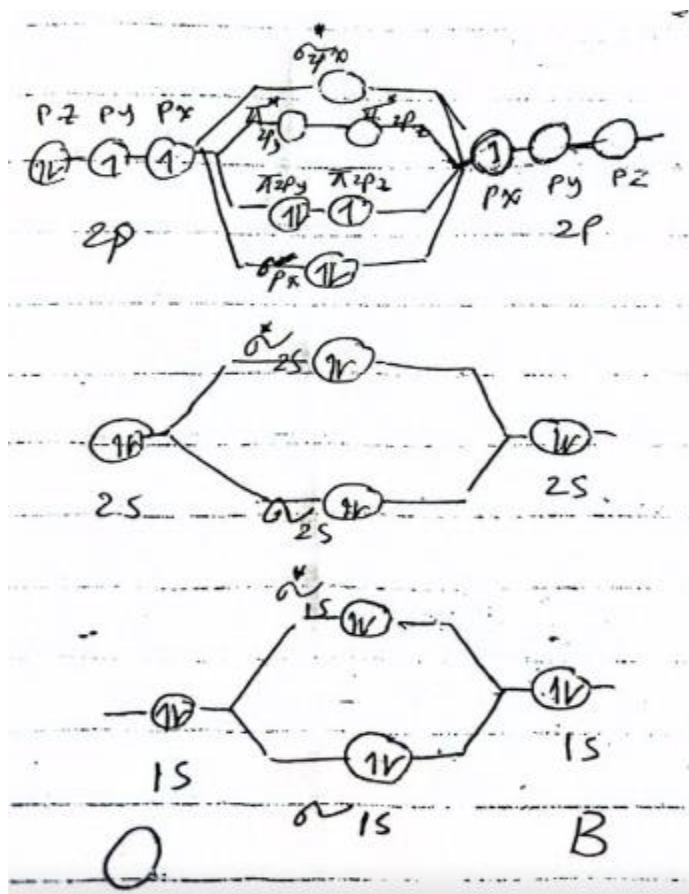
Increased ionic character and decreased covalent character.



100% It has covalent properties because there is no difference in electronegativity. 100% covalent bond.

The arrangement and characteristics of the energy levels in molecules consisting of two different atoms within the same period **ns np**:

- 1. The energy and the bond order increases and its length shortens as the number of bonding molecular orbitals increases at the expense of anti-bonding molecular orbitals.**
2. The bond energy increases as the radii of the atoms that make up the molecule decrease, and its length decreases as well.
3. If the bond order = 1/2 or 1, it is a bond type, and if it is equal to more than one it means it is a bond type σ + part of the type π .
4. If two molecules are equal in bond order, so the preference for one over the other in terms of stability is based on the following:
 - i- Total nuclear charge (positive is more stable than neutral and neutral is more stable than negative) because increasing the density of the positive charge of the molecule leads to an increase in the attraction of the nuclei of the two atoms to the electronic clouds they share the negative charge on the molecule leads to increased blocking on the two nuclei, and as a result of the repulsion with the other electrons, the length of the distance between the two atoms increases, so the stability of the molecule decreases and the bond lengthens.
 - ii- The stability of the molecule decreases compared to another molecule with the same bond order if the first molecule contains more anti-affinity electrons than the second molecule.



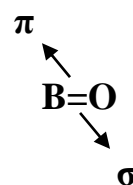
$$B=O$$

$$B.O = 9-4/2$$

$$= 5/2$$

$$= 2.5$$

It has a magnetic character due to the presence of a single electron (paramagnetic).



paramagnetic property.

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi_{2p_y} = \pi_{2p_z} < \sigma_{2p_x} < \pi^*_{2p_y} = \pi^*_{2p_z} < \sigma^*_{2p_x}$$

Home work: Draw a molecular diagram of BN & CO.

Therefore, the NO^+ molecule is considered more stable than the NO molecule because the NO^+ molecule has a high effective nuclear charge. In addition, the loss of an electron from the orbital against the bond leads to an increase in the bond order from 2.5 for NO to 3 in NO^+ .

The stability of the molecule depends on: (حفظ مهمة)

الاستقرارية حسب نظرية (MO) تعتمد على

1. The higher the bond order.
2. The greater the effective nuclear charge of the molecule.
3. The smaller the radii of the two united atoms.
4. The greater the number of bonding electrons and the smaller the number of electrons in non-bonding orbitals.

Example: Write the electronic configuration and arrange the following molecules in order to increase stability according to molecular orbital theory (MOT) and give reason?

(CN⁻, CO, NO⁺), (CN⁻, CO⁺, BO), (NO⁺, NO⁻, NO), (O₂, O₂⁻, O₂⁼), (Be, Be₂, B₂, C₂, N₂).

Example: Draw the energy levels for the following molecules according to molecular orbital theory Na₂, F₂, Cl₂ and find the bond order and magnetic properties?

Prof. Dr. Mahasin Faisal A. Alias

Hybridization

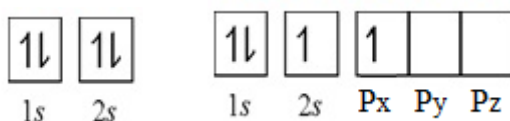
Inorganic Chemistry

7th lecture

Prof. Dr. Mahasin Faisal A. Alias

2023-2024

Hybridization



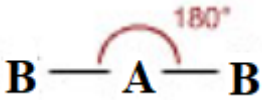
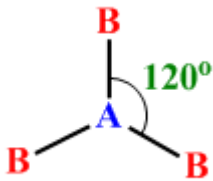
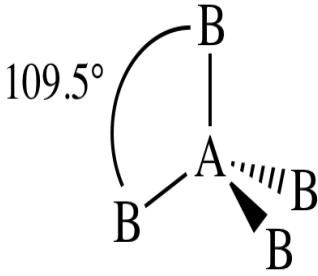

The formation of the compound **BeCl₂** is an indication that it is possible to transfer an electron from the **2S** secondary shell to the **2P** secondary shell to form (the excited atom) with a little energy. This can happen to form two bonds sigma type σ with **Be**. Each chloride atom contains an orbital, which contains one, preferably an orbital. The **P_x** is because it has a similar symmetry, which allows the formation of a sigma bond (σ).

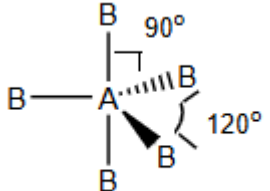
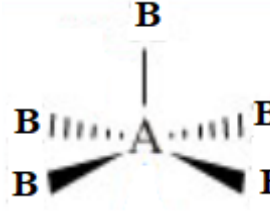
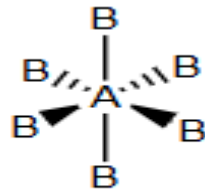
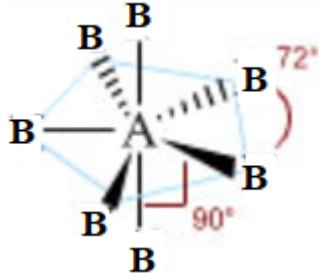
As for beryllium, it contains one electron in the **2S** orbital and one electron in **2P**. If we assume that the **2S** electron of the Be atom can form a sigma bond σ with the **P_x** secondary orbital of the first chloride atom and another sigma bond σ between the secondary **Be** orbital type **2P_x** and secondary **Cl** orbital (**P_x**) For the second **Cl** atom, there will be two unequal bonds. This means that the energy of the first **BeCl** bond differs from the energy of the second **BeCl** bond, or in other words, the first bonding electron double is not equivalent to the other bonding electron double.

In order for the two allotropic doubles (**σ bonds**) formed on both sides of the Be atom to be equivalent, the two orbitals belonging to the **Be** atom must be equivalent, and this valence will take place through the **hybridization process, which is the process of mixing and redistributing the electronic density of the atomic orbitals surrounding the central atom in the valence shell**, such that they are linked by covalent bonds. With other atoms to obtain orbitals suitable for linear correlation, the overlap of the hybrid orbitals of the central atom with the orbitals of other atoms is stronger than the non-hybridized orbitals because the extension of the hybrid orbitals in the vacuum is more strengthened by the covalent bond formed or the resulting bond.

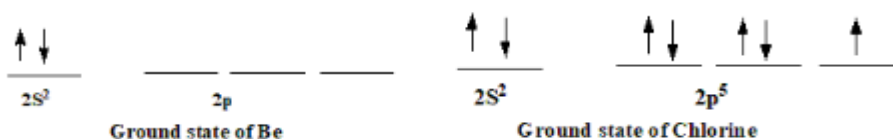
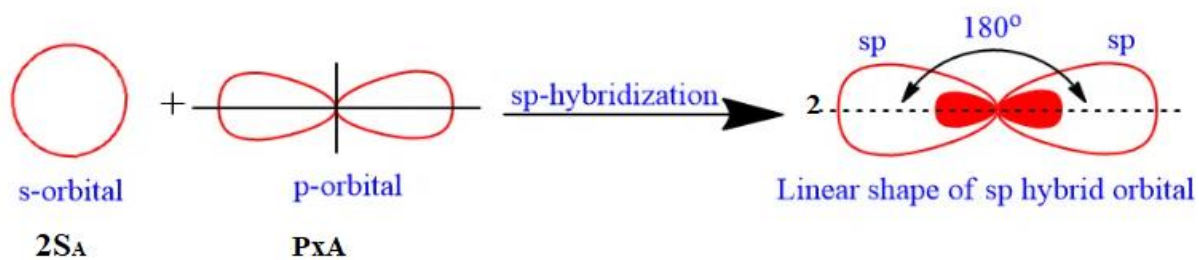
The hybridized orbitals are arranged around the central atom in a geometric and spatial manner that ensures the least repulsion between them, and the number of individual electrons in them is equivalent to the number of bonds that the central atom can form with other atoms in the elements of the second period, whose secondary shells consist of **S** and **P**. we can obtain three types of hybridization. Depending on the type of molecule.

This table show molecules conation a central atom (A) with bonding pairs (B)

Molecule	hyb.	No. of σ bond	Geometry Shape	Example
AB_2	SP	2	 Linear	$BeCl_2$
AB_3	SP^2	3	 Planner	BCl_3
AB_4	SP^3	4	 Td	CCl_4
	dsp^2		 Sq. planner	XeF_4

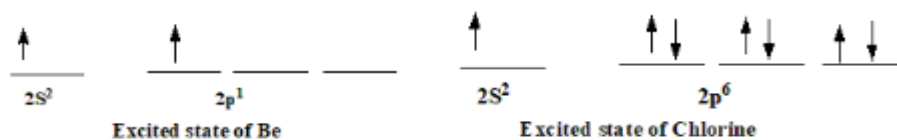
<p>AB_5</p>	<p>dSP^3</p> <p>SP^3d</p>	<p>5</p>	 <p>Trigonal bipyramid (TbP)</p>  <p>Square pyramid</p>	<p>PCl_5</p>
<p>AB_6</p>	<p>SP^3d^2</p> <p>d^2sp^3</p>	<p>6</p>	 <p>octahedral</p>	<p>SF_6</p>
<p>AB_7</p>	<p>d^3sp^3</p> <p>sp^3d^3</p>	<p>7</p>	 <p>Pentagonal bipyramid</p>	<p>IF_7</p>

1- Sp- Hybridization AB₂ (BeCl₂)

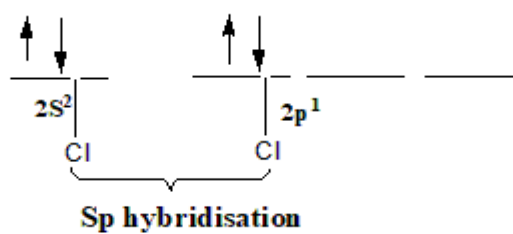


Ground state of Be and Cl

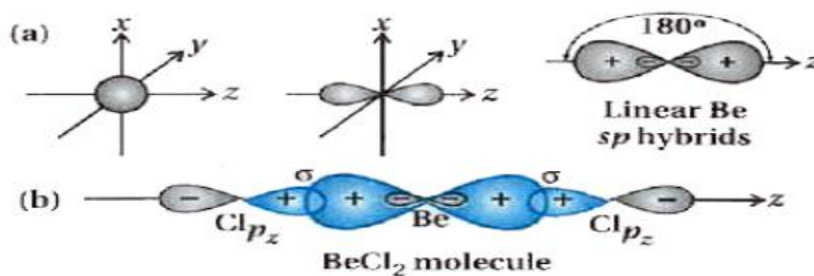
- Excited state of Be and Cl



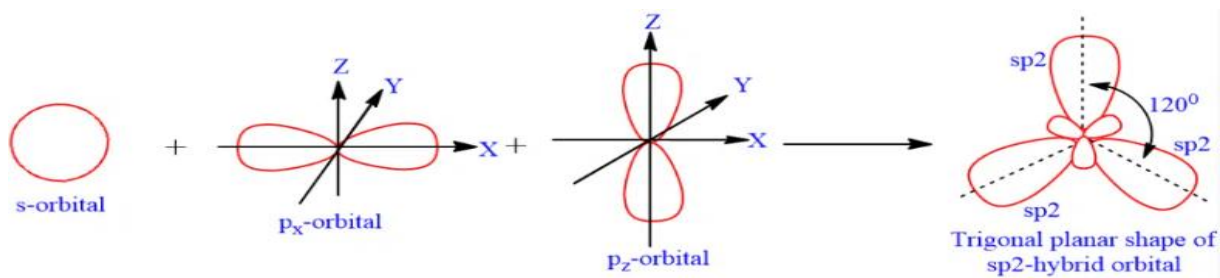
Representation of excited states of Be and Cl



Formation of BeCl₂



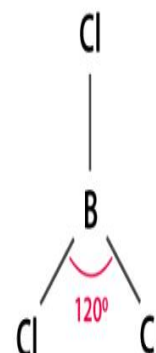
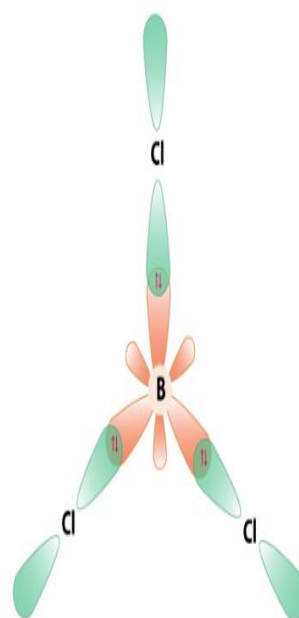
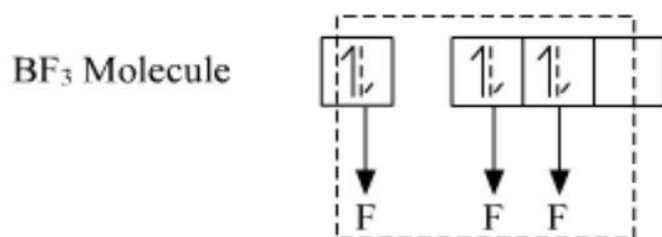
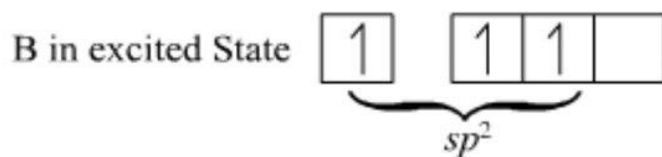
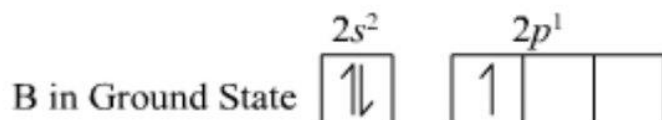
2- Sp²- Hybridization (AB₃) (BCl₃, BF₃)



