Set II

MJ -1 (Chemistry)

Full Marks: 60

Time: 3 Hours

Answer the questions as per instruction given.
The figures in the right-hand margin indicate marks.
Candidates are required to give answers in their own words as far as practicable.

Group A

(Short Answer Type Questions)

Answer all the following questions.

1. Answer the following questions in a few words or maximum in one sentence. (5x1=5)

a) How many electrons are present in bonding π molecular orbitals of O_2 molecule?
b) Which element has the highest electron affinity?
c) Which metal is the most abundant in the earth's crust?
d) How many unpaired electrons are present in C_2 molecule?
e) How does the solubility of hydroxides of alkaline earth metals in water vary on moving down the group?

2. What is Fajan's rule? Lithium iodide is soluble in organic solvents, why? (5)

3. Explain the shape of CO_2 and SO_2 molecule with the help of hybridisation. (5)

Group B

(Long/Descriptive Answer Type Questions)

Answer any three of the following questions.

4. a) What is Aufbau principle?
b) Explain Hund's rule of maximum spin- multiplicity with suitable example.
c) Write down electronic configurations of Ti (Z = 22), Cr (Z= 24), and Fe^{2+} (Z = 26). (4+5+6)

5. a) Define electron affinity and illustrate with an example.
b) Discuss the variation of electron affinity in the periodic table.
c) The electron affinity of fluorine is lower than that of chlorine, why? (5+5+5)

6. a) What is dipole moment? What is its unit?
b) What do you mean by polar and non-polar molecules?
c) Classify the following molecules into polar and non-polar categories:
CO_2, SO_2, BF_3 and ClF_3

(6+5+4)

7. a) What is metallic bond?

b) Explain the free electron model for metallic bond.
b) The electrical conductivity of metal decreases with increase in temperature, why?

(3+8+4)

8. Write short notes on any three of the following:
   a) Silicones
   b) Borazine
   c) Pauli’s exclusion principle
   d) Hydrogen bonding
   e) van der Waals forces

(3x5)

Answer:

1. a) 4
   b) Chlorine
   c) Aluminium
   d) 0
   e) The solubility of hydroxides of alkaline earth metals in water increases on moving down the group.
2. **Fajan’s rule:**

   Fajan presented a set of four rules to summarise the factors favouring the polarisation of anion leading to the covalent character in the ionic bond as follows:
   i) A small positive ion (cation) causes greater polarisation of anion favouring covalency.
   ii) A large negative ion (anion) is polarised to a greater extent favouring covalency.
   iii) High charge on cation or on anion or on both causes greater polarisation of anion favouring covalency.
   iv) A positive ion having non-noble gas electronic configuration such as Cu^+(2,8,18) has greater polarising power than the positive ion having noble gas electronic configuration such as Na^+(2,8) if they have comparable size.

   These are called Fajan’s rules.

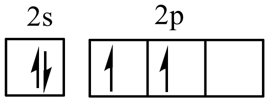
   Lithium iodide is has high covalent character due to larger anion (I^-) and smaller cation (Li^+) which leads to greater polarisation of the anion. This is why, LiI is soluble in organic solvents which are covalent in nature.

3. **CO_2**

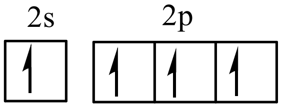
   C is the central atom in CO_2 molecule.

