5

CHAPTER

Chemical Bonding – Lewis Theory

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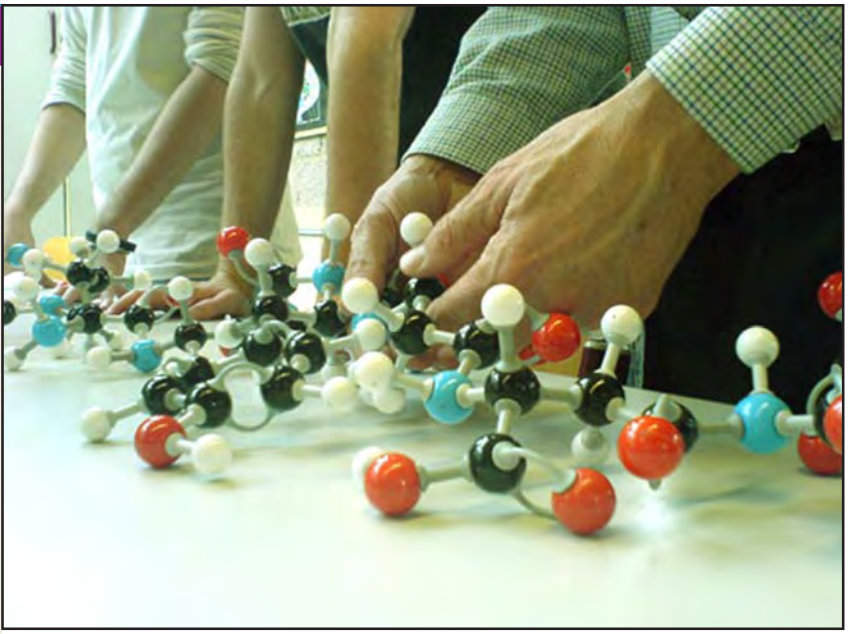


TERMS AND DEFINITIONS

Chemical Bond

Molecules of chemical substances are made of two or more atoms joined together by some force, acting between them. This force which results from the interaction between the various atoms that go to form a stable molecule, is referred to as a *Chemical Bond*.

A chemical bond is defined as a force that acts between two or more atoms to hold them together as a stable molecule.

As we will study later, there are three different types of bonds recognised by chemists :

(1) Ionic or Electrovalent bond
(2) Covalent bond
(3) Coordinate covalent bond

There is a fourth type of bond, namely, the metallic bond which we will consider later in this chapter.

Definition of Valence

The term valence (or valency) is often used to state the potential or capacity of an element to combine with other elements.

At one time, it was useful to define valence of an element as : the number of hydrogen atoms or twice the number of oxygen atoms with which that element could combine in a binary compound (containing two different elements only).

In hydrogen chloride (HCl), one atom of chlorine is combined with one atom of hydrogen and the valence of chlorine is 1. In magnesium oxide (MgO), since one atom of magnesium holds one atom of oxygen, the valence of magnesium is 2.

By the above definition, we would assign a valence of 2 to sulphur in H_2S, but 4 to sulphur in SO_2. Some elements have fractional valence in certain compounds, while there are elements that have variable valencies. The concept of valence as a mere number could not explain these facts. This concept, in fact, was very confusing and has lost all value.

As already stated, there are three different type of bonds that are known to join atoms in molecules. Although no precise definition of valence is possible, we can say that : **Valence is the number of bonds formed by an atom in a molecule.**

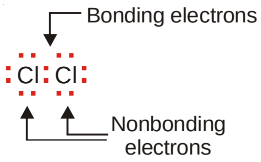
Valence Electrons

The electrons in the outer energy level of an atom are the ones that can take part in chemical bonding. These electrons are, therefore, referred to as the valence electrons.

The electronic configuration of Na is 2, 8, 1 and that of Cl is 2, 8, 7. Thus sodium has one valence electron and chlorine 7. It is important to remember that **for an A group element of the periodic table (H, O, K, F, Al etc.) the group number is equal to the number of valence electrons.**

Bonding and Non-bonding Electrons

The valence electrons actually involved in bond formation are called bonding electrons. The remaining valence electrons still available for bond formation are referred to as non-bonding electrons. Thus :



Lewis Symbols of Elements

A Lewis symbol of an element consists of an element's symbol and surrounding dots to represent the number of valence electrons. In this notation, **the symbol of an element represents the nucleus plus the inner normally filled levels (or shells) of the atom.** For illustration, the symbol Na stands for the nucleus of sodium atom plus 2, 8 electrons in the inner two levels.

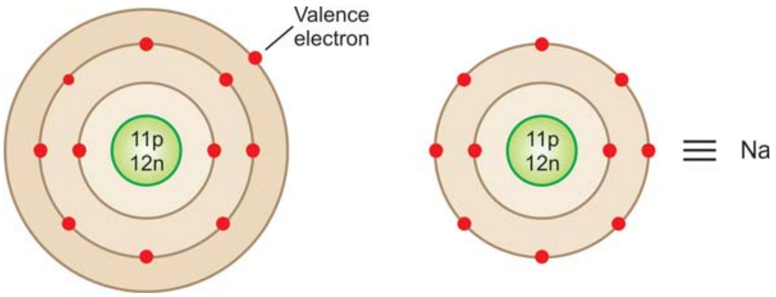


Figure 5.1
The Lewis symbol Na represents the nucleus and the electrons arranged in the inner two levels as 2, 8, minus the valence electrons.

To represent a Lewis symbol for an element, write down the symbol of the element and surround the symbol with a number of dots (or crosses) equal to the number of valence electrons. The position of dots around the symbol is not really of any significance. The bonding electrons are shown at appropriate positions, while the rest of the electrons are generally given in pairs. The Lewis symbols for hydrogen, chlorine, oxygen and sulphur may be written as :

The structural formulae of compounds built by union of Lewis symbols for the component atoms, are referred to as Electron-dot formulas, or Electron-dot structures or Lewis structures. For this purpose, the valence electrons actually involved in bond formation may be shown by crosses (x) or dots (·) for the sake of distinction.

Now we will proceed to discuss the common types of chemical bonds in the light of the electronic theory of valence.

ELECTRONIC THEORY OF VALENCE

As Bohr put forward his model of the atom so electronic configuration of elements was known. G.N. Lewis and W. Kossel, working independently, used this knowledge to explain 'why atoms joined to form molecules'. They visualised that noble gas atoms had a stable electronic configuration, while atoms of all other elements has unstable or incomplete electronic configuration. In 1916, they gave **the electronic theory of valence.** It states that : **In chemical bond formation, atoms interact by losing, gaining, or sharing of electrons so as to acquire a stable noble gas configuration.** Each noble gas, except helium, has a valence shell of eight electrons (Table 5.1).

TABLE 5.1. ELECTRONIC CONFIGURATION OF NOBLE GASES

Noble gas	At. No.	Electrons in principal shells
He	2	2
Ne	10	2, 8
Ar	18	2, 8, 8
Kr	36	2, 8, 18, 8
Xe	54	2, 8, 18, 18, 8
Rn	86	2, 8, 18, 32, 18, 8

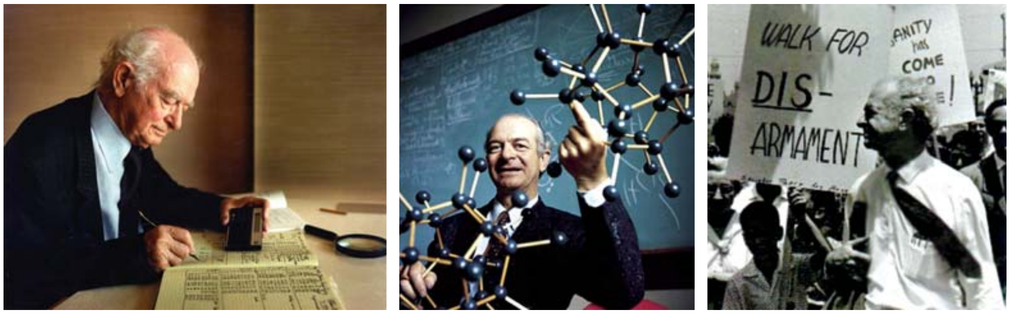
While atoms of noble gases possess a stable outer shell of eight electrons or **octet,** atoms of most other elements have incomplete octets. They may have less than 8 electrons or in excess. Thus, the electronic theory or valence could well be named as the **Octet theory of Valence.** It may be stated as : **Atoms interact by electron-transfer or electron-sharing, so as to achieve the stable outer shell of eight electrons.**

The tendency for atoms to have eight electrons in the outer shell is also known as the **Octet Rule** or the **Rule of Eight.** Since helium has two electrons in the outer shell, for hydrogen and lithium, having one and three (2, 1) electrons respectively, it is the **Rule of two** which will apply. We will see later in this chapter that there are quite a few exceptions to the rule of eight in covalent compounds.

IONIC BOND

This type of bond is established by transfer of an electron from one atom to another. Let us consider a general case when an atom *A* has one electron in the valence shell and another atom *B* has seven electrons. *A* has one electron in excess and *B* has one electron short than the stable octet. Therefore, *A* transfers an electron to *B* and in this transaction both the atoms acquire a stable electron-octet. The resulting positive ion (cation) and negative ion (anion) are held together by electrostatic attraction.