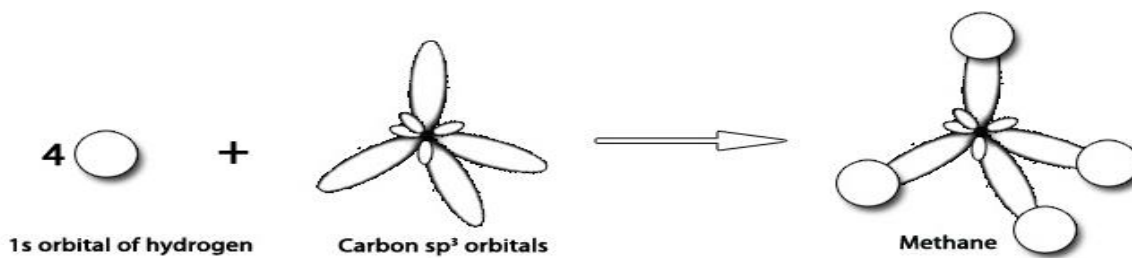
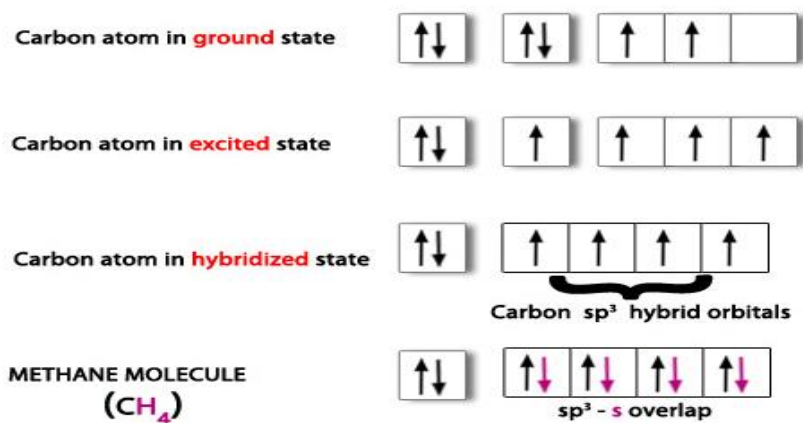
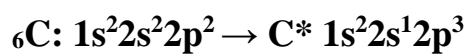
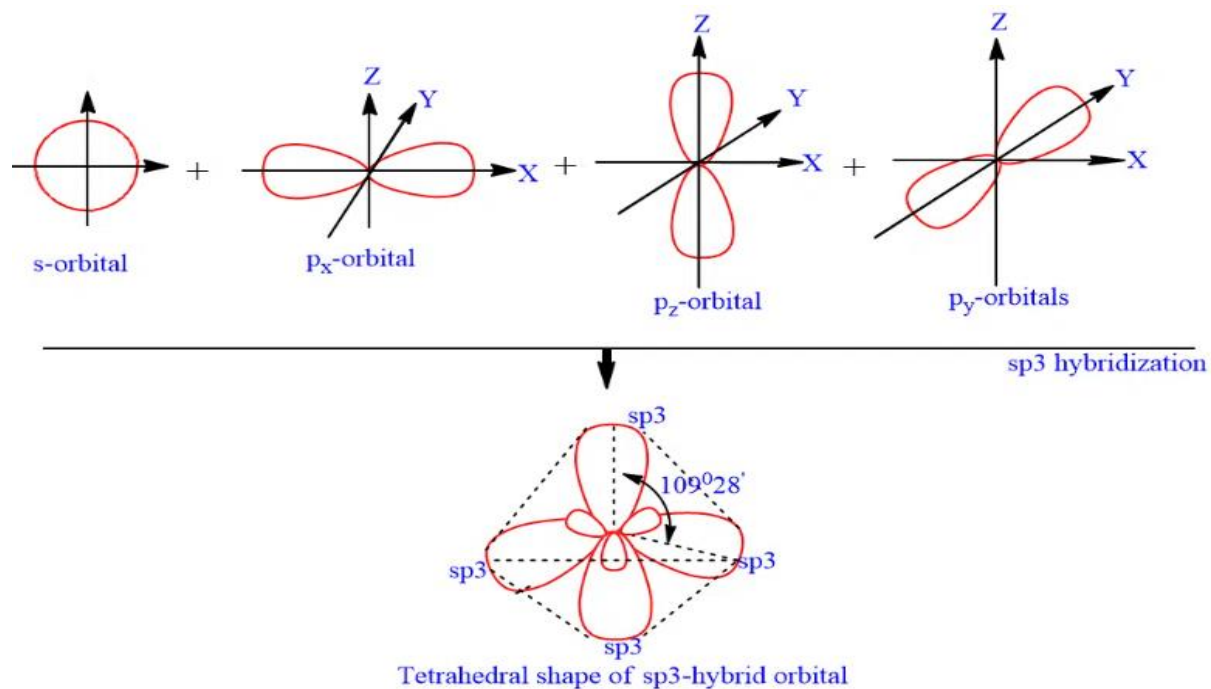
At normal state, B (5): $1s^2 2s^2 2p_x^1 2p_y^0 2p_z^0$

At excited state. B* (5): $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^0$

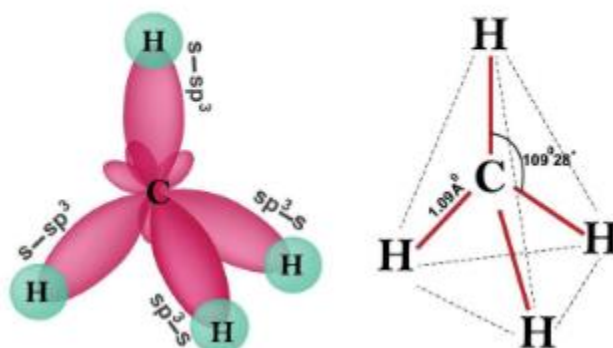
$5B = 1s^2, 2s^2, 2p^1$



3- Sp³-Hybrdization AB₄ (CH₄)



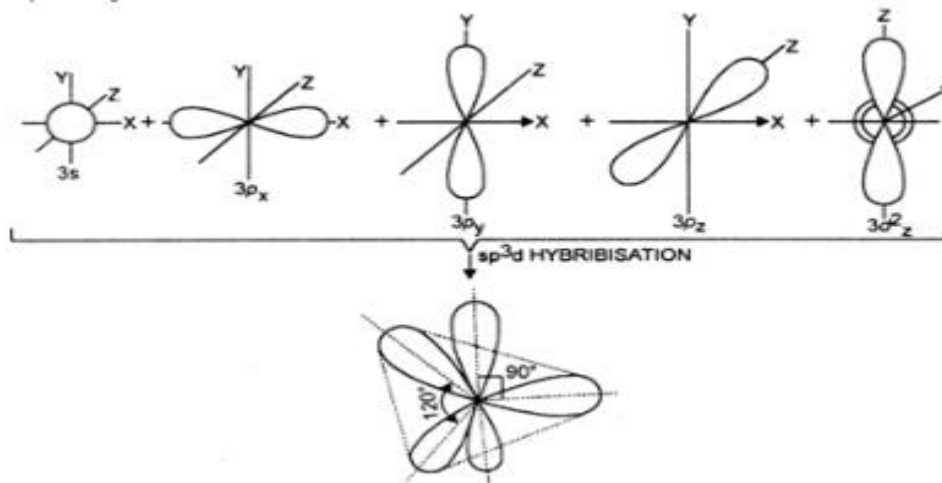
- Hybridisation of C is sp^3
- C-H bond length is 1.09 \AA



Note: that the central atom contains orbitals and includes several types AB_7 , AB_6 , AB_5 .

4- sp^3d -Hybridization AB_5 (PCl_5)

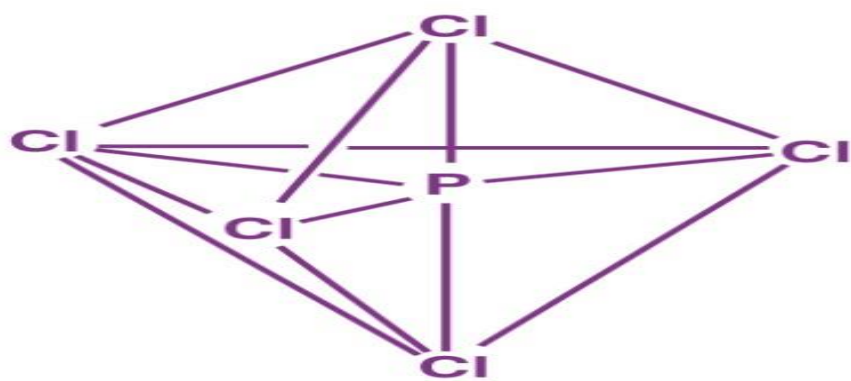
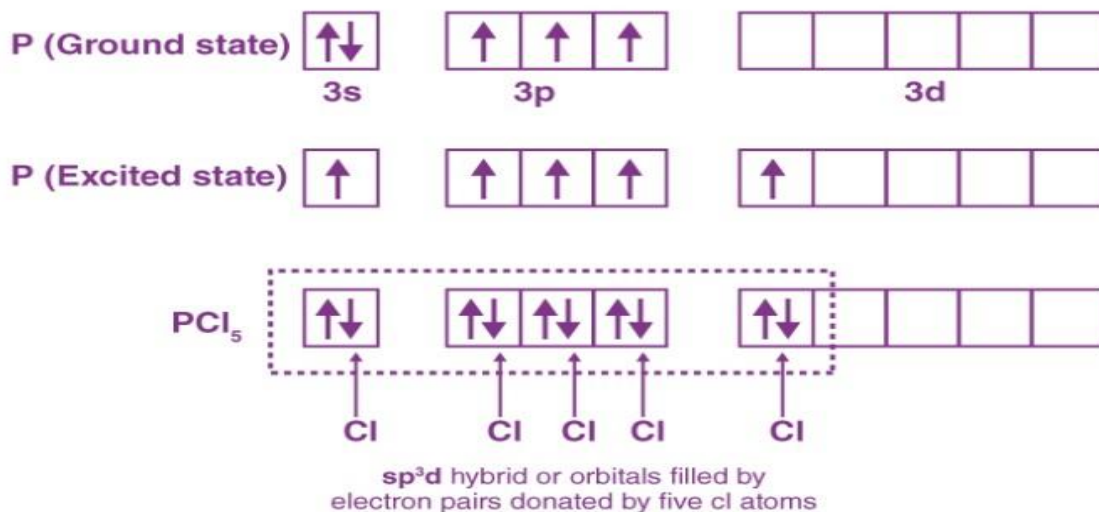
sp^3d hybridisation:



$AB_5: PCl_5$

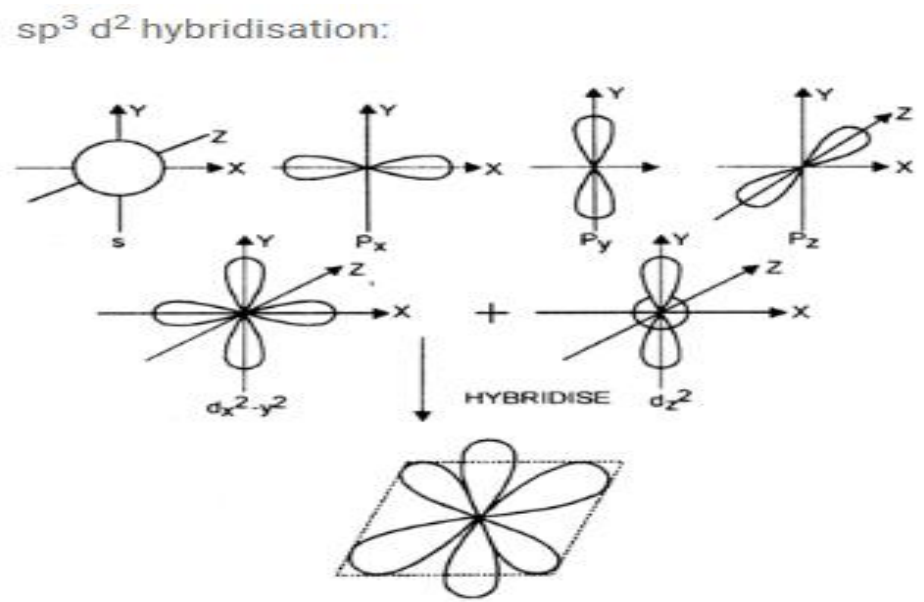
${}_{15}P: 1s^2 2s^2 2p^6 3s^2 3p^3$

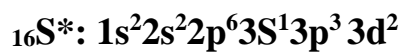
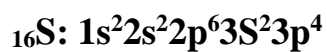
${}_{15}P^*: 1s^2 2s^2 2p^6 3s^1 3p^3 3d^1$