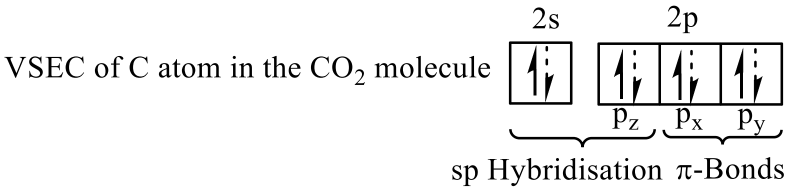
   C (6) [He]$2s^2\,2p^2$

VSEC of C atom in the GS

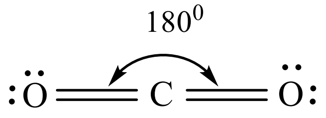


VSEC of C atom in the ES





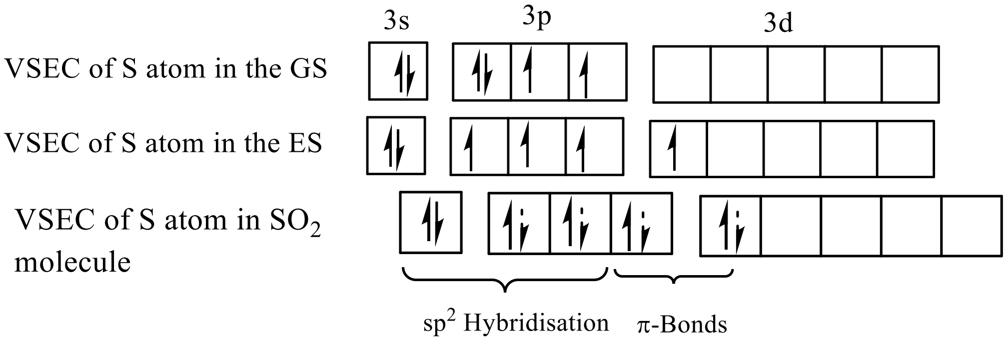
Thus, CO_2 molecule will have linear shape arising from sp hybridisation on the central C atom.



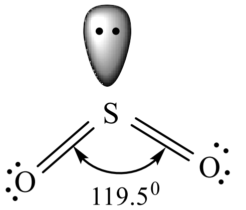
Shape: Linear

SO_2

S is the central atom in SO_2 molecule.
S(16) $[Ne]3s^23p^4$



Thus, SO_2 molecule will have bent /angular shape arising from sp^2 hybridisation on the central S atom which contains a lone pair of electrons also.



Shape: Bent or angular

4. **a) Aufbau principle:**

Aufbau is a German word, which means to build up. Thus, aufbau principle means the principle of building up. According to this principle, "During build- up of electronic configuration of an atom, the subshell having minimum energy is filled first by electrons and then the subshells with higher energies are filled successively."

The aufbau principle can be explained as follows:

i) $(n + l)$ rule:The subshell having minimum value of $(n + l)$ has minimum energy and hence filled first by electrons and hence filled first by electrons. The subshells having higher values of $(n + l)$ are filled successively. Let us consider 3d and 4s subshells.

	3d	4s
n+l	3+2 = 5	4+ 0 = 4

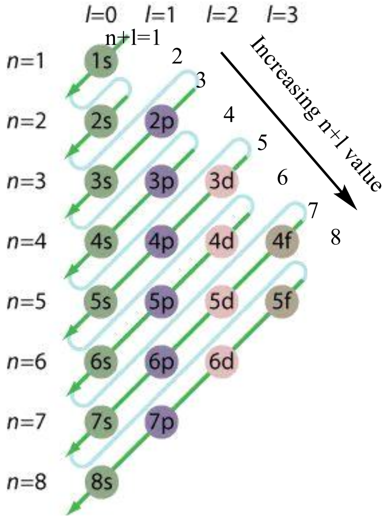
4s subshell has lower value of $(n + l)$ and hence lower energy than 3d subshell. Therefore, 4s subshell is filled before 3d subshell.

ii) n-rule: If two or more subshells have the same value of $(n+l)$, the subshell having minimum value of n has minimum energy and hence is filled first by electrons and then the subshells with higher values of n are filed successively.

$$\begin{array}{cccc} & 3d & 4p & 5s \\ n+l & 3+2=5 & 4+1=5 & 5+0=5 \end{array}$$

$$\xrightarrow[\text{Energy increases}]{\hspace{12em}}$$

It is obvious that 3d subshell will fill up before 4p subshell which, in turn, will fill up before 5s subshell. According to aufbau principle, the sequence of filling up of different subshells is given in the following figure :



b) Hund's rule of maximum spin- multiplicity:

"In a given set of degenerate orbitals, i.e., in a given set of orbitals having the same energy, the electrons fill up in such a way that there is maximum number of unpaired electrons with parallel spins so that there is maximum spin- multiplicity and minimum energy so that the molecule/ion may have maximum stability."

It is known as Hund's rule of maximum spin- multiplicity. Let us illustrate it by taking example of the filling up of electrons in the p-subshell, which is nothing but a set of three degenerate orbitals.