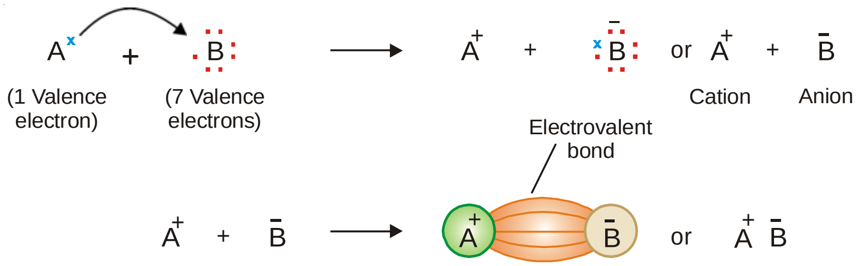
LINUS CARL PAULING



Linus Pauling won the Nobel Prize in Chemistry in 1954 for his work on chemical bonding. He also received the Nobel Peace Prize in 1962 for his campaign against nuclear testing.

Linus Carl Pauling (February 28, 1901 – August 19, 1994) was an American quantum chemist and biochemist. Pauling is widely regarded as the premier chemist of the twentieth century. He pioneered the application of quantum mechanics to chemistry and in 1954 was awarded the Nobel Prize in chemistry for his work describing the nature of chemical bonds. He also made important contributions to crystal and protein structure determination, and was one of the founders of molecular biology. He came near to discovering the "double helix," the ultrastructure of DNA, when Watson and Crick made the discovery in 1953.

Pauling received the Nobel Peace Prize in 1962 for his campaign against above-ground nuclear testing, and is the only person to win two unshared Nobel prizes. Later in life, he became an advocate for greatly increased consumption of vitamin C and other nutrients. He generalized his ideas to define orthomolecular medicine, which is still regarded as unorthodox by conventional medicine. He popularized his concepts, analyses, research and insights in several successful but controversial books centered around vitamin C and orthomolecular medicine.



The electrostatic attraction between the cation (+) and anion (–) produced by electron-transfer constitutes an Ionic or Electrovalent bond.

The compounds containing such a bond are referred to as **Ionic** or **Electrovalent Compounds.**

CONDITIONS FOR FORMATION OF IONIC BOND

The conditions favourable for the formation of an ionic bond are :

(1) Number of valence electrons

The atom *A* should possess 1, 2 or 3 valence electrons, while the atom *B* should have 5, 6 or 7 valence electrons. The elements of group IA, IIA and IIIA satisfy this condition for atom *A* and those of groups VA, VIA, and VIIA satisfy this condition for atom *B*.

(2) Net lowering of Energy

To form a stable ionic compound, there must be a net lowering of the energy. In other words energy must be released as a result of the electron transfer and formation of ionic compound by the following steps :

(*a*) The removal of electron from atom *A* ($A - e^- \rightarrow A^+$) requires input of energy, which is the ionization energy (IE). It should be low.

(*b*) The addition of an electron to *B* ($B + e^- \rightarrow B^-$) releases energy, which is the electron affinity of *B* (EA). It should be high.

(*c*) The electrostatic attraction between A^+ and B^- in the solid compound releases energy, which is the electrical energy. It should also be high.

If the energy released in steps (*b*) and (*c*) is greater than the energy consumed in step (*a*), the overall process of electron transfer and formation of ionic compound results in a net release of energy. Therefore, ionisation of *A* will occur and the ionic bond will be formed. For example, in case of formation of sodium chloride (NaCl), we have

$$\begin{aligned}
\mathrm{Na} &- e^- \longrightarrow \mathrm{Na}^+ - 119\ \mathrm{kcal}\\
\mathrm{Cl} &+ e^- \longrightarrow \mathrm{Cl}^- + 85\ \mathrm{kcal}\\
\mathrm{Na}^+ &+ \mathrm{Cl}^- \longrightarrow \mathrm{Na}^+\mathrm{Cl}^- + 187\ \mathrm{kcal}
\end{aligned}$$

The net energy released is 187 + 85 – 119 = 153 kcal. Since the overall process results in a lowering of energy, the ionic bond between Na and Cl will be formed.

(3) Electronegativity difference of A and B

From the line of argument used in (2), we can say that atoms *A* and *B* if they have greatly different electronegativities, only then they will form an ionic bond. In fact, a difference of 2 or more is necessary for the formation of an ionic bond between atoms *A* and *B*. Thus Na has electronegativity 0.9, while Cl has 3.0. Since the difference is (3.0 – 0.9) = 2.1, Na and Cl will form an ionic bond.

FACTORS GOVERNING THE FORMATION OF IONIC BOND

(1) Ionisation Energy

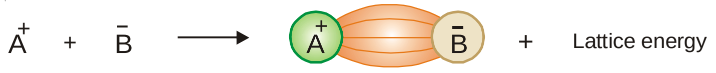
The ionisation energy of the metal atom which looses electron(s) should be low so that the formation of +vely charged ion is easier. *Lower the ionisation energy greater will be the tendency of the metal atom of change into cation and hence greater will be the ease of formation of ionic bond*. That is why *alkali metals and alkaline earth metals form ionic bonds easily*. Out of these two, alkali metals form ionic bonds easily as compared to alkaline earth metals. *In a group the ionisation energy decreases as we move down the group and therefore, the tendency to form ionic bond increases in a group downward*. Due to this reason Cs is the most electropositive atom among the alkali metals.

(2) Electron Affinity

The atom which accepts the electron and changes into anion should have high electron affinity. *Higher the electron affinity more is the energy released and stable will be the anion formed*. The elements of group VI A and VII A have, in general, higher electron affinity and have high tendency to form ionic bonds. Out of these two, *the elements of group* VII A (*halogens*) *are more prone to the formation of ionic bond than the elements of group* VI A. In moving down a group the electron affinity decreases and, therefore, the tendency to form ionic bond also decreases.

(3) Lattice Energy

After the formation of cations and anions separately, they combine to form ionic compound.



In this process, energy is released. It is called Lattice Energy. It may be defined as "*the amount of energy released when one mole of an ionic compound is formed from its cations and anions.*"

Greater the lattice energy, greater the strength of ionic bond. The value of lattice energy depends upon the following two factors :

(*a*) Size of the ions

In order to have the greater force of attraction between the cations and anions their size should be small as the force of attraction is inversely proportional to the square of the distance between them.

(*b*) Charge on Ions

Greater the charge on ions greater will be the force of attraction between them and, therefore, greater will be the strength of the ionic bond.

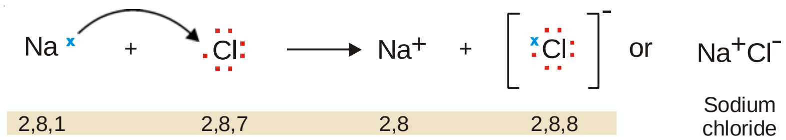
Necessary for the formation of an ionic bond between atoms *A* and *B*. Thus Na has electronegativity 0.9, while Cl has 3.0. Since the difference is (3.0 – 0.9) = 2.1, Na and Cl will form an ionic bond.

SOME EXAMPLES OF IONIC COMPOUNDS

Here we will discuss the formation of **Lewis formula** or **Electron dot formula** of some binary ionic compounds, for illustration.

Sodium Chloride, NaCl

A simple sodium chloride molecule is formed from an atom of sodium (Na) and one atom of chlorine (Cl). Na (2, 8, 1) has one valence electron, while Cl (2, 8, 7) has seven. Na transfers its valence electron to Cl, and both achieve stable electron octet. Thus Na gives Na^+ and Cl gives Cl^- ion, and the two are joined by an ionic bond.



Ionic Compounds Exist as Crystals. The (+) and (–) ions attract each other with electrostatic force that extends in all directions. This means that ions will be bonded to a number of oppositely charged ions around them. Therefore in solid state, single ionic molecules do not exist as such. Rather many (+) and (–) ions are arranged systematically in an alternating cation-anion pattern called the crystal lattice. The crystal lattice of NaCl is shown in Fig. 5.2. It will be noticed that here a large number of Na^+ and Cl^- ions are arranged in an orderly fashion so as to form a cubic crystal. Each Na^+ ion is surrounded by 6 Cl^- ions and each Cl^- ion is surrounded by 6 Na^+ ions. This makes a network of Na^+ and Cl^- ions which are tightly held together by electrostatic forces between them.

Although discrete molecules Na^+Cl^- do not exist in the solid form of ionic compounds, independent molecules do exist in the vapour form of such compounds.

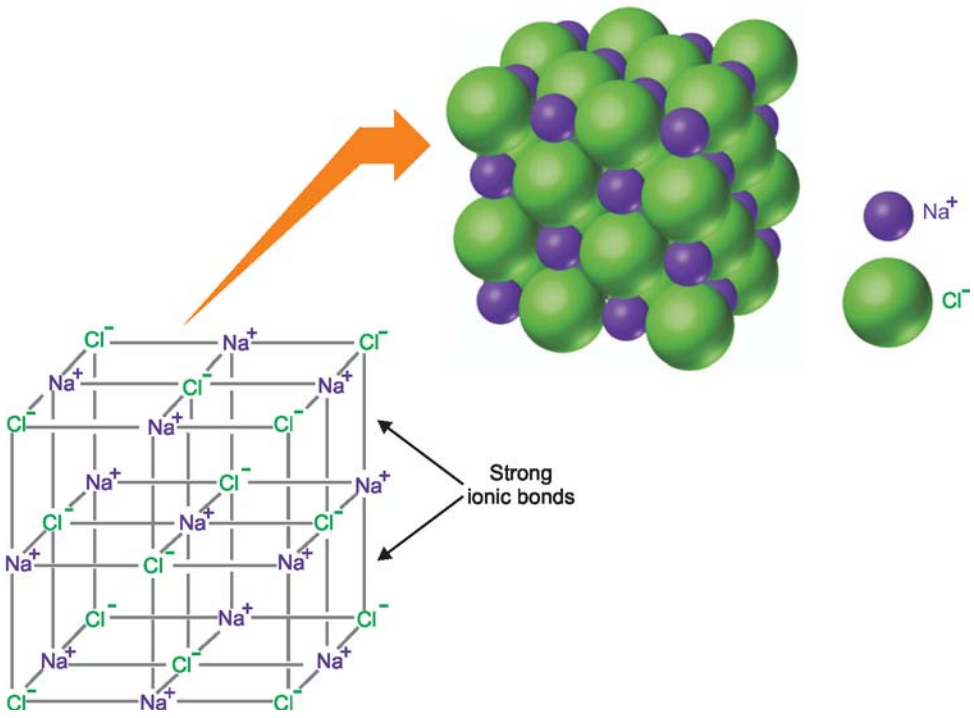
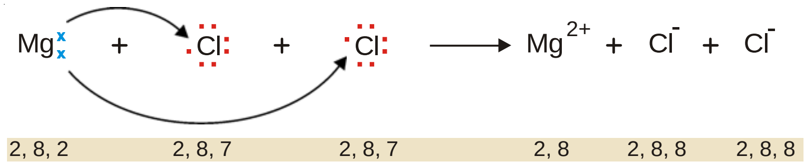


Figure 5.2
Ionic crystal of Sodium Chloride.