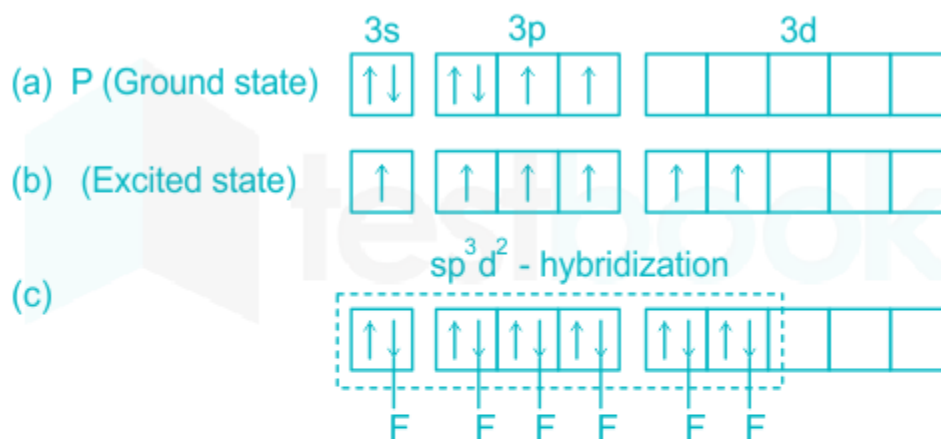
Triangle bipyramide

5- Sp³d²-Hybridization

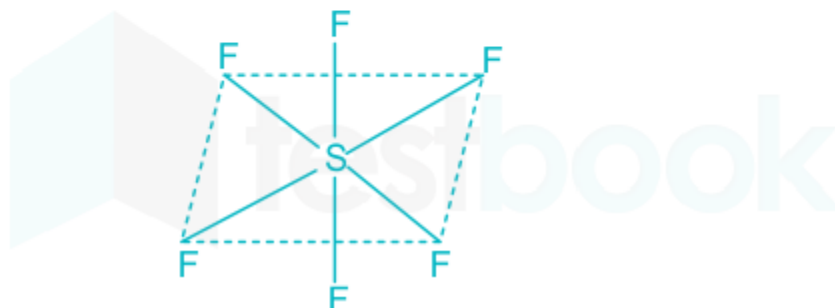




sp³d² Hybridization - Geometry of SF₆ molecule



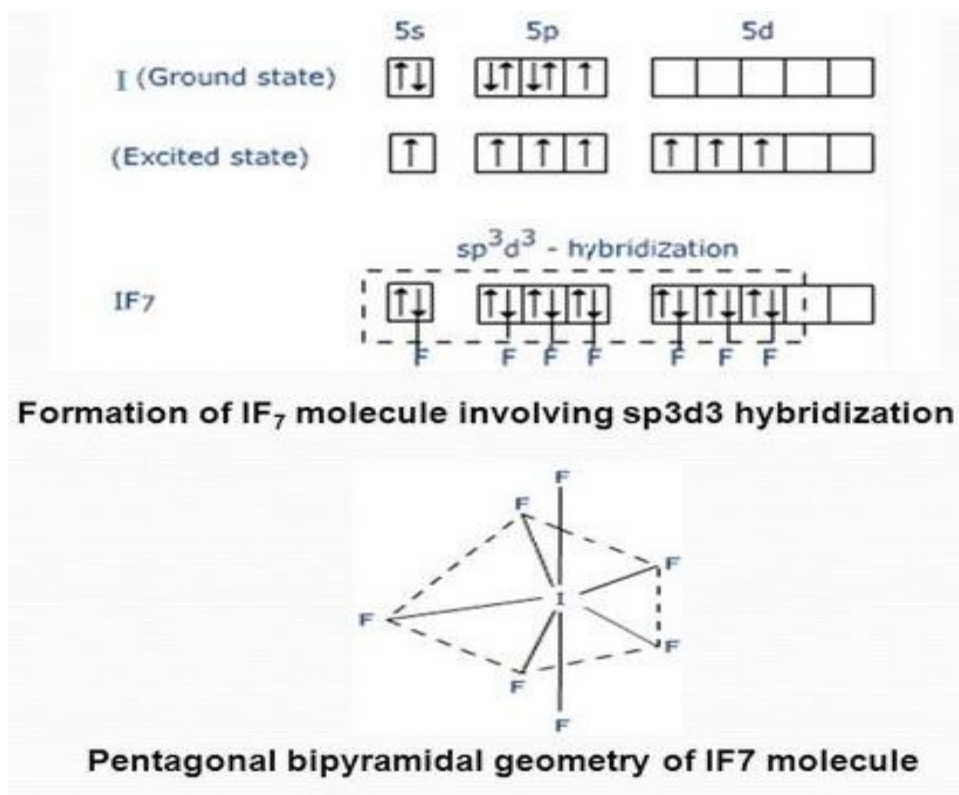
Formation of SF₆ molecule involving sp³d² Hybridization



Octahedral (Oh)

6- Sp³d³-Hybridization





Homework: Explain the hybridization of the following molecules: BrF₇, ClF₇, ICl₇.

Hybridization of Transition Metals

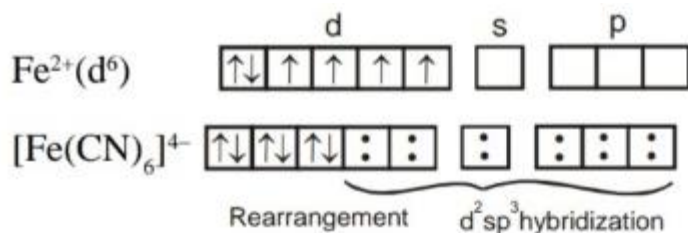
In the transition elements for hybridization in the orbitals of the central atom, according to the type of complexes formed with the transition elements containing empty d-orbitals, which can coordinate or form electronic doubles from elements or groups that donate these electrons, they are called (**Lewis bases**). The element or group that donates or donates electrons is called (**ligands**) and the resulting bonds are coordination bonds. The method of hybridization in the transition elements depends on the type of ligand, whether it has a strong field or a weak field for the purpose of providing empty orbitals and does not require individual electrons. It also depends on the charge and size of the metal. To form bonds, we need empty orbitals. It accepts electronic doublets if the Lewis base is strong (a strong-field ligand). The strong bases are as follows: CO, CN⁻, NH₃, NO₂⁻, en.

Example: $[\text{Fe}(\text{CN})_6]^{4-}$

${}_{26}\text{Fe}: {}_{18}[\text{Ar}]3d^6 4s^2$.

Since the ligand is strong, it pairs electrons

$\text{Fe}^{2+}: {}_{18}[\text{Ar}]3d^6 4s^0$.



All orbitals are doubly occupied, hence it is diamagnetic in nature.

Octahedral shape, inner- complex.

Complexes containing four symmetrical ligands are hybridized either tetrahedral SP^3 or square planar dsp^2 .

Note: Weak ligands are $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{H}_2\text{O}, \text{OH}^-, \text{C}_2\text{O}_4^{2-}$.

Example: SP^3 ($[\text{CuCl}_4]^{2-}, [\text{Ni}(\text{CO})_4], [\text{NiCl}_4]^{2-}, [\text{CoCl}_4]^{2-}$).

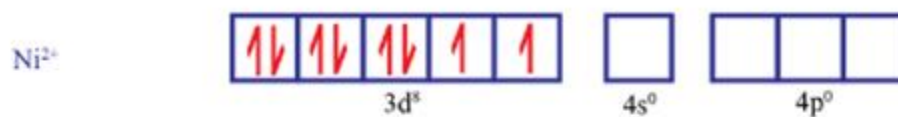
dsp^2 ($[\text{PtCl}_4]^{2-}, [\text{Ni}(\text{CN})_4]^{2-}$)

Example: $[\text{Ni}(\text{CN})_4]^{2-}$

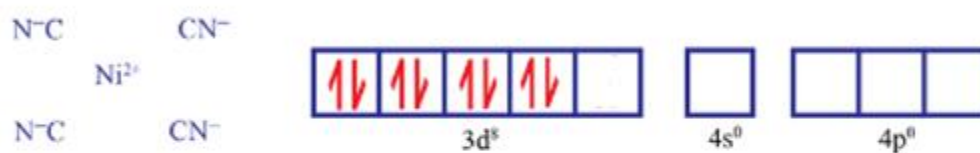
$_{28}\text{Ni}: 18[\text{Ar}]3d^8 4s^2$.

$\text{Ni}^{2+}: 18[\text{Ar}]3d^8 4s^0$.

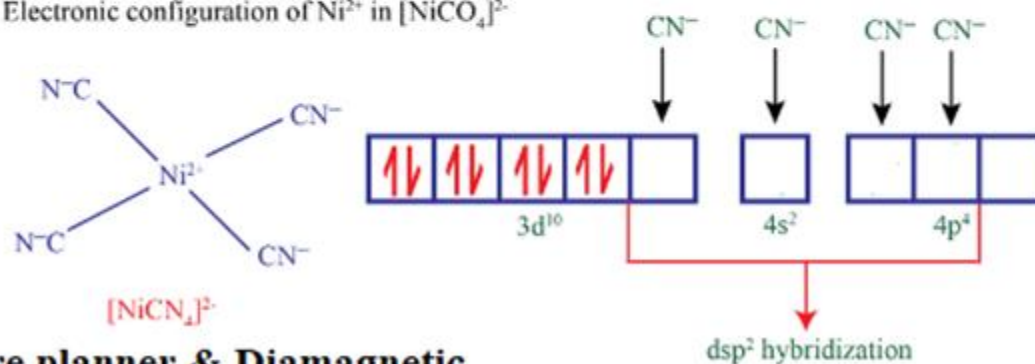
Electronic configuration of Ni^{2+} ion



Change in electronic configuration of Ni^{2+} ion when CN^- ligands approach it



Electronic configuration of Ni^{2+} in $[\text{Ni}(\text{CN})_4]^{2-}$



Example: Ni(CO)₄

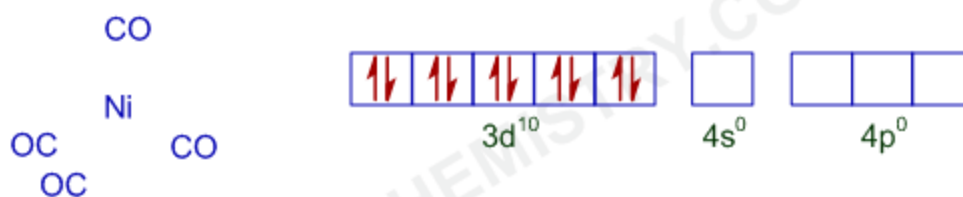
²⁸Ni: $18[\text{Ar}]3d^8 4s^2$.

Ni⁰: $18[\text{Ar}]3d^8 4s^2$.

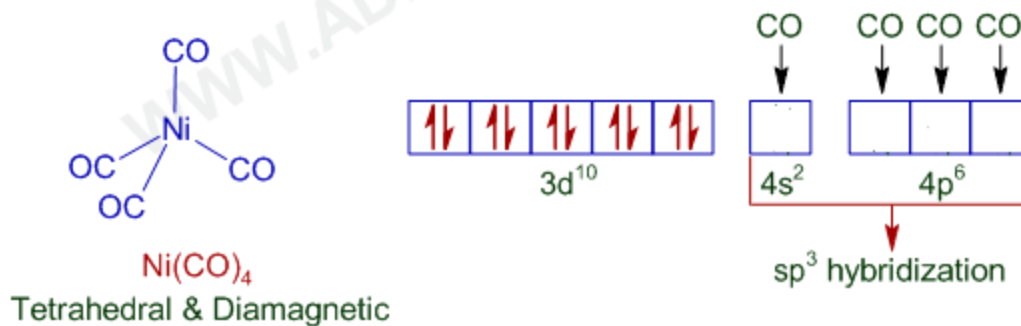
Electronic configuration of Ni atom in ground state



Change in electronic configuration of Ni atom when CO ligands approach it



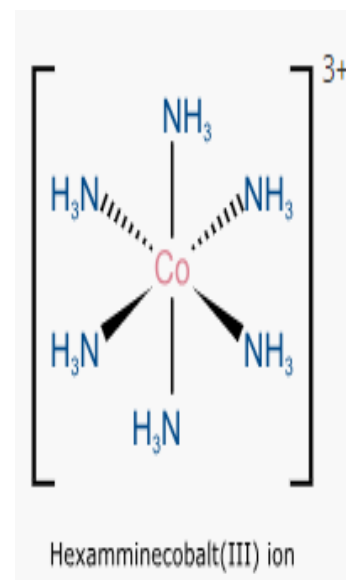
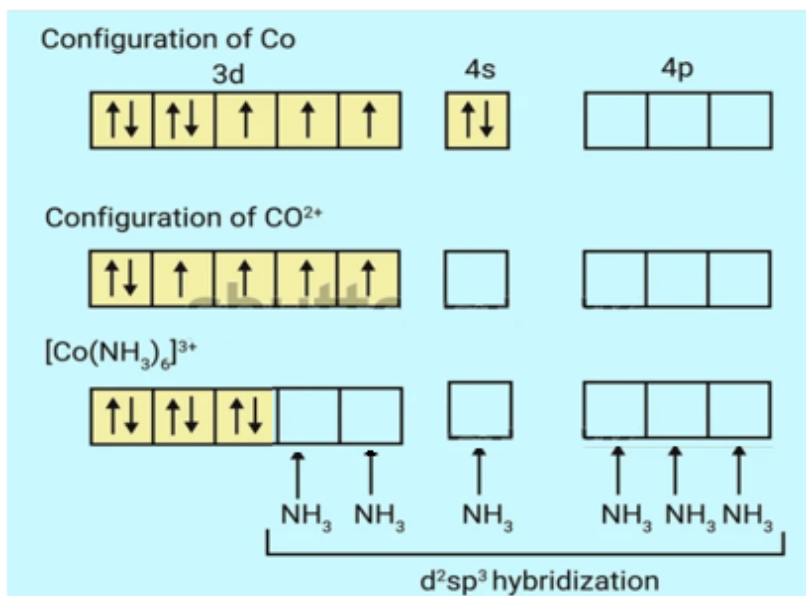
Electronic configuration of Ni atom in Ni(CO)₄



Example: $[\text{Co}(\text{NH}_3)_6]^{3+}$

$_{27}\text{Co}: 18[\text{Ar}]3d^7 4s^2$.

$\text{Co}^{3+}: 18[\text{Ar}]3d^6 4s^0$.

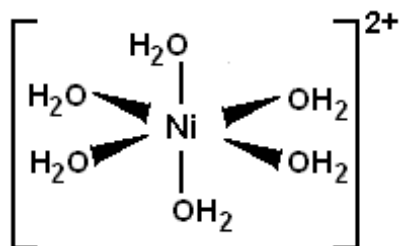
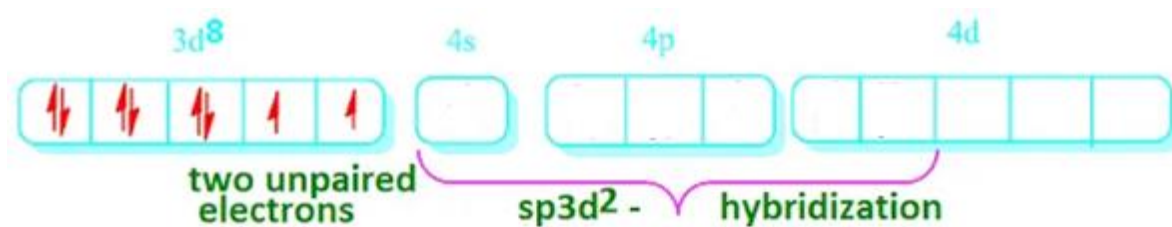


d^2sp^3 octahedral & diamagnetic

Example: $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

$_{28}\text{Ni}: 18[\text{Ar}]3d^8 4s^2$.