Electronic configuration	Electronic arrangement	No. of unpaired electrons with parallel spins	S	Spin-multiplicity (2S+1)
p^1	$\boxed{\uparrow}\boxed{}\boxed{}$	1	$\frac{1}{2}$	2(Doublet)
P^2	$\boxed{\uparrow}\boxed{\uparrow}\boxed{}$	2	1	3(Triplet)
P^3	$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$	3	$\frac{3}{2}$	4(Quartet)
P^4	$\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$	2	1	3(Triplet)

P^5	[↑↓][↑↓][↑]	1	$\frac{1}{2}$	2(Doublet)
P^6	[↑↓][↑↓][↑↓]	0	0	1(Singlet)

The Hund's rule can be stated in other words also as follows:

"In *a given set of degenerate orbitals, i.e., in a given set of orbitals having the same energy, the electrons fill up one by one and when all the orbitals become singly occupied the pairing up of electrons starts."*

c) Electronic configuration of Ti (22) : $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^2, 4s^2$
Electronic configuration of Cr (24) : $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$
Electronic configuration of Fe^{2+} : $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6$
No. of electrons in Fe^{2+} ion = 26-2 = 24

5. a) Electron affinity:

"The amount of energy released when an extra electron is introduced to an isolated neutral gaseous atom of an element in its ground state to produce a gaseous anion is called the electron affinity of that element." It is abbreviated as EA. It is expressed in kJ/mole.

$$\overset{\text{Electrostatic attraction}}{\overset{\curvearrowright\ \curvearrowleft}{X(g) \quad + \quad e^-}} \longrightarrow X^-(g) \ + \ \text{Energy}$$

When an electron is brought near an atom, the nucleus of atoms exerts electrostatic attractive force on the electron. Therefore, when an extra electron is added to an atom, generally energy is released which is called electron affinity. Let us illustrate it taking the following example:

$$\overset{\text{Electrostatic attraction}}{\overset{\curvearrowright\ \curvearrowleft}{Cl(g) \quad + \quad e^-}} \longrightarrow Cl^-(g) \ + \ 349\ \text{kJ/mole} \ ;\ \text{EA of Cl} = -349\ \text{kJ/mole}$$

The negative sign is used before electron affinity because energy is released during adding electron. The greater the negative value of electron affinity of an atom, the greater will be its tendency to gain electron. The stronger the electrostatic attractive force acting on the electron to be added towards the nucleus of the atom, the greater will be the electron affinity.

b) Variation of electron affinity in the periodic table:

On moving down a group in the periodic table, the Z_{eff} remains almost constant but atomic radius increases. As a result, the electrostatic attractive force acting on the electron to be added towards the nucleus becomes increasingly weaker and hence the electron affinity goes on decreasing as illustrated below:

Group 17	
Elements	**EA(kJ/mole)**
F	-333
Cl	-349
Br	-325

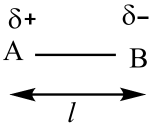
I	-296

On moving from left to right in a period in the periodic table, the atomic radius decreases and the Z_{eff} increases. As a result, the electrostatic attractive force acting on the electron to be added towards the becomes increasingly stronger and hence the electron affinity goes on increasing as illustrated below:

c) The electron affinity of fluorine is lower than that of chlorine due to the fact that the addition of electron to F atom leads to the formation of F^-ion while the addition of electron to Cl atom leads to the formation of Cl^- ion. There is greater interelectronic repulsion in much smaller F^- ion than in larger Cl^- ion. Therefore, F atom has lower tendency to accept electron than Cl atom.

6. **a) Dipole moment:**

The polarity of a covalent bond is expressed in terms of dipole moment, which is defined by the expression:



$$\mu = \delta \times l$$

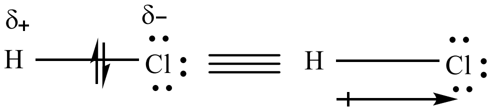
Where,

$\mu =$ Dipole moment

$\delta =$ Magnitude of charge on either end of the bond

$l =$ Separation between the centres of charges or the bond length

Dipole moment is a vector quantity. It is denoted by an arrow in the direction of the displacement of electron. It is called dipole moment vector or simply dipole vector.