Magnesium Chloride, $Mg^{2+}Cl_2^{1-}$ ($MgCl_2$)

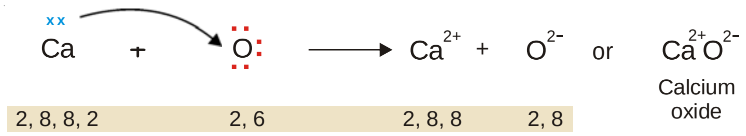
Magnesium (Mg) has two valence electrons, while chlorine (Cl) has seven. The magnesium atom transfers its two electrons, one to each chlorine atom, and thus all the three atoms achieve the stable octet. In this way Mg atom gives Mg^{2+} ion and the two Cl atoms give $2Cl^{1-}$, forming $Mg^{2+}\ Cl_2^{1-}$ (or $MgCl_2$).



$$\text{or} \quad Mg + 2Cl \longrightarrow Mg^{2+} + 2Cl^- \quad \text{or} \quad Mg^{2+}Cl_2^{1-}$$

Calcium Oxide, $Ca^{2+}O^{2-}$ (CaO)

Calcium (Ca) has two valence electrons, while oxygen (O) has six. Calcium atom transfers its two valence electrons to the same oxygen atom. Thus both Ca and O achieve the stable electron-octet, forming Ca^{2+} and O^{2-} ions. Thus is obtained the molecule of calcium oxide, $Ca^{2+}O^{2-}$.

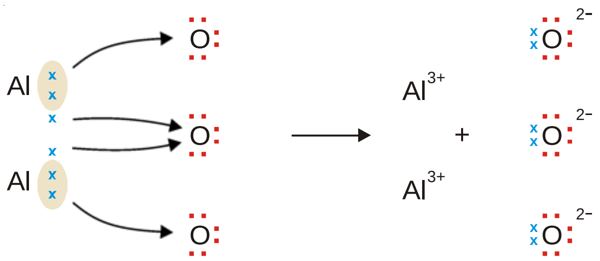


Aluminium Oxide, $Al_2^{3+}O_3^{2-}$ (Al_2O_3)

Here the aluminium atom (Al) has three electrons in the valence shell (2, 8, 3), while oxygen has six (2, 6). Two atoms of aluminium transfer their six electrons to three oxygen atoms. Thus are the electron-octets of the two Al atoms and three O atoms achieved. The two Al atoms deprived of three electrons each, give $2Al^{3+}$ ions, while the three O atoms having gained two electrons each give $3O^{2-}$ ions. In this way, we get $Al_2^{3+}O_3^{2-}$ or Al_2O_3.

CHARACTERISTICS OF IONIC COMPOUNDS

The ionic compounds are made of (+) and (–) ions held by electrostatic forces in a crystal lattice. Each ion is surrounded by the opposite ions in alternate positions in a definite order in all directions. This explains the common properties of ionic compounds.



or $2Al + 3O \longrightarrow 2Al^{3+} + 3O^{2-}$ or $2Al_2^{3+}O_3^{2-}$
Aluminium oxide

(1) Solids at Room Temperature

On account of strong electrostatic forces between the opposite ions, these ions are locked in their allotted positions in the crystal lattice. Since they lack the freedom of movement characteristic of the liquid state, they are solids at room temperature.

(2) High Melting Points

Ionic compounds have high melting points (or boiling points). Since the (+) and (–) ions are tightly held in their positions in the lattice, only at high temperature do the ions acquire sufficient kinetic energy to overcome their attractive forces and attain the freedom of movement as in a liquid. Thus ionic compounds need heating to high temperatures before melting.

(3) Hard and brittle

The crystals of ionic substances are hard and brittle. Their hardness is due to the strong electrostatic forces which hold each ion in its allotted position.

These crystals are made of layers of (+) and (–) ions in alternate positions so that the opposite ions in the various parallel layers lie over each other. When external force is applied to a layer of ions (Fig. 5.3), with respect to the next, even a slight shift brings the like ions in front of each other. The (+) and (–) ions in the two layers thus repel each other and fall apart. The crystal cleaves here.

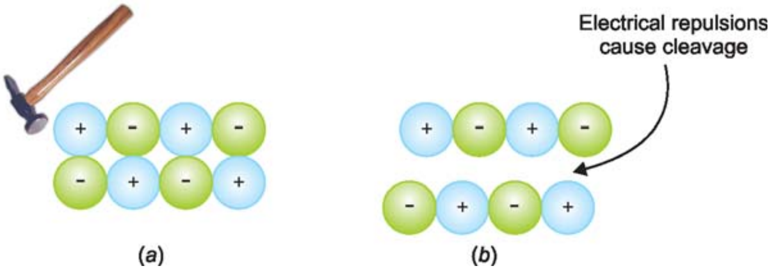


Figure 5.3
(*a*) Two layers of (+) and (–) ions in a crystal. (*b*) When force is applied to one layer it slips over the other so that similar ions come above one another and electrical repulsions between them cause cleavage of the crystal.

(4) Soluble in water

When a crystal of an ionic substance is placed in water, the polar water molecules detach the (+) and (–) ions from the crystal lattice by their electrostatic pull. These ions then get surrounded by water molecules and can lead an independent existence and are thus dissolved in water. By the same reason, non-polar solvents like benzene (C_6H_6) and hexane (C_6H_{14}) will not dissolve ionic compounds.

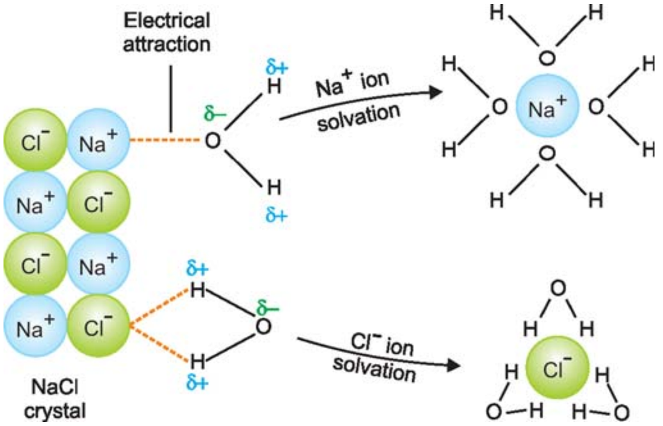


Figure 5.4
Solvation of NaCl in water.

(5) Conductors of electricity

Solid ionic compounds are poor conductors of electricity because the ions are fixed rigidly in their positions. In the molten state and in water solutions, ions are rendered free to move about. Thus molten ionic compounds or their aqueous solutions conduct a current when placed in an electrolytic cell.

(6) Do not exhibit isomerism

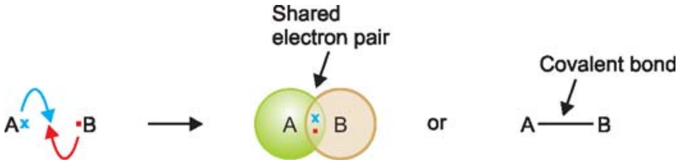
The ionic bond involving electrostatic lines of force between opposite ions, is non-rigid and non-directional. The ionic compounds, therefore, are incapable of exhibiting stereoisomerism.

(7) Ionic reactions are fast

Ionic compounds give reactions between ions and these are very fast.

COVALENT BOND

The electron transfer theory could not explain the bonding in molecules such as H_2, O_2, Cl_2 etc., and in organic molecules, that had no ions. It was G.N. Lewis who suggested that two atoms could achieve stable 2 or 8 electrons in the outer shell by sharing electrons between them. Let us consider a general case where an atom *A* has one valence electron and another atom *B* has seven valence electrons. As they approach each other, each atom contributes one electron and the resulting electron pair fills the outer shell of both the atoms. Thus *A* acquires stable 2 electrons and *B*, 8 electrons in the outer shell.



The shared pair is indicated by a dash (–) between the two bonded atoms. A shared pair of electrons constitutes a **Covalent bond** or **Electron-pair bond.**

In fact, the positive nuclei of atoms *A* and *B* are pulled towards each other by the attraction of the shared electron pair. At the same time, the nuclei of two atoms also repel each other as do the two electrons. It is the net attractive force between the shared electrons and the nuclei that holds the atoms together. Thus an alternative definition of a covalent bond would be :

The attractive force between atoms created by sharing of an electron-pair.