$\text{Ni}^{2+}: 18[\text{Ar}]3d^8 4s^0$.



Outer complex and paramagnetic.

Valance Shell Electronic Pair Repulsion (VSEPR)

Inorganic Chemistry (2)

8th lecture

Prof. Dr. Mahasin Faisal A. Alias

2023-2024

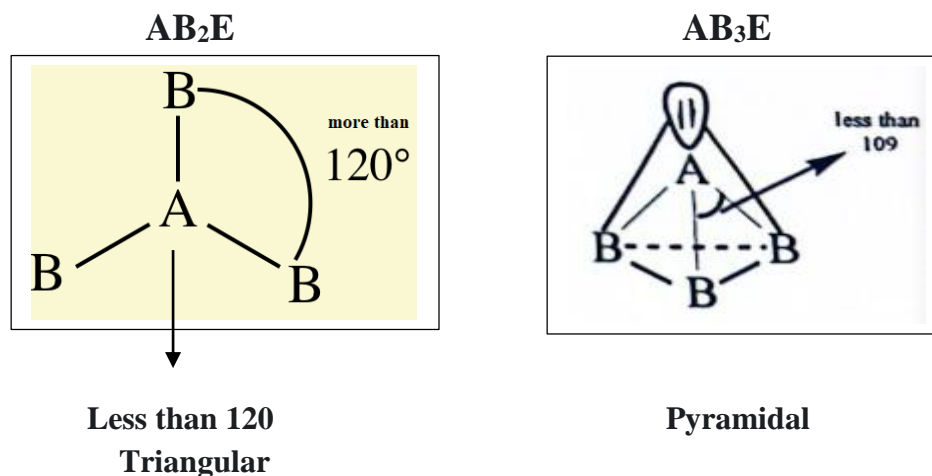
Valance shell electronic pair repulsion (VSEPR)

Theory of repulsion of electronic pairs in the valence shell to determine the shapes of molecules:

There are four main rules that result in determining the shapes of molecules according to the **VSEPR** theory, and these rules are:

1. The nonbonding electronic doubles are as far apart in the valence region of the central atom as if they are repelling each other.
2. The space occupied by the non-isotropic electronic bonding is larger than the space occupied by the influencing electronic bonding.
3. The size of the space occupied by the influencing electronic bonding decreases with the increase in the electronegativity of the element that is in contact with the central atom. The amount of space occupied by the allosteric electronic double also decreases as the electronegativity of the central atom decreases.
4. Bonds of the type's σ & π double or triple type occupy more space than bonds σ alone.

If we assume that the symbol of the central atom is **A**, and the atoms that are linked to it with bonding electronic of the type only are **B**, and if, in addition to the central atom **A**, there are non-bonding electronic doubles (**E**), then the general composition of the molecule will change according to the number of these non-bonding electronic doubles because they are of a large size, taking into account these electronic doubles are non-dissimilar as long as they affect the general shape of the molecule and are included in the hybridization process. All of these electronic doubles surrounding the central atom must be as far apart as possible. Therefore, to calculate the hybridization of the central atom, it is necessary to know its shape, and since the true shape of the molecule is done by measuring the angles between the σ bonds. That is, between the bonding electronic doubles, and this means that the true shape of the molecule will be determined after finding the number of non-bonding electronic doubles, because these doubles do not appear in X-ray measurements because they are not specified for another atom, as is the case with σ bonds. Hybridization can be calculated and the shape of the molecule and the angles between them can be known as follows:



The number of bonds is calculated by counting the number of electrons in the valence shell of the central atom and the number of electrons that the peripheral atoms contribute to form bonds as much as the number of individual electrons.

5. If the molecule is positively or negatively charged, an electron is given or σ bonds with drawn from the atom. If the total number of electron pairs is = **2**, then the hybridization is **sp**. If it is = **3** the hybridization is **sp²**. If it is = **4** the hybridization is **sp³** or **dsp²**. If it is = **5** the hybridization is **sp³d** or **dsp³**. If it is = **6** the hybridization is of the type **sp³d²** or **d²sp²**.

Example: Draw the geometry or geometric and write or find the type of hybridization of the following molecules according to the VESPR.

1- BeCl₂



hybridization= sp.

No. of σ bonds= 2

No non-bonding pair of electrons.

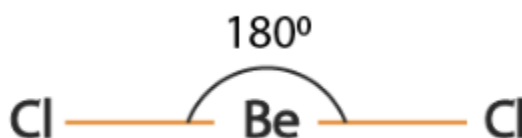
Geometry shape: linear molecule.

$$\text{Be} = 2 \text{ e}$$

$$2\text{Cl} = 2 \text{ e}$$

$$4 \text{ e} / 2 = 2 \text{ pair}$$

$$2 = \sigma \text{ no. of bonds}$$



2- BCl₃

${}_{5}\text{B}: 1s^2 2s^2 2p^1$

hybridization= sp^2 .

No. of σ bonds= 3

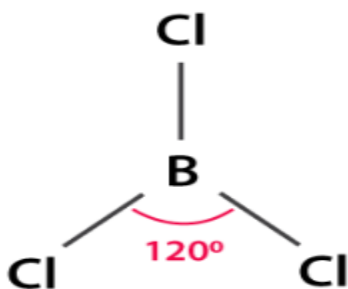
No non-bonding pair of electrons.

Geometry shape: triangular planer molecule.

Be= 3 e

3Cl= 3 e

6 e/2= 3 pair



3- SnCl₂

${}_{50}\text{Sn}: {}_{36}[\text{Kr}] 4d^{10} 5s^2 5p^2$

hybridization= sp^2 .

No. of σ bonds= 2

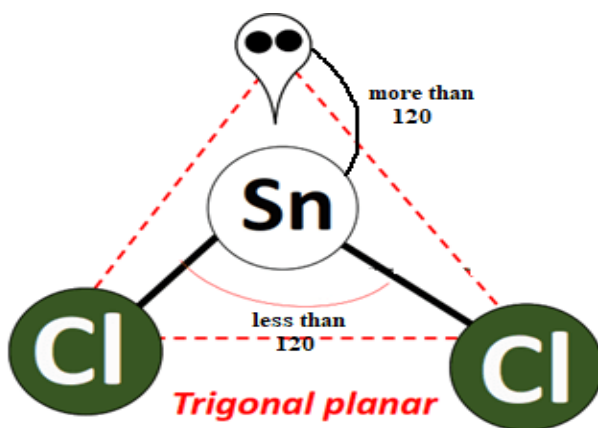
one non-bonding pair of electrons.

Geometry shape: triangular molecule.

Sn= 4 e

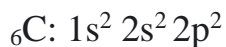
2Cl= 2 e

6 e/2= 3 pair



Home work: SiF₄, GeCl₂, GeF₂ same above steps.

4- CH₄



hybridization= sp^3 .

No. of σ bonds= 4

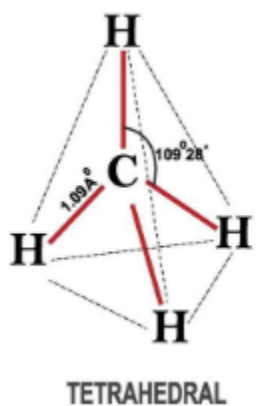
No non-bonding pair of electrons.

Geometry shape: Tetrahedral molecule.

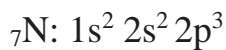
$$\text{C} = 4 e$$

$$4\text{H} = 4 e$$

$$\frac{8 e}{2} = 4 \text{ pair}$$



5- NH₃



hybridization= sp^3 .

No. of σ bonds= 3

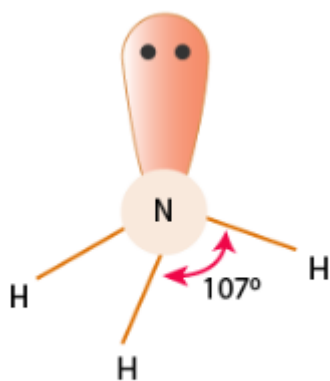
one non-bonding pair of electrons.

Geometry shape: Pyramid molecule.

$$\text{N} = 5 e$$

$$3\text{H} = 3 e$$

$$\frac{8 e}{2} = 4 \text{ pair}$$



Example: PH₃, PCl₃, AsH₃, AsBr₃, SbCl₃, PF₃.

PH₃

¹⁵P: 1s² 2s² 2p⁶ 3s² 3p³

hybridization= sp³.

No. of σ bonds= 3

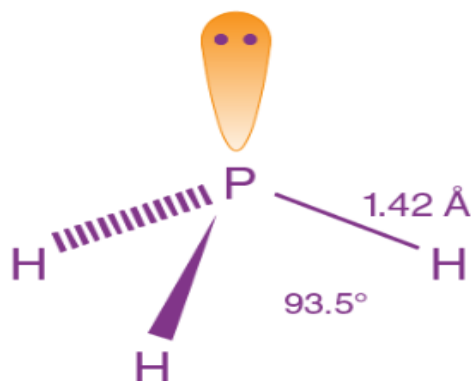
one non-bonding pair of electrons.

Geometry shape: Pyramid molecule.

P= 5 e

3H= 3 e

8 e/2= 4 pair



6- H₂O, H₂S AB₂E₂

⁸O: 1s² 2s² 2p⁴

hybridization= sp³.

No. of σ bonds= 2

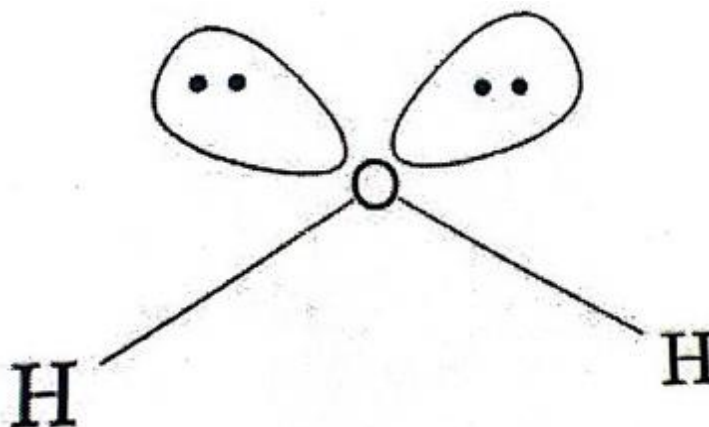
two non-bonding pair of electrons.

Geometry shape: V-shape or angular molecule.

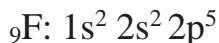
O= 6 e

2H= 2 e

8 e/2= 4 pair



HF ABE₃



hybridization= sp^3 .

No. of σ bonds= 1

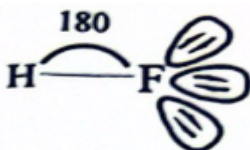
three non-bonding pair of electrons.

Geometry shape: linear molecule.

$$\text{F} = 7 \text{ e}$$

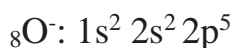
$$1\text{H} = 1 \text{ e}$$

$$\frac{8 \text{ e}}{2} = 4 \text{ pair}$$



Same solution: HCl, HBr, HI, OH⁻.

OH⁻



hybridization= sp^3 .

No. of σ bonds= 1

three non-bonding pair of electrons.

Geometry shape: linear molecule.

$$\text{O}^- = 7 \text{ e}$$

$$1\text{H} = 1 \text{ e}$$

$$\frac{8 \text{ e}}{2} = 4 \text{ pair}$$



7- PCl₅



hybridization= sp^3d .

No. of σ bonds= 5

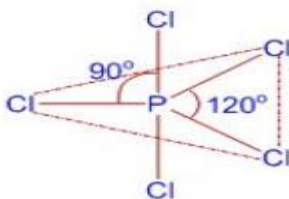
Non non-bonding pair of electrons.

Geometry shape: Trigonal bipyramide molecule.

$$\text{P} = 5 \text{ e}$$

$$5\text{Cl} = 5 \text{ e}$$

$$\frac{10 \text{ e}}{2} = 5 \text{ pair}$$



Tbp

8- SF₄



hybridization= sp^3d .

No. of σ bonds= 4

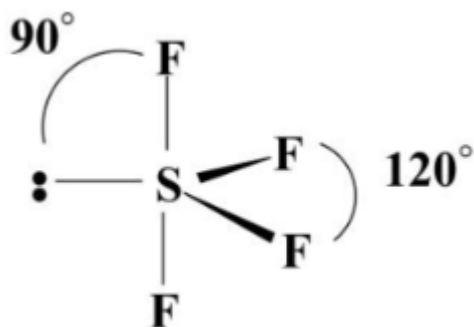
one non-bonding pair of electrons.

Geometry shape: Distortion tetrahedral molecule (Distortion).

$$\text{S} = 6 \text{ e}$$

$$4\text{F} = 4 \text{ e}$$

$$\frac{10 \text{ e}}{2} = 5 \text{ pair}$$



9- ClF₃



hybridization= sp^3d .

No. of σ bonds= 3

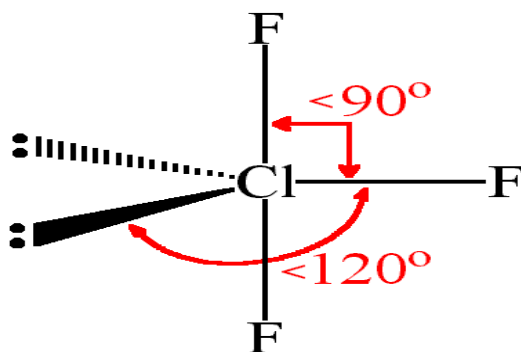
two non-bonding pair of electrons.

Geometry shape: T-shape molecule.

$$\text{Cl} = 7 \text{ e}$$

$$3\text{F} = 3 \text{ e}$$

$$\frac{10 \text{ e}}{2} = 5 \text{ pair}$$



10- ICl₂⁻



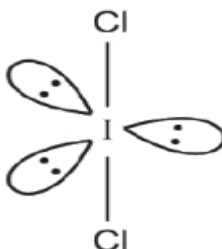
hybridization= sp³d.

No. of σ bonds= 2

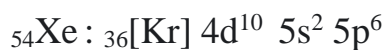
three non-bonding pair of electrons.

Geometry shape: T-shape molecule.

$$\begin{array}{r} \text{I} = 8 \text{ e} \\ 2\text{Cl} = 2 \text{ e} \\ \hline 10 \text{ e}/2 = 5 \text{ pair} \end{array}$$



Home work: XeF₂, ClBr₂⁻, ClF₂⁻, IF₂⁻, I₃⁻, KrF₃.