Unit of dipole moment: δ is of the order 10^{-10} esu and l is of the order 10^{-8}cm and, therefore, μ is of the order 10^{-18}esu cm. It is unit of dipole moment. It is called debye and denoted by D.

$$1\,D = 10^{-18} esu\ cm$$

The SI unit of dipole moment is coulomb metre, which is denoted by C m.

$$1\,D = 3.33 \times 10^{-30}\ C\ m$$

The dipole moment of a covalent bond is called bond moment.

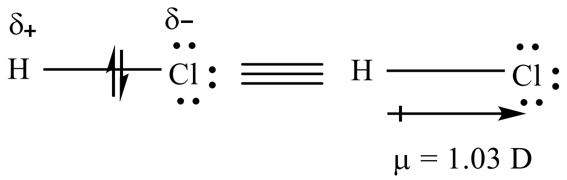
b) Polar and non-polar molecules:

Molecules are of two types on the basis of their polarity or dipole moment :

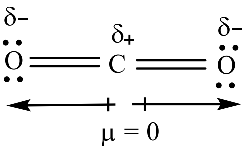
i. **Non-polar molecules:** The molecule whose net dipole moment is equal to zero is called a non-polar molecule. Example: H_2, O_2, Cl_2, etc.
ii. **Polar molecule:** The molecule whose net dipole moment is not equal to zero is called a polar molecule. Any molecule is polar only when it contains polar covalent bond. But a molecule containing polar covalent bond is not essentially polar.

Examples:

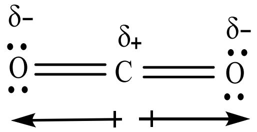
i. HCl molecule contains polar covalent bond and it is a polar molecule.



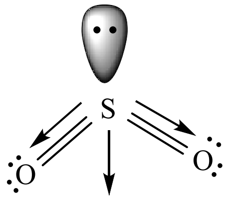
ii. **CO_2** molecule contains polar covalent bonds whose dipole vectors are in opposite directions, the net dipole moment is zero, and hence it is a non-polar molecule.



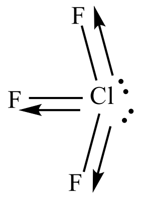
c) CO_2 : Non-polar, Linear shape
SO_2 : Polar, Bent shape
BF_3 : Non-polar, Triangular planar shape
ClF_3 : Polar, T-shape



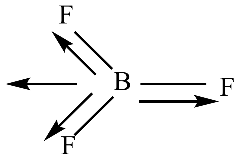
Linear molecule
μ = 0
Non-polar



Bent or angular molecule
μ ≠ 0
Polar



T-Shaped molecule
μ ≠ 0
Polar



Triangular planar molecule
μ = 0
Non-polar

7. a) Metallic bond:

The attractive force which binds the metal atoms together in a metallic solid is called metallic bond. For example, in the crystal of sodium, the Na atoms are held together by an attractive force which is called metallic bond.

There are various theories to explain the nature of metallic bond viz.

i. Electron pool theory or free electron theory
ii. Valence bond theory
iii. Molecular orbital theory or band theory

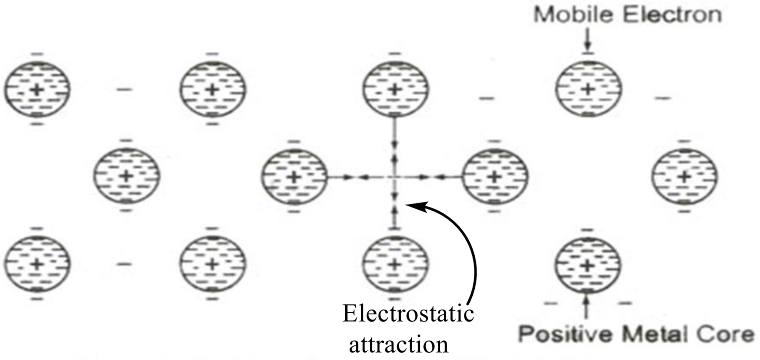
b) Free electron model for metallic bond:

According to the electron-pool theory, the metal atoms lose all their valence electrons during the formation of metal crystal forming positive metal core.