The compounds containing a covalent bond are called **covalent compounds.**

CONDITIONS FOR FORMATION OF COVALENT BOND

The conditions favourable for the formation of covalent bonds are :

(1) Number of valence electrons

Each of the atoms *A* and *B* should have 5, 6 or 7 valence electrons so that both achieve the stable octet by sharing 3, 2 or 1 electron-pair. H has one electron in the valence shell and attains duplet. The non-metals of groups VA, VIA and VIIA respectively satisfy this condition.

(2) Equal electronegativity

The atom *A* will not transfer electrons to *B* if both have equal electronegativity, and hence electron sharing will take place. This can be strictly possible only if both the atoms are of the same element.

(3) Equal sharing of electrons

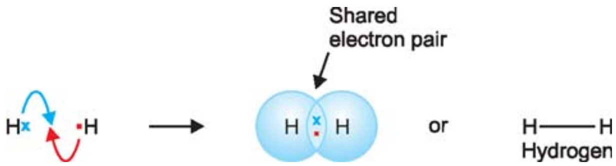
The atoms *A* and *B* should have equal (or nearly equal) electron affinity so that they attract the bonding electron pair equally. Thus equal sharing of electrons will form a nonpolar covalent bond. Of course, precisely equal sharing of electrons will not ordinarily occur except when atoms *A* and *B* are atoms of the same element, for no two elements have exactly the same electron affinity.

SOME EXAMPLES OF COVALENT COMPOUNDS

The construction of Lewis structures of simple covalent compounds will be discussed.

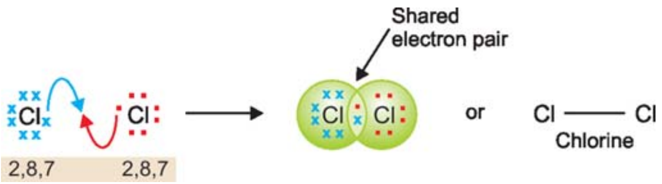
Hydrogen, H_2

Hydrogen molecule is made of two H atoms, each having one valence electron. Each contributes an electron to the shared pair and both atoms acquire stable helium configuration. Thus stable H_2 molecule results.



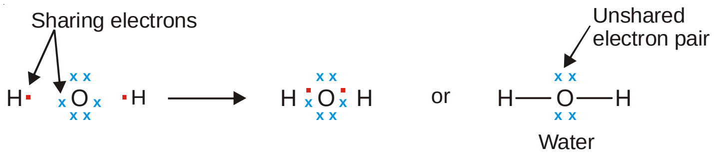
Chlorine, Cl_2

Each Cl atom (2, 8, 7) has seven valence electrons. The two Cl atoms achieve a stable electron octet by sharing a pair of electrons.



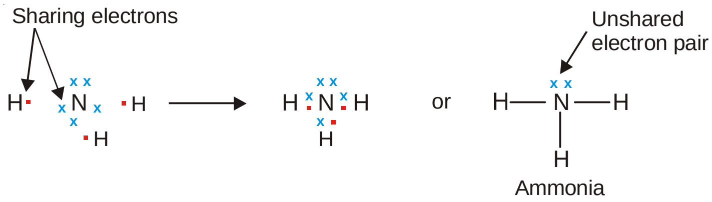
Water, H_2O

Oxygen atom (2, 6) has six valence electrons and can achieve the stable octet by sharing two electrons, one with each H atom. Thus Lewis structure of water can be written as :



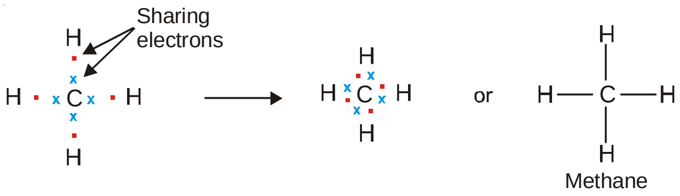
Ammonia, NH_3

Nitrogen atom (2, 5) has five valence electrons and can achieve the octet by sharing three electrons, one each with three H atoms. This gives the following Lewis structure for ammonia :



Methane, CH_4

Carbon atom (2, 4) has four electrons in the valence shell. It can achieve the stable octet by sharing these electrons with four H atoms, one with each H atom. Thus the Lewis structure of methane can be written as :

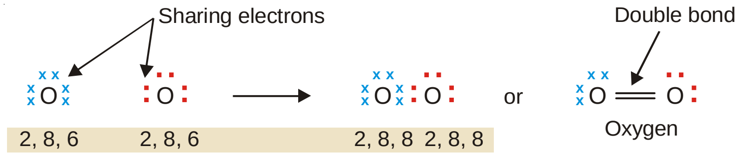


EXAMPLES OF MULTIPLE COVALENT COMPOUNDS

In many molecules, we find that in order to satisfy the octet, it becomes necessary for two atoms to share two or three pairs of electrons between the same two atoms. The sharing of two pairs of electrons is known as a **Double bond** and the sharing of three pairs of electrons a **Triple bond.** Let us consider some examples of compounds containing these multiple covalent bonds in their molecules.

Oxygen, O_2

The conventional Lewis structure of oxygen is written by sharing of two pairs of electrons between two O atoms (2, 6). In this way both the O atoms achieve the octet.

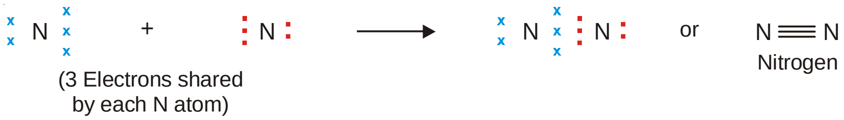


The above structure of oxygen implies that all the electrons in oxygen, O_2, are paired whereby the molecule should be diamagnetic. However, experiment shows that O_2 is paramagnetic with two unpaired electrons. This could be explained by the structure.

Although writing Lewis structures work very well in explaining the bonding in most simple molecules, it should be kept in mind that it is simply the representation of a theory. In this case, the theory just doesn't work.

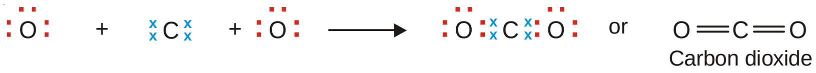
Nitrogen, N_2

The two atoms of nitrogen (2, 5), each having five electrons in the valence shell, achieve the octet by sharing three electron pairs between them.



Carbon Dioxide, CO_2

Carbon (2, 4) has four valence electrons. It shares two electrons with each O atom (having six valence electrons). Thus the C atom and both the O atoms achieve their octet.



CHARACTERISTICS OF COVALENT COMPOUNDS

While the atoms in a covalent molecule are firmly held by the shared electron pair, the individual molecules are attracted to each other by weak van der Waals forces. Thus the molecules can be separated easily as not much energy is required to overcome the intermolecular attractions. This explains the general properties of covalent compounds.

(1) Gases, liquids or solids at room temperature

The covalent compounds are often gases, liquids or relatively soft solids under ordinary conditions. This is so because of the weak intermolecular forces between the molecules.

(2) Low melting points and boiling points

Covalent compounds have generally low melting points (or boiling points). The molecules are held together in the solid crystal lattice by weak forces. On application of heat, the molecules are readily pulled out and these then acquire kinetic energy for free movement as in a liquid. For the same reason, the liquid molecules are easily obtained in the gaseous form which explains low boiling points of covalent liquids.

(3) Neither hard nor brittle

While the ionic compounds are hard and brittle, covalent compounds are neither hard nor brittle. There are weak forces holding the molecules in the solid crystal lattice. A molecular layer in the crystal easily slips relative to other adjacent layers and there are no 'forces of repulsion' like those in ionic compounds. Thus the crystals are easily broken and there is no sharp cleavage between the layers on application of external force.

(4) Soluble in organic solvents

In general, covalent compounds dissolve readily in nonpolar organic solvents (benzene, ether). The kinetic energy of the solvent molecules easily overcomes the weak intermolecular forces.

Covalent compounds are insoluble in water. Some of them (alcohols, amines) dissolve in water due to hydrogen-bonding.

(5) Non-conductors of electricity

Since there are no (+) or (–) ions in covalent molecules, the covalent compounds in the molten or solution form are incapable of conducting electricity.

(6) Exhibit Isomerism

Covalent bonds are rigid and directional, the atoms being held together by shared electron pair and not by electrical lines of force. This affords opportunity for various spatial arrangements and covalent compounds exhibit stereoisomerism.

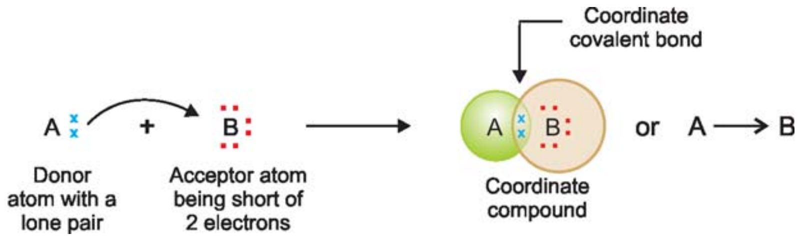
(7) Molecular reactions

The covalent compounds give reactions where the molecule as a whole undergoes a change. Since there are no strong electrical forces to speed up the reaction between molecules, these reactions are slow.