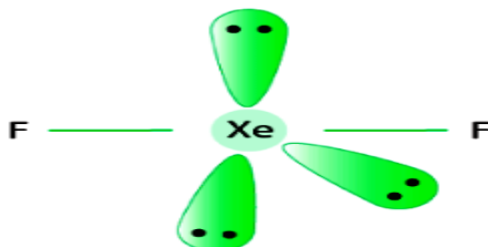


hybridization= sp³d.

No. of σ bonds= 2

three non-bonding pair of electrons.

$$\begin{array}{r} \text{Xe} = 8 \text{ e} \\ 2\text{F} = 2 \text{ e} \\ \hline 10 \text{ e}/2 = 5 \text{ pair} \end{array}$$



11- SOCl₂



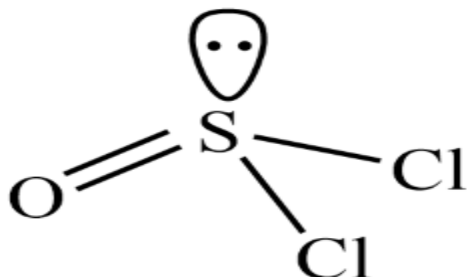
hybridization= sp³.

No. of σ bonds= 3

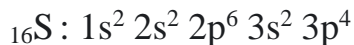
one non-bonding pair of electrons.

Geometry shape: Pyramid molecule.

$$\begin{array}{r} \text{S} = 6 \text{ e} \\ \text{O} = \text{Zero} \\ 2\text{Cl} = 2 \text{ e} \\ \hline 8 \text{ e}/2 = 4 \text{ pair} \end{array}$$



SF₆



hybridization = sp^3d^2 .

No. of σ bonds = 6

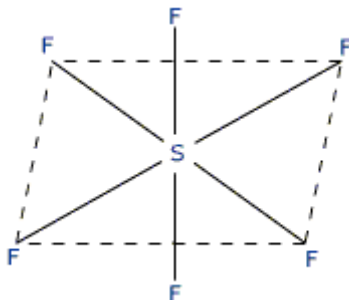
No non-bonding pair of electrons.

Geometry shape: Octahedral molecule.

$$\text{S} = 6 e$$

$$6\text{F} = 6 e$$

$$\frac{12 e}{2} = 6 \text{ pair}$$



IF₅



hybridization = sp^3d^2 .

No. of σ bonds = 5

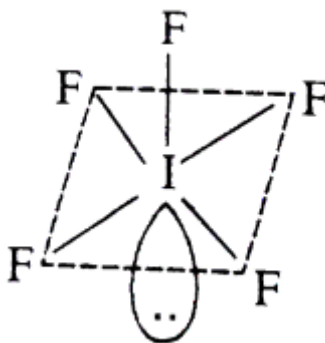
one non-bonding pair of electrons.

Geometry shape: Distorted square pyramid.

$$\text{I} = 7 e$$

$$5\text{F} = 5 e$$

$$\frac{12 e}{2} = 6 \text{ pair}$$



Square pyramid

Home work: ICl₅, BrI₅, ClF₅, ClBr₅.

XeF₄

${}_{54}\text{Xe} : {}_{36}[\text{Kr}] 4d^{10} 5s^2 5p^6$

hybridization = sp^3d^2 .

No. of σ bonds = 4

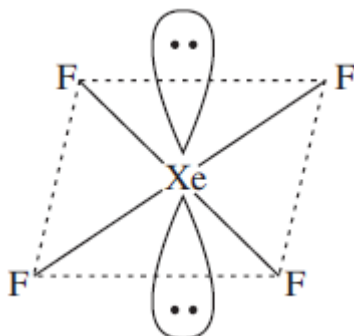
two non-bonding pair of electrons.

Geometry shape: square planer molecule.

Xe = 8 e

4F = 4 e

$\frac{12 e}{2} = 6 \text{ pair}$



The size of the vacuum space of the allosteric electronic pairs decreases as the **EN** of the central atom decreases, because increasing **EN** leads to increased repulsion between the peripheral atoms, and this is also the case for the **O** group (oxygen).

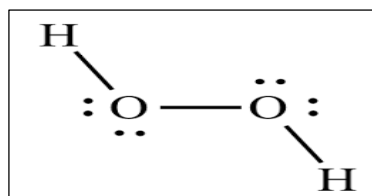
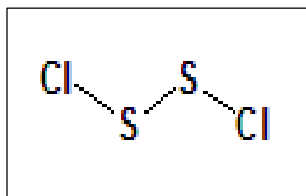
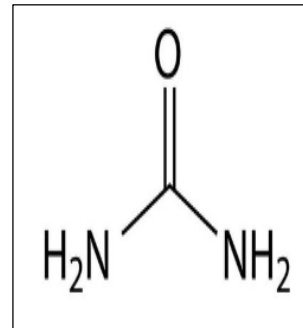
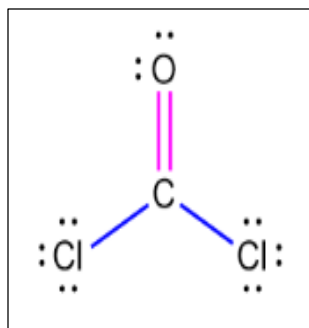
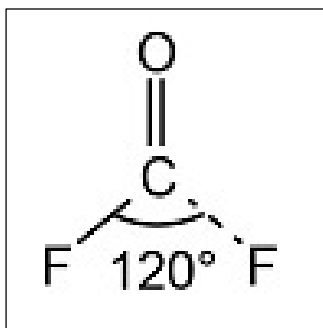
BAB	AB₃E	BAB	AB₂E
107	NH₃	105	H₂O
93.3	PH₃	92	H₂S
92	AsH₃	91	H₂Se
91	SbH₃	90	H₂Te

Note: The third reason why the difference is so large between **NH₃ = 107°** and the rest of the elements in the same group is that the rest have empty orbitals, such as orbital (**d**). Also, the non-bonding electron double, if it exists, can be transferred to these orbitals, which leads to a reduction in the angle. The space occupied by the allosteric electron pair decreases as the **EN** of the atoms attached to the central atom increases.

Molecule	BAB
NH ₃	107
NF ₃	102
PF ₃	98
AsF ₃	96
PCl ₃	100
PBr	101
PI ₃	104
H ₂ O	105
OF ₂	102
OCl ₂	111

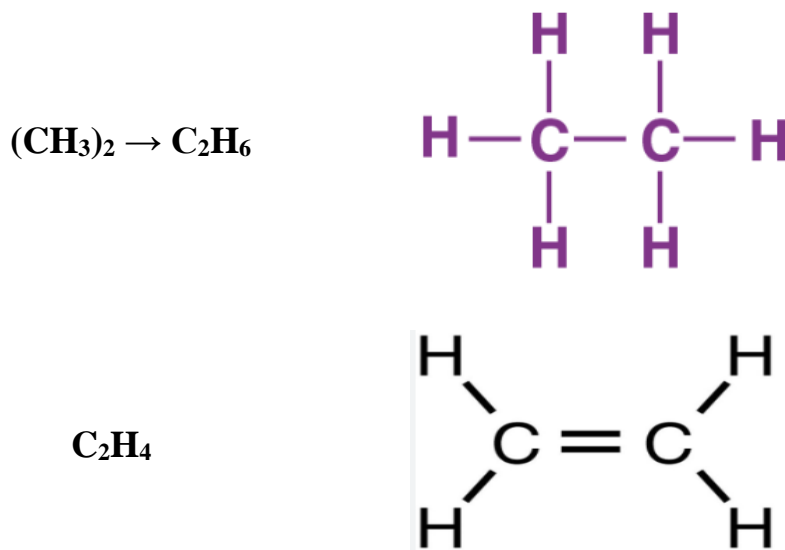
Draw the following Molecules:

F₂CO, Cl₂CO, (NH₂)₂CO, S₂Cl₂, H₂O₂

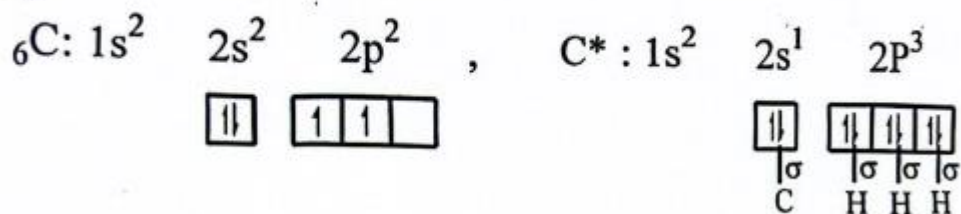


Bonds σ & bonds π and states of resonance

1. Sigma bonds are formed after the hybridization procedure, and the shape of the resulting molecule from the hybridization takes place after the bonding and non-bonding electronic pairs are arranged, and both are included in the hybridization. As for the pi bond, it is formed after the sigma bond is formed, i.e. is that the π bond is formed after the hybridization process, so the π orbitals are not hybridized, that is, they result from $p_{zA} + p_{zB}$ or $p_{yA} + p_{yB}$. That is, after the molecule takes its general shape in space, and since the π bond is parallel or in line with the σ bond, it does not affect the shape of the molecule much. First, the number of σ bonds is calculated, and the remaining number of electrons belong to π , meaning the last orbitals are the ones that form π bonds.

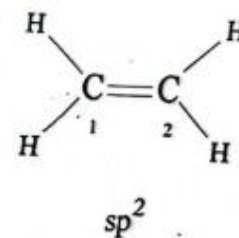
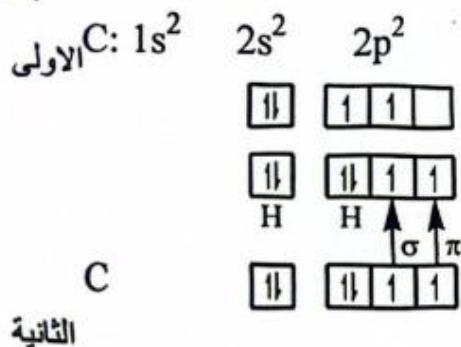


The central atom is any carbon atom now, one of which is hybridized at a specific center that is the same as the other in the same compound.



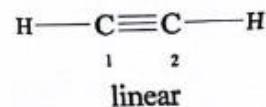
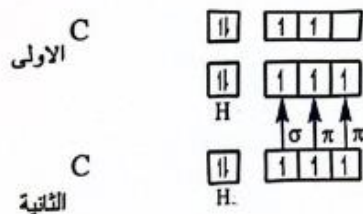
$$\begin{array}{r} \text{C} = 4 e \\ 3\text{H} = 3 e \\ 1\text{C} = +1 e \\ \hline 8 e^- / 2 = 4 \text{ pair} \end{array}$$

Tetrahedral



no. of σ bonds = 3
 sp^2 hybridization
 No non-bonding pair of electrons.
 No. of π bonds = 1

$$\begin{array}{r} \text{C} = 4 e \\ 2\text{H} = 2 e \\ \text{الثانية C} = 1 e \\ \hline (7-1) / 2 = 3 \text{ pair} \end{array}$$



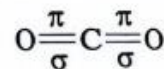
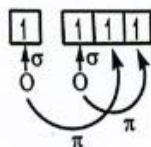
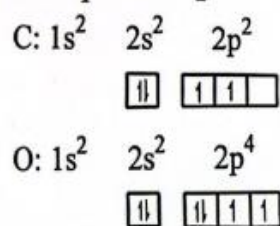
no. of σ bonds = 2
 sp hybridization
 No non-bonding ion pair of electrons.

$$\begin{array}{r} \text{الاولى C} = 4 e \\ \text{H} = 1 e \\ \text{الثانية C} = 1 e \\ \hline 6-2/2 = 2 \text{ pair} \end{array}$$

No. of π bonds = 2

2. If the central atom is bonded to the O atom by a π bond or by a σ and π bond, then the oxygen's contribution of electrons is calculated to be equal to zero (if the oxygen atom is peripheral and non-central).

Example: CO_2

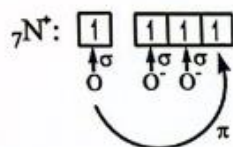
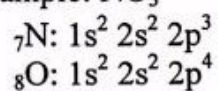


no. of σ bonds = 2
 sp hybridization
 Linear molecule
 No non-bonding ion pair of electrons.

$$\begin{array}{r} \text{C} = 4 e \\ 2\text{O} = \text{zero} \\ \hline 4 e/2 = 2 \text{ pair} \end{array}$$

If the molecule containing the oxygen atom is negative, the negative charge is added to the molecule when calculating the hybridization, and when drawing the molecule, the negative charge is placed according to the resonance state that exists between the atoms that suffer from this condition.