$M \rightarrow M^{n+} + ne^-$

Positive metal core   Valence electron

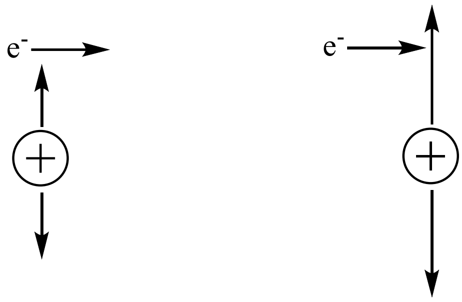
These valence electrons constitute a pool of electrons in which the positive metal cores are immersed. An electrostatic attractive force acts between the positive metal core and the electrons of the electron pool which binds them together.



Representation of sea of mobile electrons

The positive metals cores are held at equilibrium distances from one another while the electrons of the electron pool are free to move throughout the crystal. These mobile electrons provide various properties to metals such as thermal and electrical conductivity and metallic lustre.

c) The electrical conductivity of metallic solid decreases with increase in temperature. This is due to the fact that the amplitude and frequency of the positive metal core increases with increase in temperature. It produces greater resistance towards the flow of electrons, i.e., towards the flow of electric current.

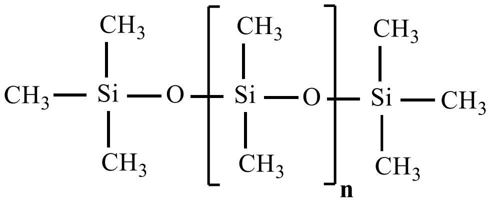


Lower temperature
Smaller resistance towards
the flow of electrons

Higher temperature
Greater resistance towards
the flow of electrons

8. a) Silicones:

The silicones are a group of organosilicon polymers containing Si-O-Si links. An example of silicone polymer is given below:



$$CH_3-Si(CH_3)_2-O-\left[Si(CH_3)_2-O\right]_n-Si(CH_3)_2-CH_3$$

Silicones have a number of characteristic features such as

i. good thermal and oxidative stability
ii. valuable resistance to high and low temperature
iii. excellent water repelling property

iv. good dielectric properties
v. desirable anti-stick and anti-foam properties
vi. chemical inertness
vii. prolonged resistance to UV irradiation and weathering
viii. complete physiological inertness

Preparation: The starting material for the manufacture of silicones are alkyl/aryl substituted chlorosilanes – $RSiCl_3$, R_2SiCl_2 and R_3SiCl. These can be prepared by using Grignard's reagent.

$SiCl_4 + CH_3MgCl \rightarrow CH_3SiCl_3 + MgCl_2$

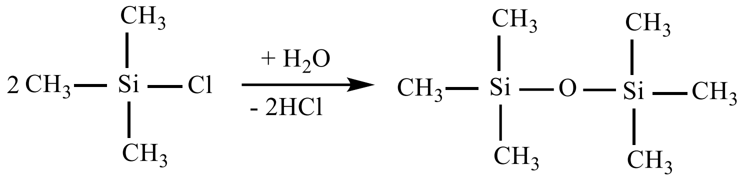
$CH_3SiCl_3 + CH_3MgCl \rightarrow (CH_3)_2SiCl_2 + MgCl_2$

$(CH_3)_2SiCl_2 + CH_3MgCl \rightarrow (CH_3)_3SiCl + MgCl_2$

$(CH_3)_2SiCl_2$ is best prepared as follows:

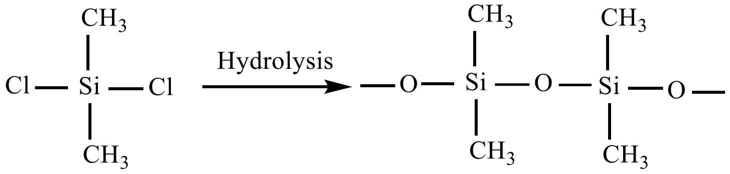
$2CH_3Cl + Si \xrightarrow{Cu\ catalyst, 300\ ^0C} (CH_3)_2SiCl_2$

The hydrolysis of $(CH_3)_3SiCl$ produces hexamethyl siloxane.



$$2\,CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-Cl \xrightarrow[-\ 2HCl]{+\ H_2O} CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

The hydrolysis of $(CH_3)_2SiCl_2$ gives rise to straight chain polymers of high length.



$$Cl-\overset{CH_3}{\underset{CH_3}{Si}}-Cl \xrightarrow{Hydrolysis} -O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-$$

If some $(CH_3)_3SiCl$ is added to the reaction mixture, the chain length is limited. On the other hand, if CH_3SiCl_3 is added to the reaction mixture, cross-linking is produced.