CO-ORDINATE COVALENT BOND

In a normal covalent bond, each of the two bonded atoms contributes one electron to make the shared pair. In some cases, a covalent bond is formed when both the electrons are supplied entirely by one atom. Such a bond is called **co-ordinate covalent** or **dative bond.** It may be defined as : **a covalent bond in which both electrons of the shared pair come from one of the two atoms (or ions).** The compounds containing a coordinate bond are called **coordinate compounds.**

If an atom *A* has an unshared pair of electrons (**lone pair**) and another atom *B* is short of two electrons than the stable number, coordinate bond is formed. *A* donates the lone pair to *B* which accepts it. Thus both *A* and *B* achieve the stable 2 or 8 electrons, the lone pair being held in common.



The atom *A* which donates the lone pair is called the **donor,** while *B* which accepts it the **acceptor.** The bond thus established is indicated by an arrow pointing from *A* to *B*. Although the arrow head indicates the origin of the electrons, once the coordinate bond is formed it is in no way different from an ordinary covalent bond.

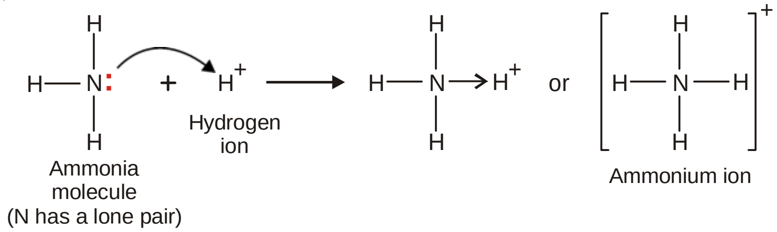
The molecule or ion that contains the donor atom is called the ligand.

SOME EXAMPLES OF COORDINATE COMPOUNDS OR IONS

Lewis structures of some common molecules or ions containing a coordinate covalent bond are listed below.

Ammonium ion, NH_4^+

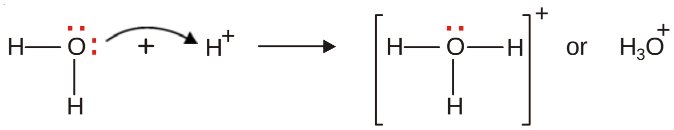
In ammonia molecule, the central N atom is linked to three H atoms and yet N has an unshared pair of electrons. The H^+ ion furnished by an acid has no electron to contribute and can accept a pair of electrons loaned by N atom. Thus, NH_3 donates its unshared electrons to H^+ forming ammonium ion.



All the N–H bonds in NH_4^+ are identical, once the coordinate bond $N \rightarrow H^+$ is established.

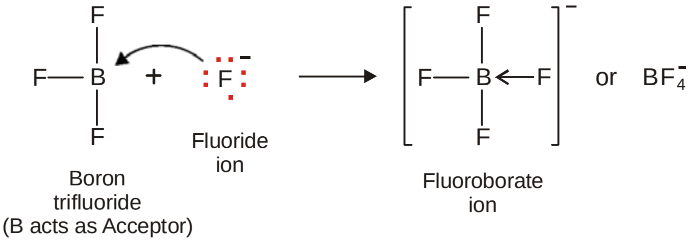
Hydronium ion, H_3O^+

The oxygen atom in water molecule is attached to two H atoms by two covalent bonds. There are still two unshared pairs of electrons with the O atom. The O atom donates one of these pairs of electrons to H^+ ion and the hydronium ion is thus formed.



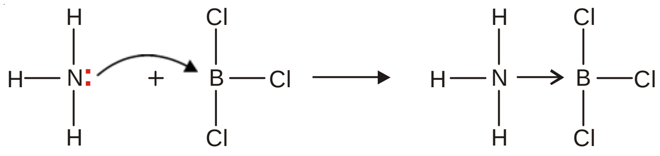
Fluoroborate ion, BF_4^-

It is formed when a boron trifluoride molecule (BF_3) shares a pair of electrons supplied by fluoride ion (F^-).



Addition compound of NH_3 with BCl_3

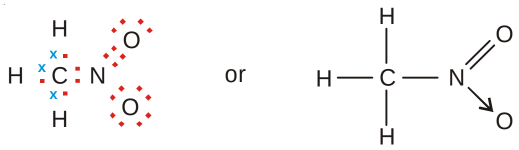
The N atom of ammonia molecule (NH_3) has lone pair while B atom in boron trichloride (BCl_3) is short of two electrons than stable octet. An addition compound is formed as the N atom donates its lone pair to B atom of BCl_3.



(N is Donor) (B is Acceptor) Addition compound

Nitromethane, CH_3NO_2

The Lewis structure of nitromethane is shown below. Here the N atom has five valence electrons, three of which are used in forming a covalent bond with C atom and two covalent bonds with O atom. The N atom is still left with two unshared electrons which are donated to another O atom.

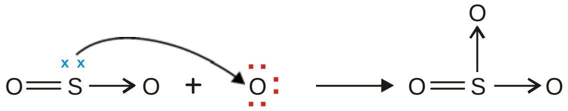


Nitromethane

Sulphur dioxide, SO_2, and Sulphur trioxide, SO_3

Sulphur achieves its octet by forming two covalent bonds with one O atom, giving SO. The S atom in SO has two lone pairs, one of which is shared with a second O atom to form sulphur dioxide, SO_2. The S atom in SO_2 still has one lone pair which it donates to a third O atom forming the sulphur trioxide (SO_3) molecule.

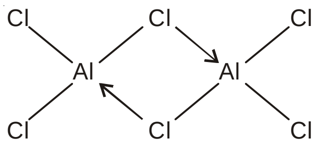
Sulphur dioxide



Sulphur trioxide

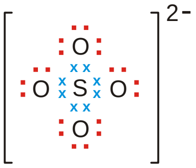
Aluminium Chloride, Al_2Cl_6

Aluminium atom has three valence electrons which it shares with three Cl atoms, forming three covalent bonds. Thus the Al atom acquires six electrons in its outer shell. Now Cl atom has three lone pairs, one of which is donated to the Al atom of another molecule $AlCl_3$. Thus both Al atoms achieve octet and stable Al_2Cl_6 results.



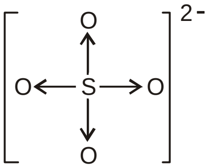
Sulphate ion, SO_4^{2-}

Sulphur has six valence electrons (2, 8, 6) and achieves the octet by gaining two electrons from metal atoms (say two Na atoms). The four pairs of electrons around the S atom are then donated to four oxygen atoms each of which has six electrons. Thus the Lewis structure for SO_4^{2-} ion may be written as :



S gains two electrons from metal atoms and completes octet

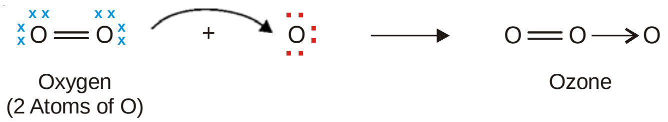
or



Sulphate ion

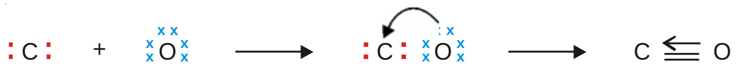
Ozone, O_3

Oxygen molecule is made of two oxygen atoms joined by two covalent bonds. Each O atom in O_2 has two unshared pairs of electrons. When one pair of these is donated to a third O atom which has only six electrons, a coordinate bond is formed. Thus the Lewis structure of ozone may be represented as :



Carbon Monoxide, CO

Carbon atom has four valence electrons while oxygen atom has six. By forming two covalent bonds between them, O atom achieves octet but C atom has only six electrons. Therefore O donates an unshared pair of electron to C, and a coordinate covalent bond is established between the two atoms. Lewis structure of CO may be written as :

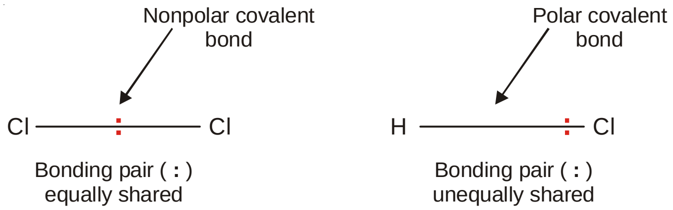


COMPARISON OF IONIC AND COVALENT BONDS

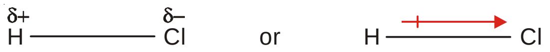
Ionic Bond	Covalent Bond
1. Formed by transfer of electrons from a metal to a non-metal atom.	**1.** Formed by sharing of electrons between nonmetal atoms.
2. Consists of electrostatic force between (+) and (–) ions.	**2.** Consists of a shared pair of electrons between atoms.
3. Non-rigid and non-directional; cannot cause isomerism.	**3.** Rigid and directional : causes stereoisomerism.
Properties of Compounds	**Properties of Compounds**
1. Solids at room temperature.	**1.** Gases, liquids or soft solids.
2. High melting and boiling points.	**2.** Low melting and boiling points.
3. Hard and brittle.	**3.** Soft, much readily broken
4. Soluble in water but insoluble in organic solvents.	**4.** Insoluble in water but soluble in organic solvents.
5. Conductors of electricity	**5.** Non-conductors of electricity.
6. Undergo ionic reactions which are fast.	**6.** Undergo molecular reactions which are slow.

POLAR COVALENT BONDS

In the H_2 or Cl_2 molecule, the two electrons constituting the covalent bond are equally shared by the two identical nuclei. Due to even distribution of (+) and (–) charge, the two bonded atoms remain electrically neutral. Such a bond is called **nonpolar covalent bond.** However, when two different atoms are joined by a covalent bond as in HCl, the electron pair is not shared equally.