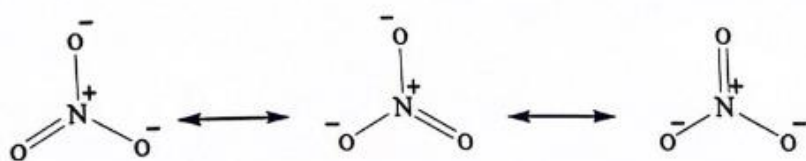
Example: NO_3^-



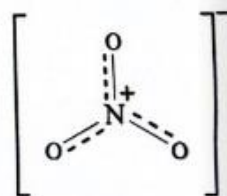
sp^2 hybridization
 no. of σ bonds = 3
 shape planner

$$\begin{aligned} \text{N} &= 5 \text{ e} \\ 3\text{O} &= \text{zero} \\ (-) &= 1 \text{ e} \end{aligned}$$

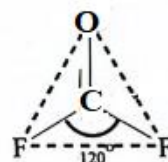
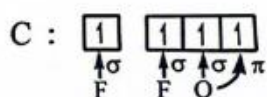
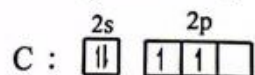
$$5 + 1/2 = 3 \text{ pair}$$



Resonance



Example: COF_2

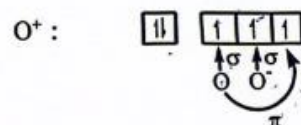
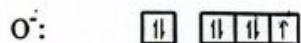
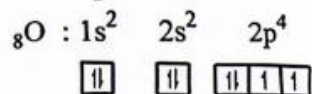


hybridization = sp^2
 no. of sigma bonds = 3
 Shape of molecule = planner
 No non-bonding pair of electrons.

$$\begin{array}{r} \text{C} = 4 e \\ \text{O} = \text{zero} \\ 2\text{F} = 2 e \\ \hline 6/2 = 3 \end{array}$$

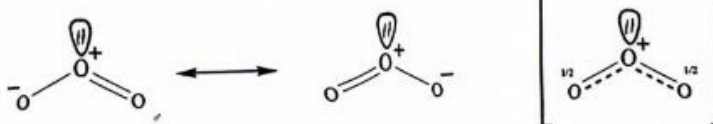
Home work: COCl_2 , H_2CO

Example: O_3

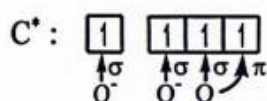


hybridization = sp^2
 no. of sigma bonds = 2
 one non-bonding pair of electrons.

$$\begin{array}{r} \text{O} = 6 e \\ 2\text{O} = \text{zero} \\ \hline 6 e/2 = 3 \text{ pair} \end{array}$$



Example: CO_3^-



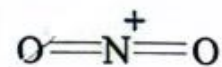
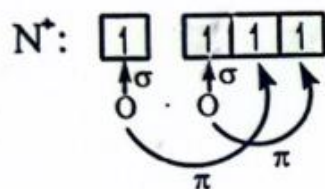
$$\begin{array}{r} \text{C} = 4 \text{ e} \\ 3\text{O} = \text{zero} \\ (-) = 2 \text{ e} \\ \hline 6 \text{ e}/2 = 3 \text{ pair} \end{array}$$

hybridization = sp^2

no. of sigma bonds = 3



Example: NO_2^+



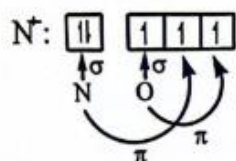
hybridization = sp

no. of sigma bonds = 2

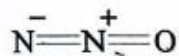
no non-bonding pair of electrons.

$$\begin{array}{r} \text{N} = 5 \text{ e} \\ 2\text{O} = \text{zero} \\ -1 \\ \hline 4 \text{ e}/2 = 2 \text{ pair} \end{array}$$

Example: N₂O



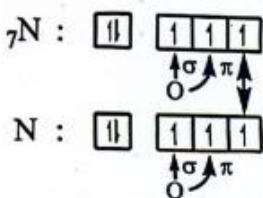
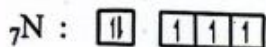
Hybridization = sp
no. of σ bond = 2



مركزية N = 5 e
N = 1 e
O = zero
 $-2\pi = -2:$

4 e/2 = 2 pair
او أصر π لا تشترك في التهجين

Example: N₂O₂



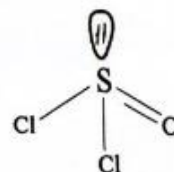
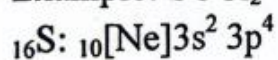
hybridization = sp²

N = 5 e
2O = zero
الثانية N = 1 e

6 e/2 = 3 pair



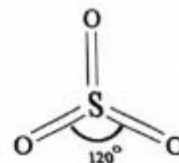
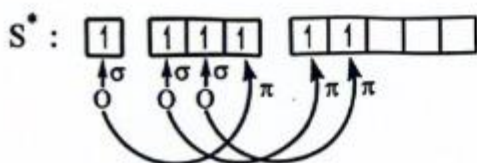
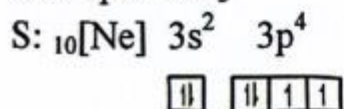
Example: SOCl₂



no. of sigma bonds = 3
 one non-bonding ion pair of electrons.
 hybridization = sp^3
 Shape of molecule = pyramid

$$\begin{array}{r} \text{S} = 6 \text{ e} \\ \text{O} = \text{zero} \\ 2\text{Cl} = 2 \text{ e} \\ \hline 8 \text{ e}/2 = 4 \end{array}$$

Example: SO_3

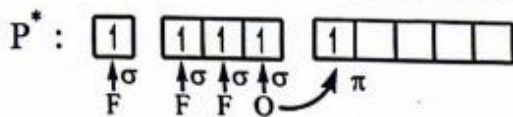
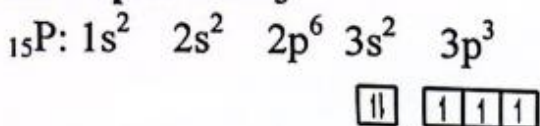


no. of sigma bonds = 3
 No non-bonding ion pair of electrons.
 hybridization = sp^2
 no. of π bonds = 3

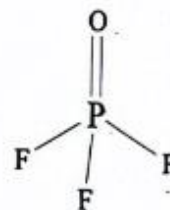
$$\begin{array}{r} \text{S} = 6 \text{ e} \\ 3\text{O} = \text{zero} \\ \hline 6 \text{ e}/2 = 3 \end{array}$$

Home work: SO_2 , POF_3 .

Example: POF_3



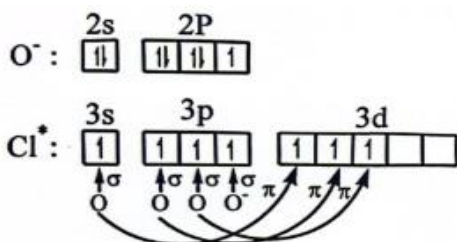
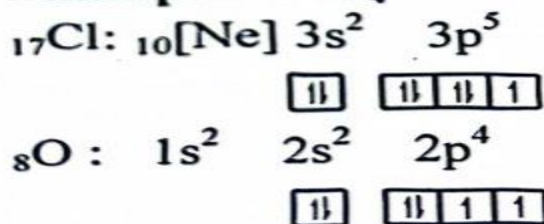
hybridization = sp^3
 no. of sigma bonds = 4



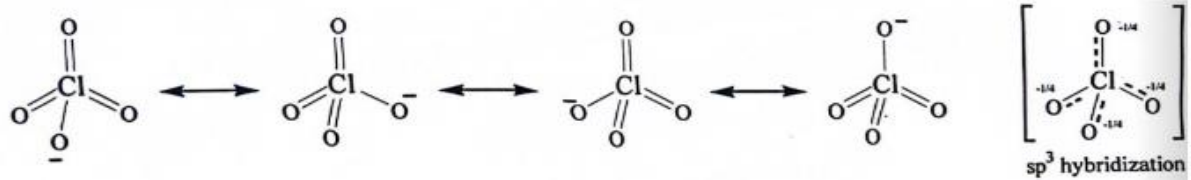
Tetrahedral

$$\begin{array}{r} \text{P} = 5 \text{ e} \\ \text{O} = \text{zero} \\ 3\text{F} = 3 \text{ e} \\ \hline 8 \text{ e}/2 = 4 \text{ pairs} \end{array}$$

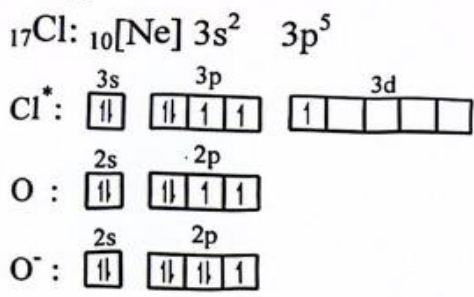
Example: ClO_4^-



$$\begin{array}{r} \text{Cl} = 7 e \\ 4\text{O} = \text{zero} \\ (-) = +e \\ \hline 7 e/2 = 4 \text{ pair} \end{array}$$

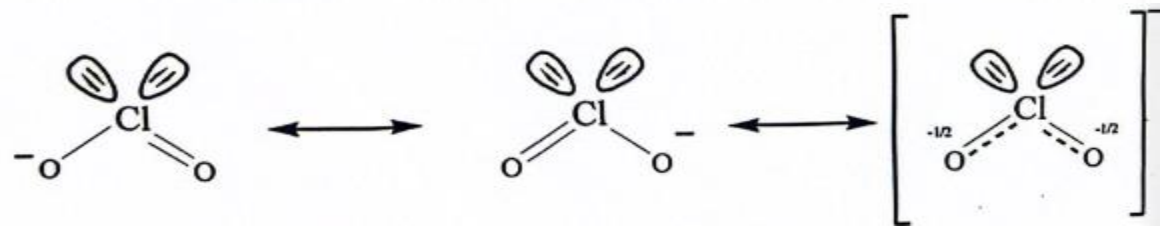


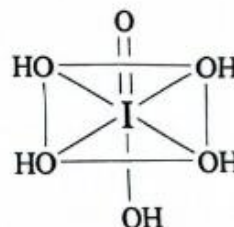
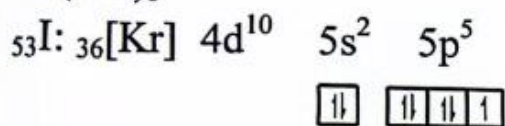
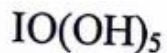
ClO_2^-



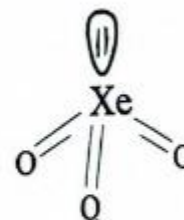
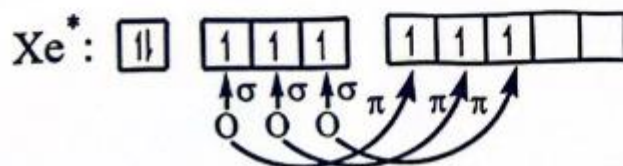
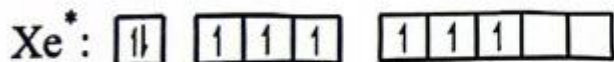
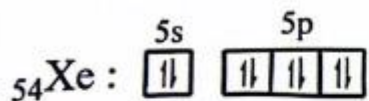
no. of sigma bond = 2
 hybridization = sp^3
 two non-bonding ion pair of electrons.
 no. of π bonds = 1
 angular molecule

$$\begin{array}{r} \text{Cl} = 7 e \\ 2\text{O} = \text{zero} \\ \hline 7+1 = 8/2 = 4 \end{array}$$





$$\begin{array}{r}
 \text{I} = 7 e \\
 \text{O} = \text{zero} \\
 5\text{OH} = 5 e \\
 \hline
 12 e/2 = 6 \text{ pairs}
 \end{array}$$

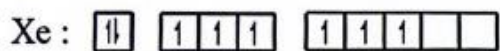


sp^3 hybridization

no. of sigma bonds = 3

one non-bonding ion pair of electrons.

$$\begin{array}{r}
 \text{Xe} = 8 e \\
 \text{O} = \text{zero} \\
 \hline
 8 e/2 = 4 \text{ pair}
 \end{array}$$



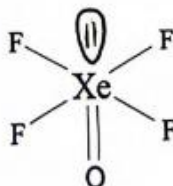
sp^3d^2 hybridization

no. of sigma bonds = 5

one non-bonding ion pair of electrons.

Square pyramid

$$\begin{array}{r} \text{Xe} = 8 e \\ \text{O} = \text{zero} \\ 4\text{F} = 4 e \\ \hline 12 e/2 = 6 \end{array}$$



$$\begin{array}{r} \text{I} = 7 e \\ 7\text{OH} = 7 e \\ \hline 14 e/2 = 7 \text{ Pair} \end{array}$$

No. of sigma bonds = 7.

Home work:

Find the type of hybridization, shape of molecule, Resonance, no. of sigma and pi bonds, ion pairs of non-bonding electrons for each of the following molecules or ions according to VSEPR.

OH^- , H_2Te , SPH_3 , OCl_2 , BrF^- , $[\text{XeO}_6]^{4-}$, XeO_4 , IO_4^- , BrO_3^- , ICl_2^- , ClF_2^- , $[\text{IO}_6]^{5-}$, H_3O^+ , PH_4^+ , BiCl_6^- , PF_6^- , FSb_5^- , SbF_5^{-2} , XeF_2 , N_2O_4 .

Prof. Dr. Mahasin Faisal A. Alias

Structural of the ionic crystals

Inorganic Chemistry


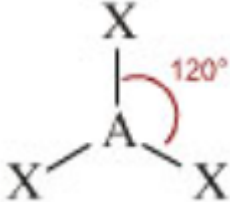


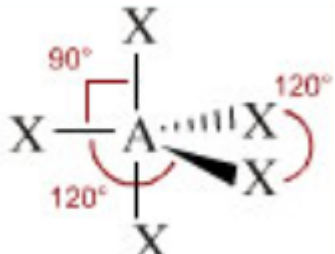
9th lecture

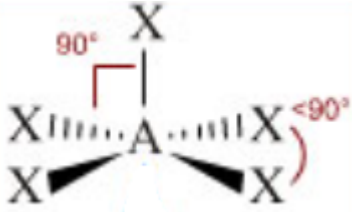
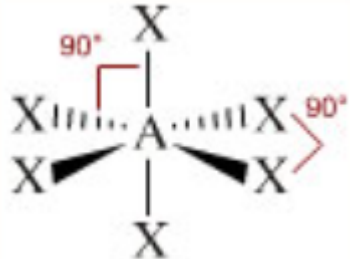
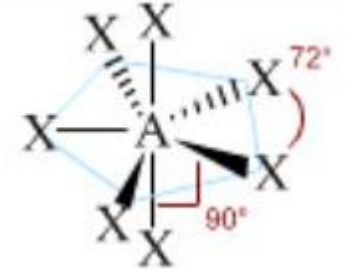

Prof. Dr. Mahasin Faisal A. Alias

2023-2024

Structure of the ionic crystals

In solid ionic compounds, each ion is bound by an electrostatic force of attraction with a number of ions of opposite charge to it, and is surrounded by a number of these electrons in a geometric arrangement called the coordination number, determined by the size of the ion, such that these ions come into contact with the ion of opposite charge (the central ion) with less Repulsion between them. If the opposite ion has a charge \mathcal{X} , the number \mathcal{X} increases when the radius of the central ion **A**, increases it decreases when the radius of the central ion decreases, through which the geometric shape of the coordination numbers can be determined based on the ratios of the radii of the positive ion and the negative ion:

Shape	Geometry	Coordination no.
	Liner	2, (AX₂)
	Triagonal planner	3, (AX₃)
	Tetrahedral	4, (AX₄)
	Square planner	4, (AX₄)
	Trigonal bipyramid	5, (AX₅)

	<p>Square pyramid</p>	<p>5, (AX₅)</p>
	<p>Octahedral</p>	<p>6, (AX₆)</p>
	<p>Pentagonal bipyramid</p>	<p>7, (AX₇)</p>
	<p>Cubic</p>	<p>8, (AX₈)</p>

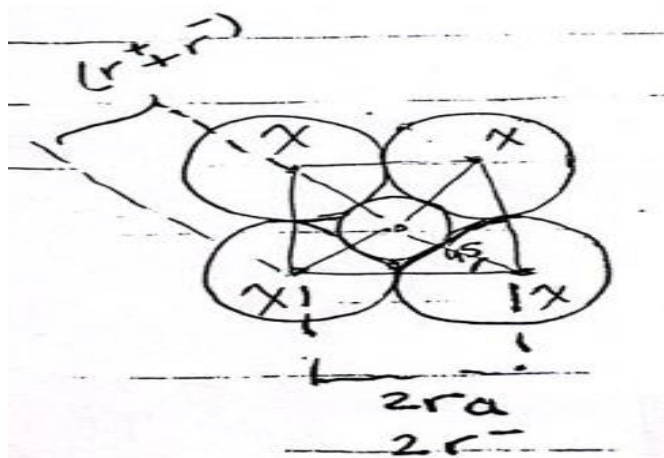
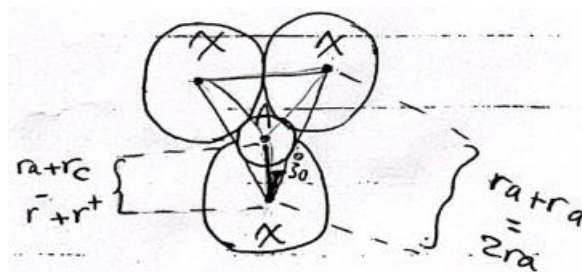
Crystal analysis using **x-ray** provides us with information about the arrangement patterns of ions and atoms in the crystal structure. For example, in metals contain a crystal.