Uses:

Silicones are used for various purposes such as:

i) As sealant
ii) As anti- frothing agent
iii) In water proofing
iv) As rubber
v) As lubricating oil

b) Borazine

Borazine is an inorganic compound with molecular formula $B_3N_3H_6$. It is also known as borazole.

Preparation: Borazine can be prepared by heating a mixture of diborane and ammonia in 1:2 molar ratio.

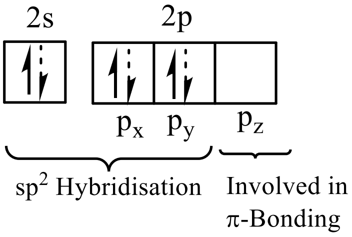
$3\ B_2H_6 + 6\ NH_3 \rightarrow 3\ [(B_2H_6)(NH_3)_2] \xrightarrow{100\ ^0C} 2B_3N_3H_6 + 12\ H_2$

Borazine can also be prepared starting from BCl_3 and NH_4Cl as follows:

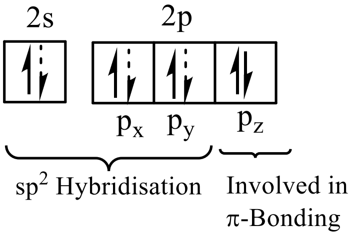
$3BCl_3 + NH_4Cl \xrightarrow[Heat\ ,-9HCl]{} (BClNH)_3 \xrightarrow{3NaBH_4} B_3N_3H_6 + 3\ NaCl + \frac{3}{2}\ B_2H_6$

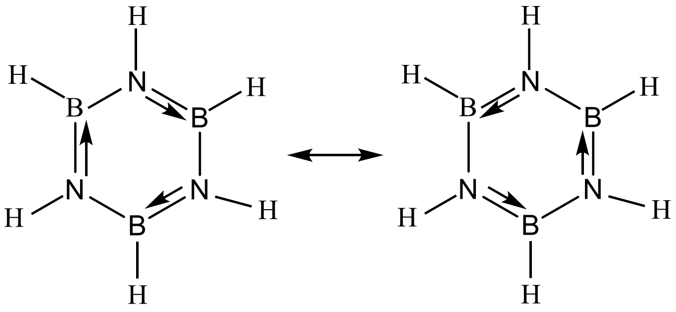
Structure: Borazine is a cyclic planar compound with benzene-like structure in which both B and N atoms are sp^2 hybridised and they form three σ-bonds with neighbouring atoms. B forms σ-bonds with neighbouring two N atoms and one H atom. Similarly, N forms σ-bonds with neighbouring two B atoms and one H atom. The filled $2p_z$ AO of N atom overlaps with vacant $2p_z$ AO of B atom forming N→B π-bond. There is resonance of π-bonds in borazine molecule.

VSEC of B atom in the $B_3N_3H_6$ molecule



VSEC of N atom in the $B_3N_3H_6$ molecule





Two resonating structures of $B_3N_3H_6$ Molecule

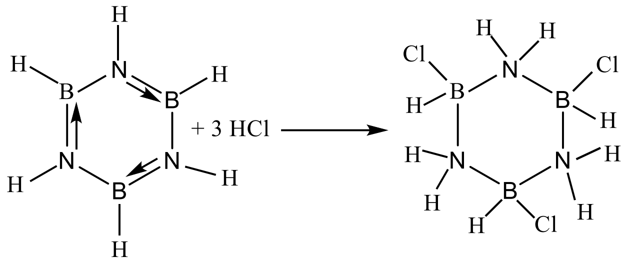
Properties:

The physical properties of borazine are similar to those of benzene as summarised in the following table:

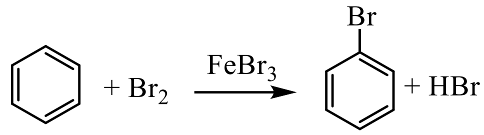
Compd.	Mol. Wt. (u)	B.P.	T_c	Density (g/ml)	Surface tension(dyne/cm)
Borazine	80.5	55^0C	252^0C	0.81 (*l*)	31.1
Benzene	78	80^0C	288^0C	0.81(*l*)	31.0