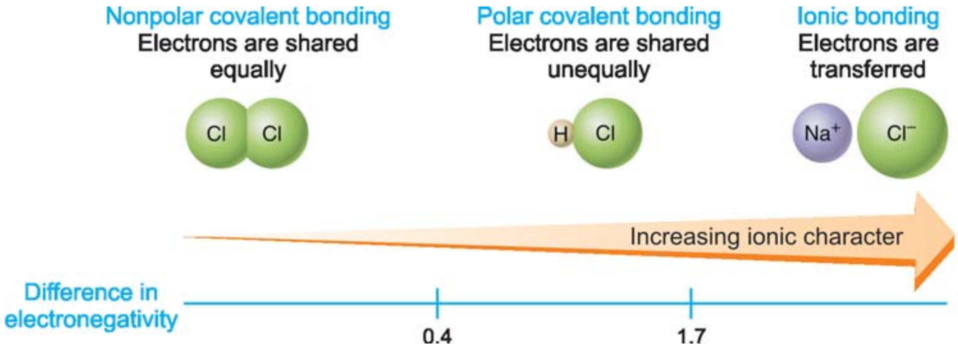
Due to a greater attraction of one nucleus (Cl) for the electrons, the shared pair is displaced towards it. This makes one end of the bond partially positive (δ+) and the other partially negative (δ–).



A covalent bond in which electrons are shared unequally and the bonded atoms acquire a partial positive and negative charge, is called a polar covalent bond.

A molecule having partial positive and negative charge separated by a distance is commonly referred to as a **Dipole** (*two poles*). The dipole of a bond is indicated by an arrow from positive to negative end with a crossed tail as shown above in HCl molecule.

Since two atoms of different elements do not have exactly the same attraction for electrons in a bond, all bonds between unlike atoms are polar to some extent. The amount of polarity of a bond is determined by the difference of electronegativity (or tendency to attract electrons) of the two bonded atoms. **The greater the difference of electronegativity between two atoms, greater the polarity.** A graph showing the % age ionic character and difference in electronegativity between the two atoms is shown in Fig. 5.5.



As a matter of fact, if this difference is around 1.9 and 2.9, the bond is generally ionic, meaning that one atom has gained complete control of the electron pair in the bond.

The percentage ionic character of a bond can be calculated by using the equation

$$\%\text{age ionic character} = 16\,[X_A - X_B] + 3.5\,[X_A - X_B]^2$$

This equation was given by Hannay and Smith.

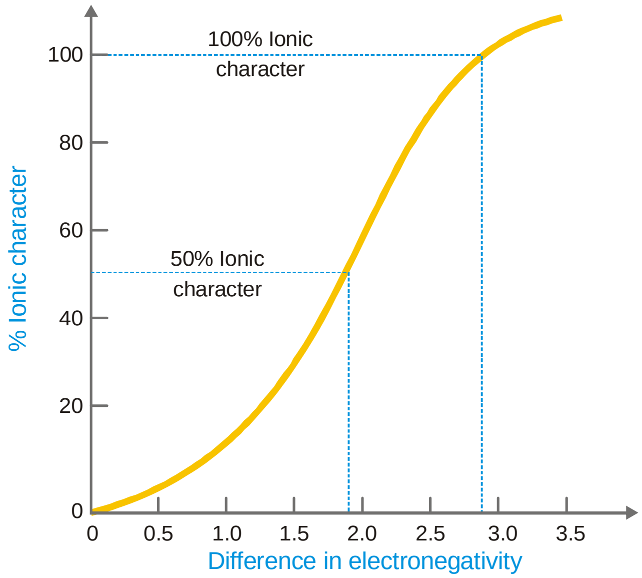


Figure 5.5
Graph between % ionic character and difference in electronegativity.

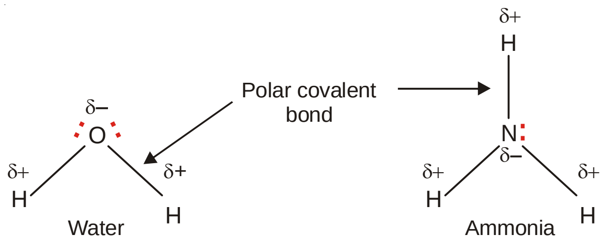
SOLVED PROBLEM. Calculate the percentage ionic character of C–Cl bond in CCl_4 if the electronegativities of C and Cl are 3.5 and 3.0 respectively.

SOLUTION

$$
\begin{aligned}
\text{\%age ionic character} &= 16\,[X_A - X_B] + 3.5\,[X_A + X_B]^2 \\
\text{Give } X_A = 3.5 \text{ and } X_B &= 3.0 \\
\therefore \quad \text{\%age ionic character} &= 16\,(3.5 - 3.0) + 3.5\,(3.5 - 3.0)^2 \\
&= 8.0 + 0.875 \\
&= \mathbf{8.875\%}
\end{aligned}
$$

Examples of Polar Covalent Bonds

Water molecule (H_2O) contains two O–H covalent bonds. The electronegativity of O is 3.5 and that of H is 2.1. Thus both the bonds are polar and water has a polar molecule.

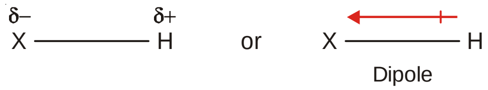


In ammonia molecule, there are three N–H bonds. The electronegativity of N is 3.0 and that of H is 2.1. Therefore all the N–H bonds are polar and ammonia has a polar molecule.

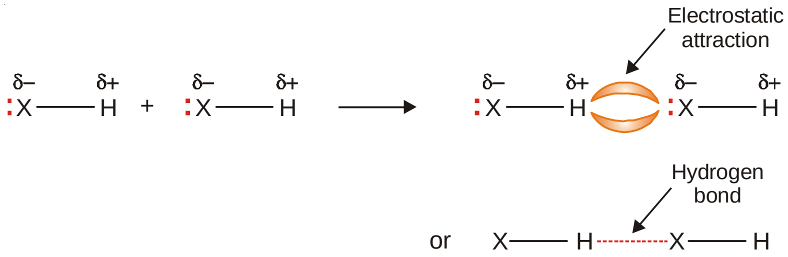
The electronegativity of fluorine (F) is 4.0 and that of H is 2.1. The difference of electronegativities being very great, the molecule H–F has a strong dipole.

HYDROGEN BONDING (H-Bonding)

When hydrogen (H) is covalently bonded to a highly electronegative atom X (O, N, F), the shared electron pair is pulled so close to X that a strong dipole results.



Since the shared pair is removed farthest from H atom, its nucleus (the proton) is practically exposed. The H atom at the positive end of a polar bond nearly stripped of its surrounding electrons, exerts a strong electrostatic attraction on the lone pair of electrons around X in a nearby molecule. Thus :



The electrostatic attraction between an H atom covalently bonded to a highly electronegative atom X and a lone pair of electrons of X in another molecule, is called Hydrogen Bonding. Hydrogen bond is represented by a dashed or dotted line.

POINTS TO REMEMBER

(1) Only O, N and F which have very high electronegativity and small atomic size, are capable of forming hydrogen bonds.

(2) Hydrogen bond is longer and much weaker than a normal covalent bond. Hydrogen bond energy is less than 10 kcal/mole, while that of covalent bond is about 120 kcal/mole.

(3) Hydrogen bonding results in long chains or clusters of a large number of ‘associated’ molecules like many tiny magnets.

(4) **Like a covalent bond, hydrogen bond has a preferred bonding direction.** This is attributed to the fact that hydrogen bonding occurs through *p* orbitals which contain the lone pair of electrons on X atom. This implies that the atoms X–H···X will be in a straight line.

CONDITIONS FOR HYDROGEN BONDING

The necessary conditions for the formation of hydrogen bonding are

(1) High electronegativity of atom bonded to hydrogen

The molecule must contain an atom of high electronegativity such as F, O or N bonded to hydrogen atom by a covalent bond. The examples are HF, H_2O and NH_3.

(2) Small size of Electronegative atom

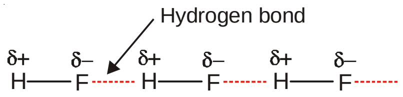
The electronegative atom attached to H-atom by a covalent bond should be quite small. Smaller the size of the atom, greater will be the attraction for the bonded electron pair. In other words, the polarity of the bond between H atom and electronegative atom should be high. This results in the formation of stronger hydrogen bonding. For example, N and Cl both have 3.0 electronegativity. But hydrogen bonding is effective in NH_3 in comparison to that in HCl. It is due to smaller size of N atom than Cl atom.

EXAMPLES OF HYDROGEN-BONDED COMPOUNDS

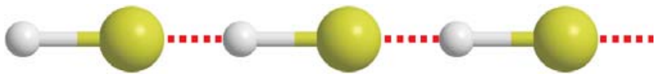
When hydrogen bonding occurs between different molecules of the same compound as in HF, H_2O and NH_3, it is called **Intermolecular hydrogen bonding.** If the hydrogen bonding takes place within single molecule as in 2-nitrophenol, it is referred to as **Intramolecular hydrogen bonding.** We will consider examples of both types.

Hydrogen Fluoride, HF

The molecule of HF contains the strongest polar bond, the electronegativity of F being the highest of all elements. Therefore, hydrogen fluoride crystals contain infinitely long chains of H–F molecules in which H is covalently bonded to one F and hydrogen bonded to another F. The chains possess a zig-zag structure which occurs through *p* orbitals containing the lone electron pair on F atom.