Therefore, the ratio of the **radii = 1**, which represents the **radius ratio= r^+/r^-** . As for ionic compounds, the crystalline arrangement is the result of small-sized positive ions and large-sized negative ions. As a result of the difference in sizes, the positive ions are concentrated in the gaps that form between the negative ions balls according to their size, meaning that there is a maximum limit to the coordination numbers that depends on the radius of the central ion. For example,

in Triple symmetry, such as AX_3 , if we consider the positive ion to be a small sphere and the negative ion to be a large sphere, it would be as follows:

$$\cos 30 = \frac{\sqrt{3}}{2}$$

$$\text{Radius ratio} = \frac{r^+}{r^-}$$



$$\cos 45 = \frac{2r}{2r^+ + 2r^-}$$

$$\cos 45 = \frac{r_c + r_a}{2r_a}$$

$$= 1/\sqrt{2}$$

r_c/r_a	Geometry	Solid State Coord. No.
Ratio value < 0.155	Liner	2(AX_2)
0.155-0.224	Triagonal	3(AX_3)
0.224-0.414	Tetrahedral	4(AX_4)
0.414-0.732	Octahedral	6(AX_6)
Ratio value > 0.732	Cubic	8(AX_8)

Note: When the ratio of charges in the solid ionic compound is **1:1**, as in the following compound Na^+Cl^- , the coordination number of the positive ion is equal to the coordination number of the negative ion, for example $Ca^{+2}S^{-2}$. Therefore, the coordination number of the two ions is equal, but if the ratio is different, as in the compound Li_2O or $Ca^{+2}F_2^-$, it must first calculate the coordination number of the positive ion, then the coordination number of the negative ion, then choose the coordination numbers that match the chemical formula of the ionic compound.

Example: for NaCl crystal find the coordination number of Na⁺ and Cl⁻ of r⁺ Na=0.95 Å, r Cl⁻ = 1.81 Å.

$$r \text{ Na}^+ / r \text{ Cl}^- = 0.95 / 0.81 = 0.524$$

Coordination number for Na⁺ = 6 = coordination number for Cl⁻.

Because the ratio of positive charges to negative charges in NaCl=1.

Example: Find the lattice structure of SrF₂ unit cell of r_{Sr²⁺}= 1.13 Å, r_{F⁻} = 1.36 Å.

$$r \text{ Sr}^{+2} / r \text{ F}^- = 1.13 / 1.36 = 0.83$$

Coordination number for Sr⁺² = 8

Coordination number for F⁻ x 2 = coordination number of Sr⁺²

Coordination number of F⁻ = 8/2 = 4.

Tight packing in crystalline compounds

Crystal close packing

Most metals crystallize (they are a cohesive arrangement of metal atoms with equal radii (i.e. spheres of equal size) and the ratio is equal to one).

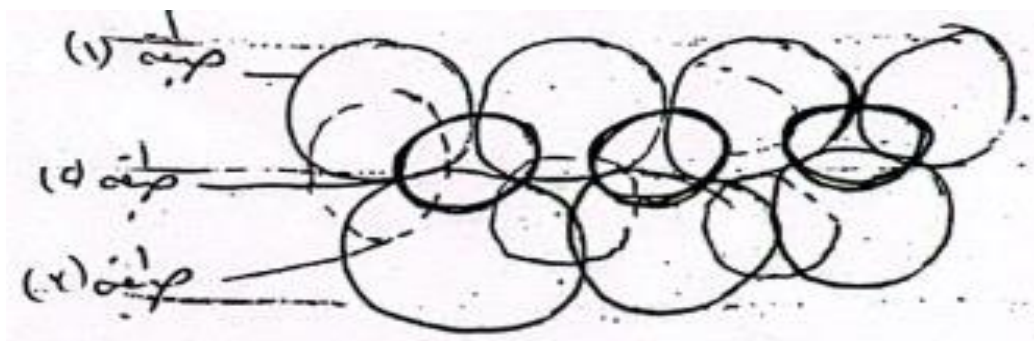
With one of three basic structures, which are the following-:

1. Facial cubic close packing (FCCP).
2. Hexagonal close packing (HCP).
3. Body central cubic (bcc).

All metallic compounds are aligned or held together by one of these three structures, and sometimes the same metals crystallize with one or more types of crystal structures. These metal structures can be used to study the crystal structure and crystalline arrangement in ionic compounds that consist of balls of varying size.

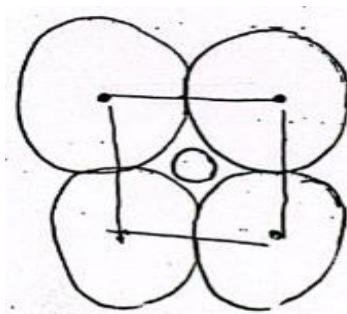
The first and second types are considered the most cohesive, and the tight crystalline arrangement is the one in which the largest percentage of empty space

in the crystal structure is filled. This can be represented in metals as follows, which shows the first type.



The second type is hexagonal tight stacking

The central ball is surrounded by four balls so that the centers of the balls are located on the corners of a square. This type of stacking involves 50% of the space being occupied. Therefore, the first type is considered more compact. The crystalline structure and method of crystal construction can be diagnosed and named by following the tight stacking.



1. Arrange balls of equal size so that each ball touches six balls in the plane.
2. Another layer of balls is stacked on top of layer **A**, which is layer **B**, so that each ball touches (from the layer **B**) three balls from layer **A**, so that each ball from layer **B** falls over the gap formed by the meeting of the three balls with each other in layer **A**, thus giving a tetrahedral-shaped cavity.

A third layer can be placed on top of the similar layer **B** so that it is directly above the balls of layer **A**, forming an arrangement called **ABABAB**----- . This type of stacking is called hexagonal tight stacking.

3. If the third layer is placed over the gaps of layer **A**, and when this type is repeated in the engineering structure, we get a repeating structure after every three layers **ABC ABC**.... This type of stacking is called a tight cubic stacking, and each ball touches twelve balls.

Body Central Cubic

In this type of stacking, every time eight balls touch each other, they fall on the corners of the cube, and this is at its center in metals. However, in ionic compounds, one of the two ions is in the center of the cube, and the other ion is located in the eight corners of the cube, and it is less cohesive than the centered stacking.

Crystal structure of NaCl

The building unit of the crystal cell of a sodium chloride crystal consists of two concentric cubic lattices for each of the sodium ions Na^+ and the chlorine ions Cl^- . Thus, two overlapping lattices of the ions are formed: the Na^+ ion is surrounded by six chloride ions, Cl^- . The same is true for the chloride ions, so a center of an octahedral pyramid is formed, and each ion is arranged in a **ABC**.

$$r_{\text{Na}^+} = 0.95 \text{ \AA}^\circ, r_{\text{Cl}^-} = 1.81 \text{ \AA}^\circ$$

$$r_{\text{Na}^+}/r_{\text{Cl}^-} = 0.95/1.81 = 0.525 \rightarrow \text{Coord. No of Na}^+=\text{Cl}^- = 6$$

Crystal structure of ZnS

$$r_{\text{Zn}^{+2}} = 0.74 \text{ \AA}^\circ, r_{\text{S}^{-2}} = 1.84 \text{ \AA}^\circ$$

$$r_{\text{Zn}^{+2}}/r_{\text{S}^{-2}} = 0.74/1.84 = 0.403 \rightarrow \text{Coord. No of Zn}^{+2}=\text{S}^{-2} = 4$$

Zinc sulfide crystallizes in one of the following two structures:

A- Zinc Blend.

B- Wurtzite.

In the **zinc blend**, the crystalline arrangement of both Zn^{+2} and S^{-2} ions is of the type of tight, centered cubic arrangement, such that the sulfide ion forms the centers or corners of the vertices of the cube, and the zinc ion is located in the gaps of the tetrahedral pyramid.

In the **wurtzite structure**, the packing of each ion is of a tight hexagonal packing type, and the coordination number of each ion is = **4**.

In the compound CaF_2 :-

The unit cell takes the coordination number of the Ca^{+2} ion to be = **8** and the coordination number of F^- = **4**. Ca^{+2} takes a tight, centered cubic arrangement, and the fluoride ions are located in the centers of the tetrahedral pyramid.

In the compound TiO_2 , the structure of titanium oxide crystallizes in the form of **anates** and takes on the **Rotile** structure, and the coordination number of Ti^{+4} = **6** and the coordination number of O^{-2} = **3**.

$$r_{\text{Ti}^{+4}} = 0.68 \text{ \AA}^\circ, r_{\text{O}^{-2}} = 1.4 \text{ \AA}^\circ$$

Comments:-

1. The expectations of the coordination number extracted from the value do not always agree. For example, the coordination number of the cadmium ion in the ionic compound **CdS** is equal to six, while in reality the coordination number of the cadmium ion Cd^{+2} in the same compound using X-rays = 4. There are other examples of compounds in which the theoretical values of Consistency differs from practical reality, and the reason for this is that sometimes the bond is not completely ionic bond, as the covalent character may appear in it, requiring that the orbital hybridization in it be of the **SP³** type. Also, the idea of tight packing of ions is based on the belief that both positive and negative ions are spheres. A solid with a fixed size, and this is far from practical reality because many ionic compounds undergo polarization. Therefore, there is no fixed radius for any ion because it depends on the type of structure within which it is located and on its polarization properties.
2. For the compounds given in the examples for **A+B⁻** type, the ratio of the radius of the positive ion to the radius of the negative ion is what determines the coordination number of the positive ion and its corresponding negative ion. The ratio of the radius of the negative ion to the radius of the positive ion appeared to be of different values, following the required coordination number of positive ion depended on r^+/r^- only.

Hydrogen

Inorganic Chemistry

10th lecture

Prof. Dr. Mahasin Faisal A. Alias

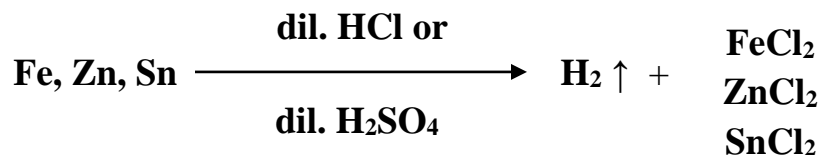
2023-2024

Hydrogen

1- Position

It is not possible to fix the position of hydrogen in the periodic table, as it takes a position independently of the other elements. On the one hand, it contains one electron in, and in this capacity it is similar to the alkaline elements. It also tends to lose this electron to form a positive ion H^+ like the rest of the alkaline elements, but at the same time, hydrogen tends to gain one electron to form the negatively charged hydride ion H^- , which is similar in its electronic distribution to the distribution of an element in this case, is similar to the group of halogens that are trying to acquire one to reach the distribution of one of the noble elements He , but the electronegativity of hydrogen.

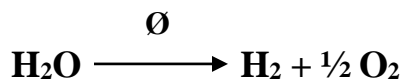
It is much higher than the electronegativity of alkali elements and much lower than the electronegativity of halogens, and for this reason hydrogen is placed in the periodic table in a separate place. Hydrogen was discovered by the scientist Henry in **1876**, who isolated the gas when some metals reacted with some dilute acids, such as dilute HCl and dilute H_2SO_4 .



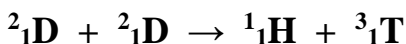
This method was called the laboratory method for preparing hydrogen.



It was found that the liberated gas is lighter than air, and it was found that it is flammable with oxygen. In **1781**, it was found that the product of combustion is water. After that, the scientist Lavoisier came and called this gas hydrogen gas, which is a Latin word consisting of two syllables **hydro** + **gen** water component. In the year **1800**, the opposite experiment was conducted, meaning that water was electrolyzed, and two types of gases were released in this experiment: H_2 and O_2 gases.



After that, hydrogen isotopes were discovered in **1932**, and the first isotope discovered was deuterium ${}^2_1\text{D}$. In **1934**, tritium ${}^3_1\text{T}$ was prepared from deuterium ${}^2_1\text{D}$.

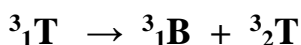


After that, it was found that the third isotope with the element hydrogen was in the atmosphere and in rainwater.

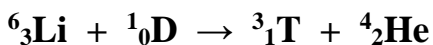
Percentage	Mass	isotope
99.98 %	1.008	${}^1_1\text{H}$ (light hydrogen)
0.956%	2.015	${}^2_1\text{D}$ (heavy hydrogen)
$10^{-17}\%$	3.017	${}^3_1\text{T}$ (Radiation element)

$t_{1/2} {}^3_1\text{T} = 12.4$ year

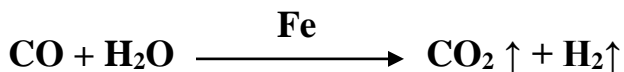
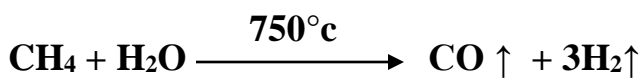
Hydrogen is generally a diatomic particle. Beta rays β can be obtained from the element tritium ${}^3_1\text{T}$.



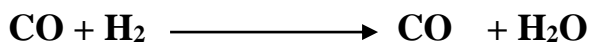
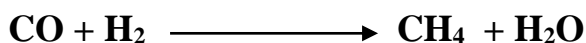
It can be prepared ${}^3_1\text{T}$ by neutron bombardment of the element lithium with the release of alpha rays.