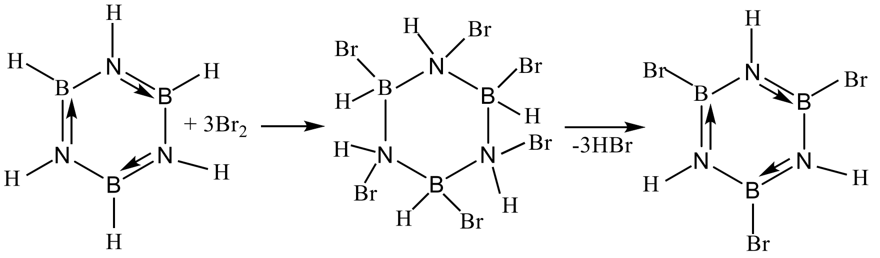
This is why borazine is also called 'Inorganic Benzene'. However, the chemical properties of borazine are quite different from those of benzene. For example, benzene is reluctant towards addition reaction while borazine undergoes addition reactions readily.

$C_6H_6 + HCl \rightarrow$ No reaction



Benzene and borazine also differ in reaction with bromine.





Uses:

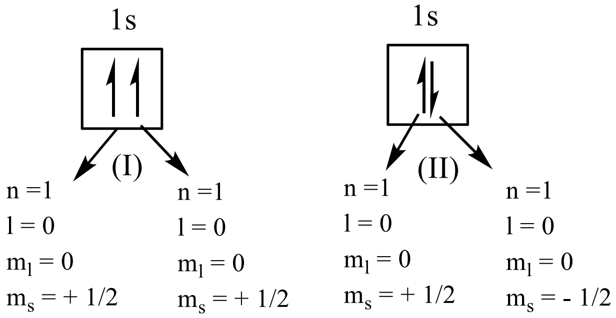
i. In ceramic industries
ii. In the manufacture of boron nitride

c) Pauli's exclusion principle:

The Pauli's exclusion principle is the quantum mechanical principle, which can be stated as follows:

"No two electrons in an atom can have the same set of all the four quantum numbers."

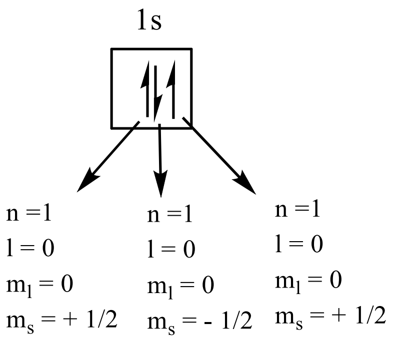
Let us consider two electronic arrangements for $1s^2$ electronic configuration of He (Z =2).



In the electronic arrangement (I), two electrons have the same set of all the four quantum numbers. Hence, it does not obey Pauli's exclusion principle and it is incorrect.

In the electronic arrangement (II), two electrons have the same set of first three quantum numbers but they differ in the fourth quantum number, i.e., the magnetic spin quantum number and thus it obeys Pauli's exclusion principle and it is correct.

Let the electronic configuration of Li (Z = 3) be $1s^3$.



It is obvious that the first and the third electrons have the same set of all the four quantum numbers. Thus, if more than two electrons are placed in a single orbital, two electrons will have the same set of all the four quantum numbers which will be against Pauli's exclusion principle. Therefore, an important conclusion can be drawn from the Pauli's exclusion principle as follows:

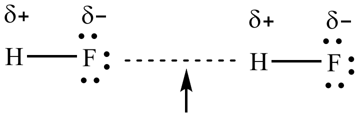
"Maximum two electrons with opposite spins can be accommodated in any orbital."

d) Hydrogen bonding

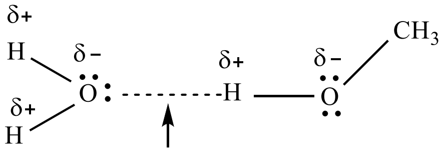
The weak electrostatic attractive force acting between the H atom which is already attached to a highly electronegative atom (F, O or N) and the lone pair of electrons of another highly electronegative atom (F, O or N) of the same molecule or the other molecule is called hydrogen bond.