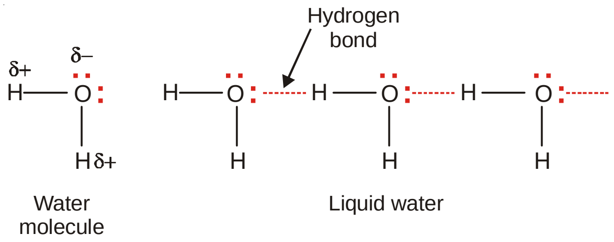


Hydrogen fluoride molecules



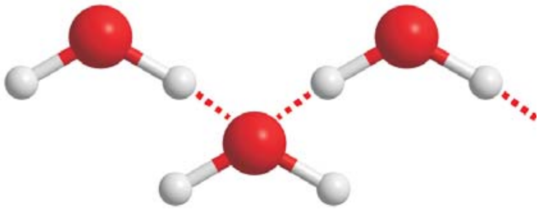
Water, H_2O

In H_2O molecule, two hydrogen atoms are covalently bonded to the highly electronegative O atom. Here each H atom can hydrogen bond to the O atom of another molecule, thus forming large chains or clusters of water molecules.



Water molecule

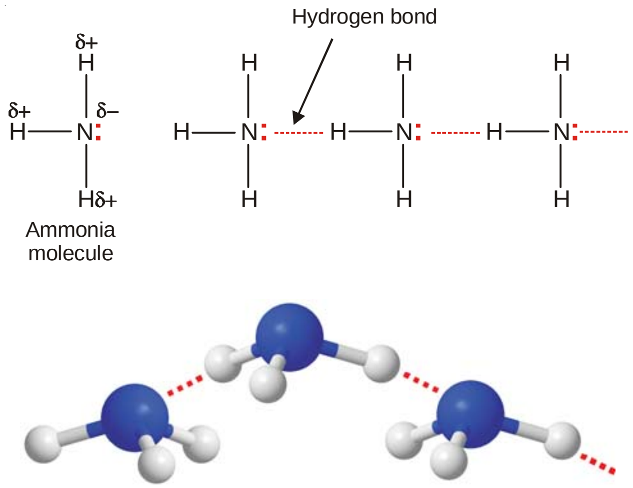
Liquid water



Each O atom still has an unshared electron pair which leads to hydrogen bonding with other water molecules. Thus liquid water, in fact, is made of clusters of a large number of molecules.

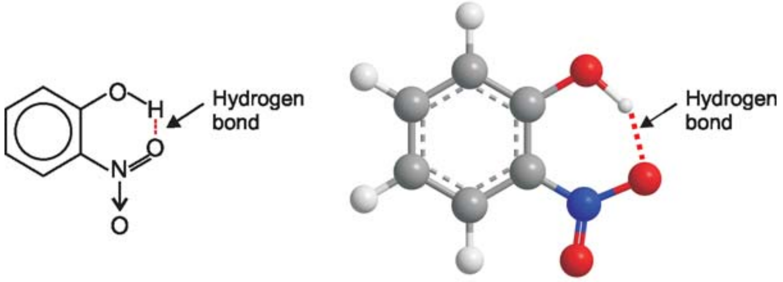
Ammonia, NH_3

In NH_3 molecules, there are three H atoms covalently bonded to the highly electronegative N atom. Each H atom can hydrogen bond to N atom of other molecules.



2-Nitrophenol

Here hydrogen bonding takes place within the molecule itself as O–H and N–H bonds are a part of the same one molecule.



TYPES OF HYDROGEN-BONDING

Hydrogen bonding is of two types :

(1) **Intermolecular Hydrogen bonding**

This type of hydrogen bonding is formed between two different molecules of the same or different substances *e.g.* hydrogen bonding in HF, H_2O, NH_3 etc. It is shown in the following diagram (Fig. 5.6).

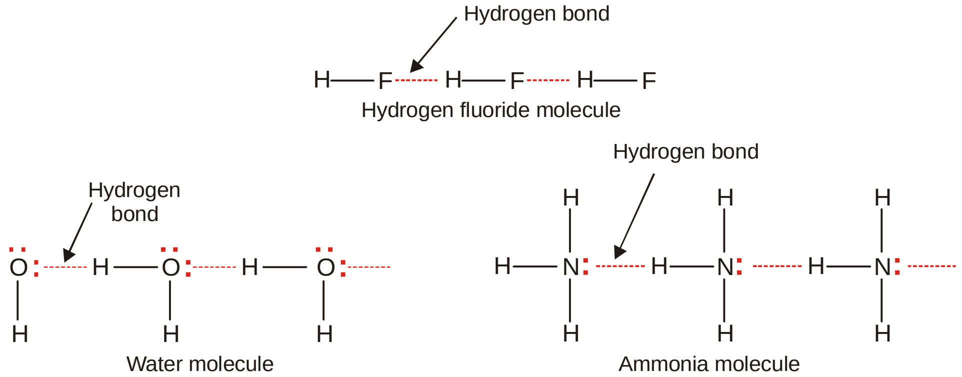


Figure 5.6
Intermolecular hydrogen bonding in HF, H_2O and NH_3.

This type of hydrogen bonding results in the formation of associated molecules. Generally speaking, the substances with intermolecular hydrogen bonding have high melting points, boiling points, viscosity, surface tension etc.

(2) Intramolecular Hydrogen bonding

This type of hydrogen bonding is formed between the hydrogen atom and the electronegative atom present within the same molecule. It results in the cyclisation of the molecule. Molecules exist as discrete units and not in associated form. Hence intramolecular hydrogen bonding has no effect on physical properties like melting point, boiling point, viscosity, surface tension, solubility etc. For example intramolecular hydrogen bonding exists in *o*-nitrophenol, 2-nitrobenzoic acid etc. as shown below :

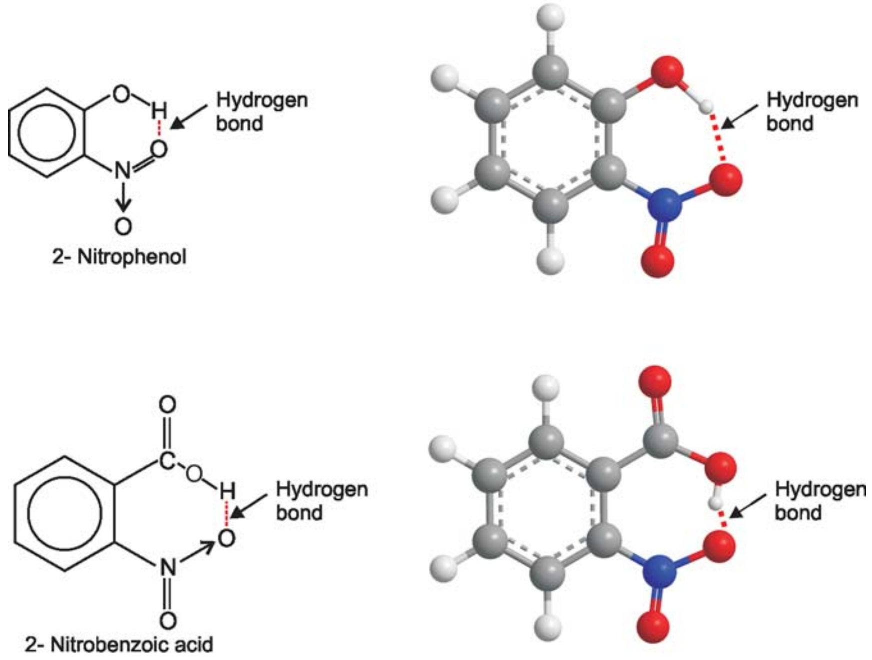


Figure 5.7
Intramolecular hydrogen bonding.

CHARACTERISTICS OF HYDROGEN-BONDED COMPOUNDS

(1) Abnormally high boiling and melting points

The compounds in which molecules are joined to one another by hydrogen bonds, have unusually high boiling and melting points. This is because here relatively more energy is required to separate the molecules as they enter the gaseous state or the liquid state. Thus the hydrides of fluorine (HF), oxygen (H_2O) and nitrogen (NH_3) have abnormally high boiling and melting points compared to other hydrides of the same group which form no hydrogen bonds. In Fig. 5.8 are shown the boiling points and melting points of the hydrides of VIA group elements plotted against molecular weights.

It will be noticed that there is a trend of decrease of boiling and melting points with decrease of molecular weight from H_2Te to H_2S. But there is a sharp increase in case of water (H_2O), although it has the smallest molecular weight. The reason is that the molecules of water are 'associated' by hydrogen bonds between them, while H_2Te, H_2Se and H_2S exist as single molecules since they are incapable of forming hydrogen bonds.

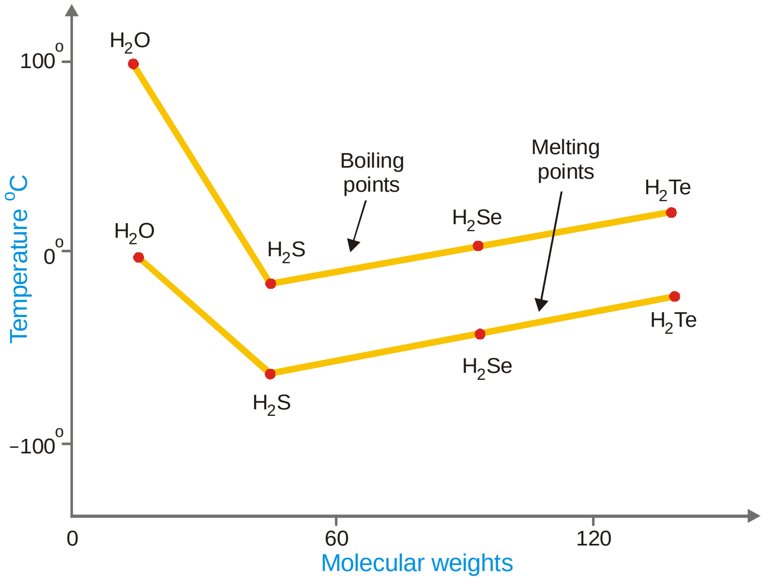
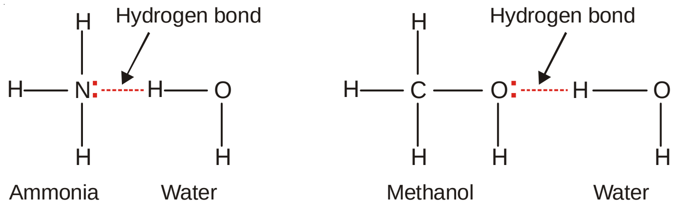


Figure 5.8

Boiling and melting point curves of the hydrides of VIA group showing abrupt increase for water (H_2O) although it has the lowest molecular weight.