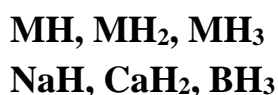
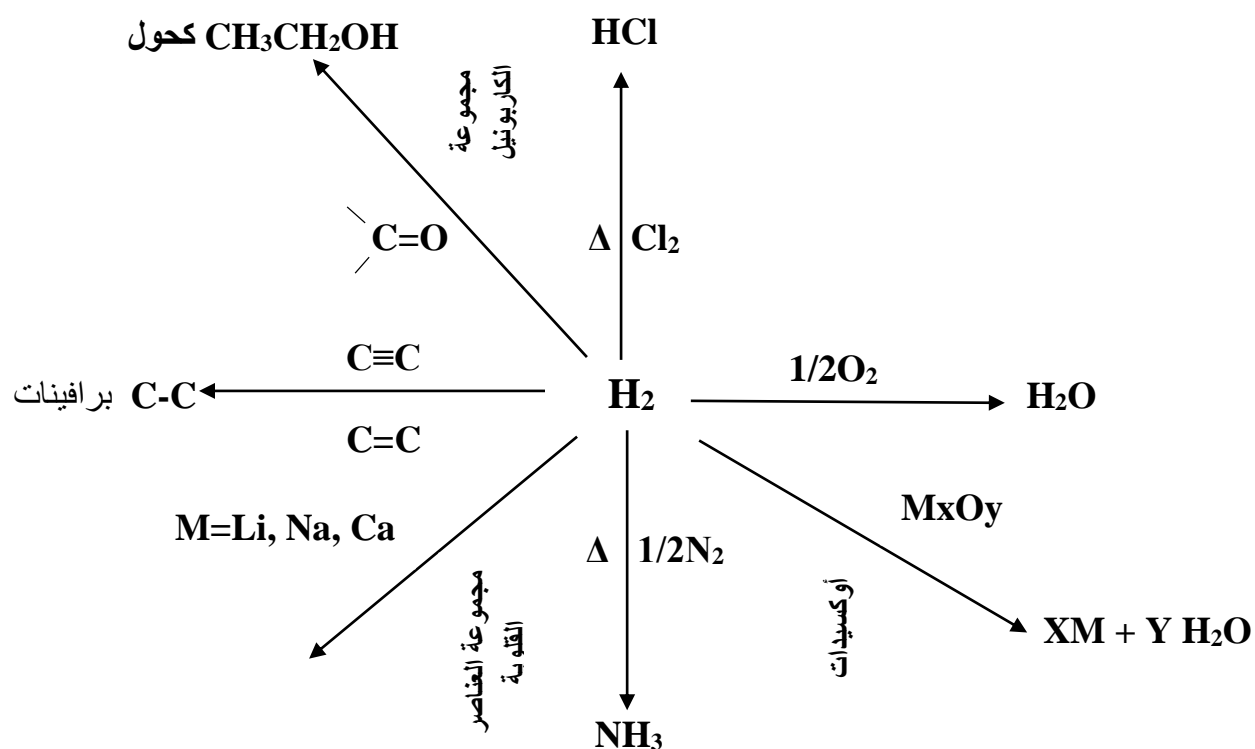
Isotopes differ from each other in physical properties. Hydrogen gas is prepared artificially.



If the previous reaction occurs in reverse, this method is called “**water shift reaction**”.



The same is true for CO_2 .



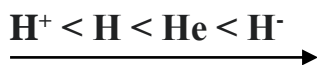
Increase of r
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rH⁺ = 10⁻⁵ Å°

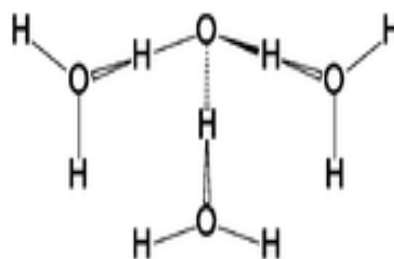
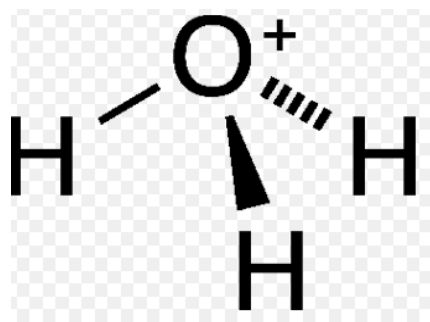
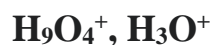
rH = 0.37 Å°

rH⁻ = 1.26 – 1.54 Å°

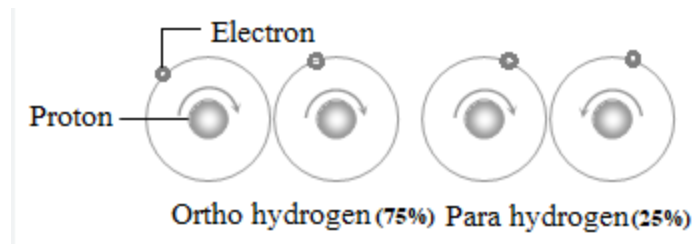


Increase of r

H⁺ has a very small radius (a nucleus without a shell), so it has **charge/ r** ratio a high concentration and therefore a high ability to polarize with respect to other molecules. For this reason, H⁺ are no exist as free ions, and it is obtained from an electrical discharge or from an electric arc inside a vacuum tube containing molecules of H₂ in an acidic environment. In aqueous form, hydrogen (proton) and hydroxide ions are formed, and the reaction produces heat, and hydroxonium ions are in the following two forms:



This results from the high ability of the H^+ ion to polarize water molecules.



These two types are similar in chemical properties but different in physical properties. This situation occurs in hydrogen and deuterium but does not occur in sodium.

Hydrides

1- Ionic hydrides

IA, IIA, (Soluble in water).

2- Covalent hydrides

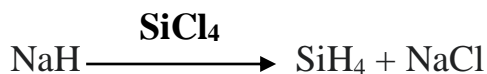
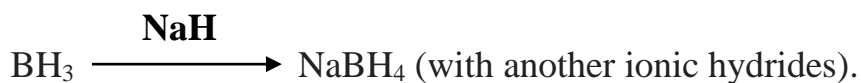
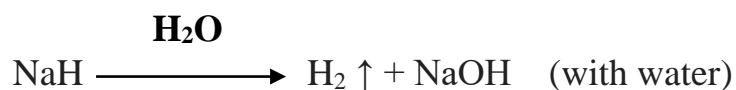
IIIB, IVB, VB, VIB, VIIB Soluble only in organic solvent.

3- Transition metal hydrides

1- Ionic hydrides

Examples include: **LiH, NaH**

These are hydrides that are formed with elements with high electronegativity or low ionization potential, and their most important reactions are the release of hydrogen gas in some reactions. The effectiveness of these halides increases greatly with the increase in the atomic number of the metal, as the ionic property increases. These hydrides exist in the solid state and have the ability to conduct electrical current at a high melting point.



Ionic hydrides must be prepared in a moisture-free environment.

2- Covalent Hydrides

These hydrides represent a transition between ionic and covalent properties and exist in the form of polymers.

Non metal hydride

IVB	VB	VIB	VIIB
CH₄	NH₃	H₂O	HF
SiH₄	BH₃	H₂S	HCl
GeH₄	AsH₃	H₂Se	HBr
SnH₄	SbH₃	H₂Te	HI

Compounds in which the element bonded to hydrogen has high electronegativity, high polarity, high oxidation potential, and the formation of hydrogen bonds. Most of them exist in a gaseous or liquid state, and a few of them exist in a solid state, and their conductivity of electric current is weaker than ionic hydrides.

The reducing ability of these hydrides increases with decreasing electronegativity.



As for the less electronegative molecules, they behave as reducing agents.



The boiling points of hydrides for groups **V**, **VI**, and **VII** increase with the increase in the molecular weight of the atoms of one group, except for the first element (**N**, **O**, **F**).



The reason for this is that the polarity of the first molecules is high due to the appearance of hydrogen bonds between the molecules, so the boiling and melting points increase, while the remaining hydrogen bonds are weak, so the boiling point becomes limited to the increase in molecular weight. As for carbon

hydrides, they do not form hydrogen bonds, as they follow an increase in melting points with increasing molecular weight.

Alkali metal hydrides are formed by heating the metal with hydrogen, and most of them deviate from chemical equilibrium.

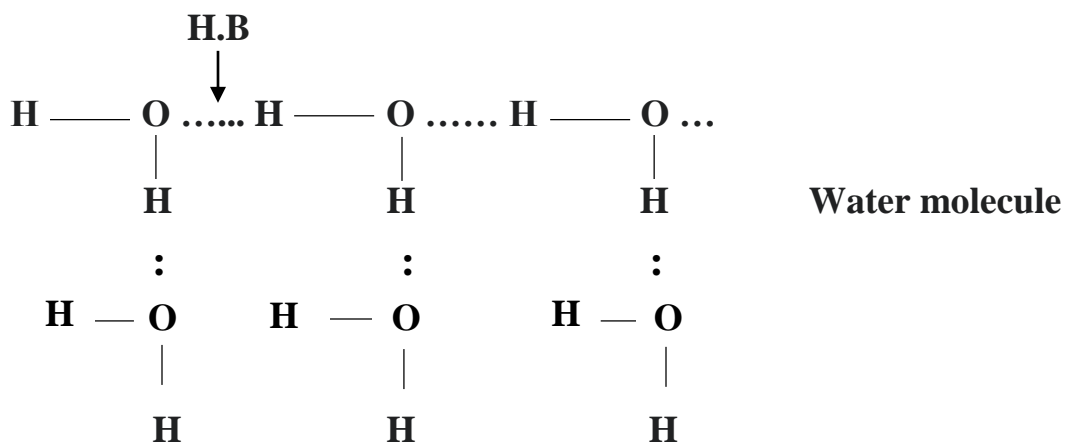
Hydrogen Bonds

1- Inter molecular H.B.

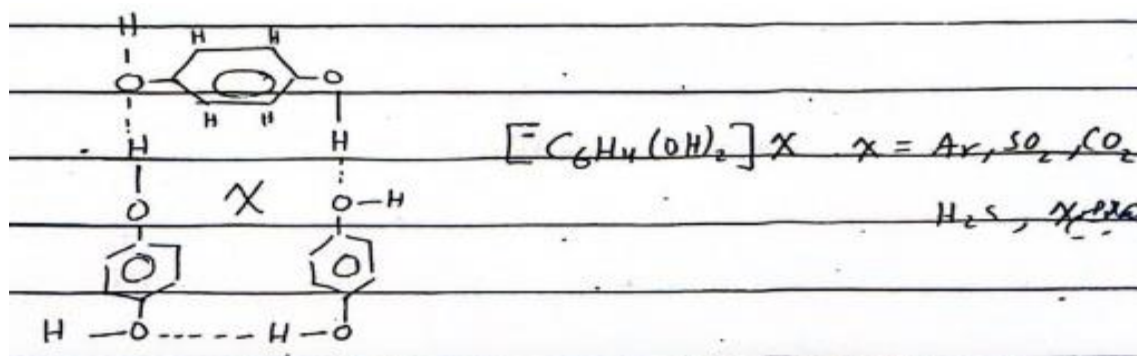
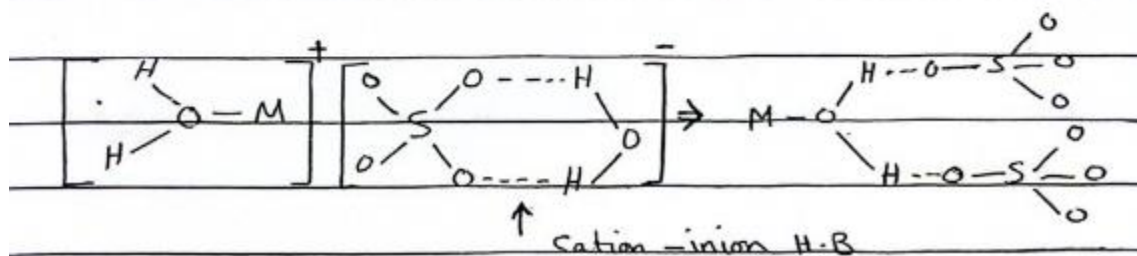
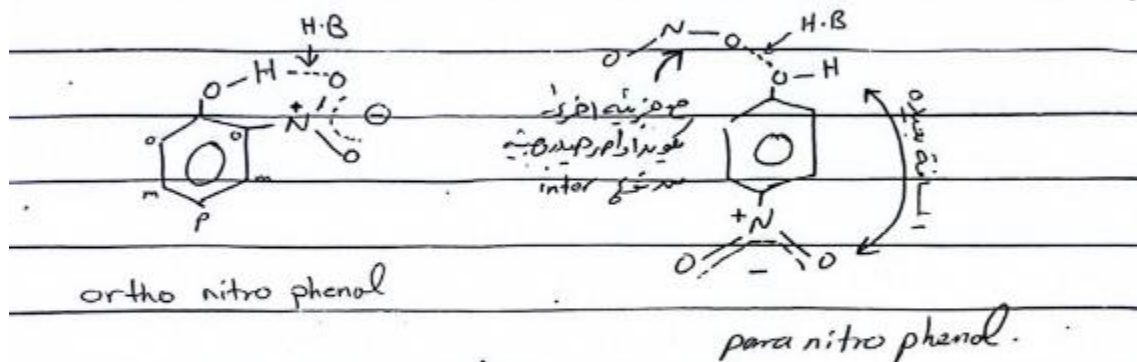
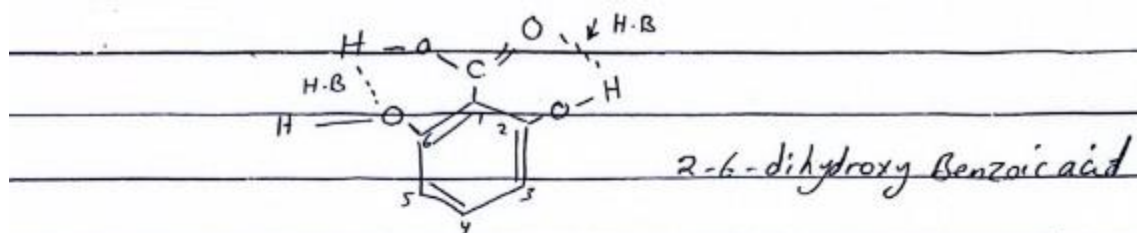
2- Intra molecular H.B.

Hydrogen bonds (**H.B**) occur in compounds in which hydrogen is bonded to a highly electronegative element such as $\text{H}^{+\delta}-\text{X}^{-\delta}$, so the molecule becomes polar, as a positive molecular charge appears on the hydrogen, and this in turn attracts a neighboring molecule through a highly electronegative element carrying non-electronic doublets. Hydrogen bonds are **stronger** than van der Waals bonds of the dipole-dipole type, and in turn, hydrogen bonds lead to **increased boiling and melting points**.

1- Inter H.B.



2- Intra H. B.



Formation of cyclic hydrogen bonds between molecules in the solid state in the presence of molecules of some gases, thus trapping the gas molecules within the innate gaps. When this gas is needed, it is obtained by heating.