The hydrogen bond is of two types:

i) **Intermolecular hydrogen bond:** The H-bond formed between two molecules- same or different is called intermolecular hydrogen bond. Examples:

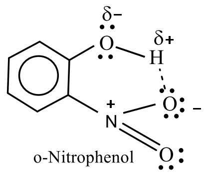


Intermolecular H-bond between two same molecules



Intermolecular H-bond between two different molecules

ii) **Intramolecular hydrogen bond:** The H-bond formed within the same molecule is called intramolecular hydrogen bond. Example: There is intramolecular H-bond between –OH and –NO$_2$ groups in o-nitrophenol.



o-Nitrophenol

Theories of hydrogen bond:

There are two important theories for hydrogen bond:

A. Electrostatic theory:

B. Valence bond theory:

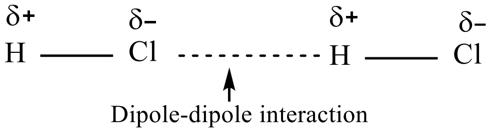
Applications of hydrogen bonding: various physical and chemical properties of compounds can be explained on the basis of hydrogen bonding such as :

i. The melting point and boiling point of compounds.
ii. Solubility of many solutes in water
iii. The strength of acids such as o-nitrophenol
iv. Stability of double-helical structure of DNA,
(And many more)

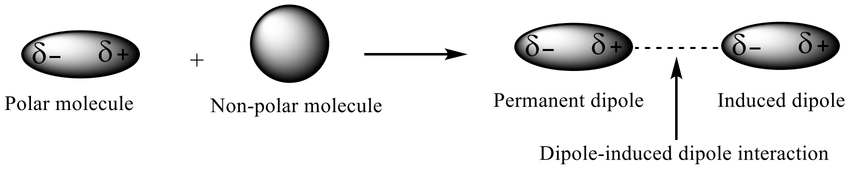
e) van der Waals forces:

The weak short-range electrostatic attractive forces acting between uncharged molecules are called van der Waals forces. These are of mainly three types:

i. **Dipole –dipole interaction:** The weak electrostatic attractive force acting between the molecules of a substance having permanent dipole moment and which cannot form hydrogen bond is called dipole-dipole interaction. Its strength increases with the increase in the magnitude of the dipole moment of polar molecules.

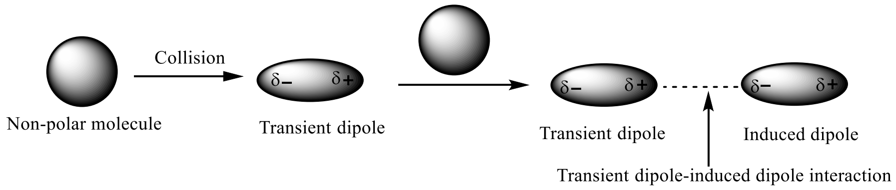


ii. **Dipole- induced interaction:** When a non-polar molecule is brought near a polar molecule, dipole moment is induced within it. The weak electrostatic attractive force acting between the molecule with permanent dipole moment and the molecule with induced dipole moment is called dipole-induced dipole interaction. It can be explained diagrammatically as follows:



For example, the attractive force acting between H_2O molecule (polar) and C_6H_6 molecule (non-polar) is dipole-induced dipole interaction. The strength of this force increases with increase in the magnitude of dipole moment of the polar molecule and the polarisability of the non-polar molecule. It is very weak force and hence polar and non-polar substances are not miscible with each other.

iii. **Transient dipole- induced dipole interaction:** In non-polar molecule, the electron cloud is symmetrical and the centres of positive & negative charges coincide at the same point. When such a molecule collides with the wall of the vessel or other molecule, its electron cloud becomes unsymmetrical and a temporary dipole is produced within it, which is called transient dipole. This transient dipole induces dipole in the neighbouring molecules. The weak electrostatic force acting between the transient dipole and the induced dipole is called transient dipole-induced dipole interaction or London Dispersion Force (LDF). It is sometimes loosely called van der Waals force.



The strength of the transient dipole-induced dipole interaction increases with increase in the

i) Surface area of molecule

ii) No. of electrons per molecule

The LDF is generally very weak, hence the substances having such intermolecular forces have low melting point and boiling point, and they are volatile.