(2) High solubilities of some covalent compounds

The unexpectedly high solubilities of some compounds containing O, N and F, such as NH_3 and CH_3OH in certain hydrogen containing solvents are due to hydrogen bonding. For example, ammonia (NH_3) and methanol (CH_3OH) are highly soluble in water as they form hydrogen bonds.



(3) Three dimensional crystal lattice

As already stated, **hydrogen bonds are directional and pretty strong to form three dimensional crystal lattice.** For example, in an ice crystal the water molecules (H_2O) are held together in a tetrahedral network and have the same crystal lattice as of diamond. This is so because the O atom in water has two covalent bonds and can form two hydrogen bonds. These are distributed in space like the four covalent bonds of carbon. The tetrahedral structural units are linked to other units through hydrogen bonds as shown in Fig. 5.6.

Since there is enough empty space in its open lattice structure ice is lighter than water, while most other solids are heavier than the liquid form.

Water as an Interesting Liquid

Water is very interesting solvent with unusual properties. It dissolves many ionic compounds and polar organic compounds. It has high heat of vaporisation, high heat of fusion, high specific heat with melting point 273 K and boiling point 373 K. Its structure as shown above is very interesting as it explains many properties :

(1) Ice (solid) is lighter than water (Liquid)

The structure of water is tetrahedral in nature. Each oxygen atom is linked to two H-atoms by covalent bonds and other two H-atoms by hydrogen bonding. In this solid state (Ice), this tetrahedral structure is packed resulting in open cage like structure with a number of vacant space. Hence in this structure the volume increases for a given mass of liquid water resulting in lesser density. Due to this reason ice floats on water.

(2) Maximum density of water at 277 K (4ºC)

On melting ice, the hydrogen bonds break and water molecules occupy the vacant spaces. This results in decrease in volume and increase in density ($d = m/v$). Hence density of water keeps on increasing when water is heated. This continues upto 277 K (4ºC). Above this temperature water molecules start moving away from one another due to increase in kinetic energy. Due to this volume increases again and density starts decreasing. This behaviour of water is shown in the fig. 5.9.

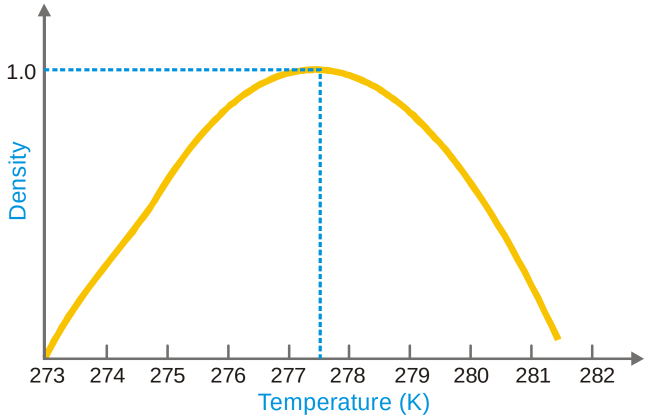


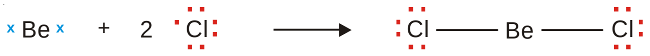
Figure 5.9
A plot of density versus temperature (water).

EXCEPTIONS TO THE OCTET RULE

For a time it was believed that all compounds obeyed the Octet rule or the Rule of eight. However, it gradually became apparent that **quite a few molecules had non-octet structures.** Atoms in these molecules could have number of electrons in the valence shell short of the octet or in excess of the octet. Some important examples are :

(1) Four or six electrons around the central atom

A stable molecule as of beryllium chloride, $BeCl_2$, contains an atom with four electrons in its outer shell.



(4 Electrons about Be)

The compound boron trifluoride, BF_3, has the Lewis structure :

(6 Electrons about B)

The boron atom has only six electrons in its outer shell.

Beryllium chloride and boron trifluoride are referred to as **electron-deficient compounds.**

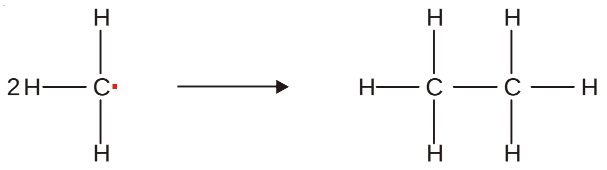
(2) Seven electrons around the central atom

There are a number of relatively stable compounds in which the central atom has seven electrons in the valence shell. A simple example is chlorine dioxide, ClO_2.

Chlorine dioxide

The chlorine atom in ClO_2 has seven electrons in its outer shell.

Methyl radical (CH_3) has an odd electron and is very short lived. When two methyl free radicals collide, they form an ethane molecule (C_2H_6) to satisfy the octet of each carbon atom. **Any species with an unpaired electron is called a free radical.**

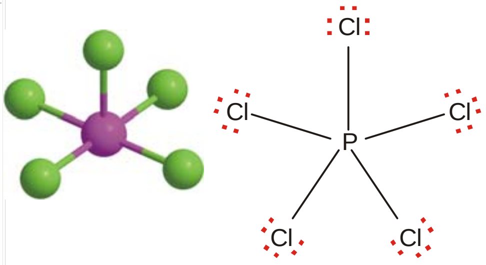


(C has 7 electrons)

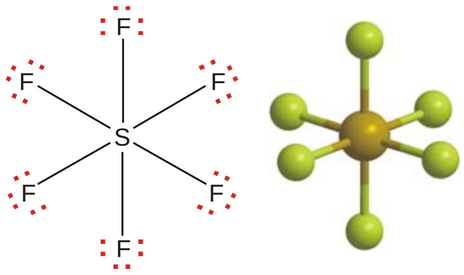
Ethane

(3) Ten or more electrons around the central atom

Non-metallic elements of the third and higher periods can react with electronegative elements to form structures in which the central atom has 10, 12 or even more electrons. The typical examples are PCl_5 and SF_6.



(10 Electrons about P)



(12 Electrons about S)

The molecules with more than an octet of electrons are called **superoctet structures.**

In elements C, N, O and F the octet rule is strictly obeyed because only four orbitals are available (one 2*s* and three 2*p*) for bonding. In the elements P and S, however, 3*s*, 3*p*, and 3*d* orbitals of their atoms may be involved in the covalent bonds they form. Whenever an atom in a molecule has more than eight electrons in its valence shell, it is said to have an **expanded octet.**

VARIABLE VALENCE

Some elements can display two or more valences in their compounds. The transition metals belong to this class of elements. The Electronic Structure of some of these metals is given below :

TABLE 5.2. ELECTRONIC STRUCTURE OF THE TWO OUTERMOST SHELLS OF SOME TRANSITION METALS

Sc	$3d^1 4s^2$	Ag	$4d^{10} 5s^1$
Cr	$3d^5 4s^1$	La	$5d^1 6s^2$
Mn	$3d^5 4s^2$	Os	$5d^6 6s^2$
Fe	$3d^6 4s^2$	Ir	$5d^7 6s^2$
Co	$3d^7 4s^2$	Pt	$5d^9 6s^2$
Cu	$3d^{10} 4s^1$	Au	$5d^{10} 6s^1$

Most of the transition metals have one or two outer-shell electrons and they form monovalent or bivalent positive ions. But because some of the *d* electrons are close in energy to the outermost electrons, these can also participate in chemical bond formation. Thus transition metals can form ions with variable valence. For example, copper can form Cu^{1+} and Cu^{2+} ions and iron can form Fe^{2+} and Fe^{3+} ions.

The complete electronic configuration of an iron atom is

$$Fe = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$$

It can form Fe^{2+} by losing two 4*s* electrons,

$$Fe^{2+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$$

When iron loses two 4*s* electrons and one of the three 3*d* electrons, if forms Fe^{3+} ion

$$Fe^{3+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$$

Copper form Cu^{1+} and Cu^{2+} ions by losing one 4*s* electron, and one 4*s* and 3*d* electron respectively

$$Cu = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$$

$$Cu^{1+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$$

$$Cu^{2+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$$

It may be noted that the structures of Fe^{2+}, Fe^{3+}, Cu^{1+}, Cu^{2+}, Cr^{3+}, etc., are not isoelectronic with any of the noble gases, and hence the *d* electrons being unstable are available for bond formation. (The atoms and ions that have the same number of electrons are said to be **Isoelectronic**).

METALLIC BONDING

The valence bonds that hold the atoms in a metal crystal together are not ionic, nor are they simply covalent in nature. Ionic bonding is obviously impossible here since all the atoms would tend to give electrons but none are willing to accept them. Ordinary covalent bonding is also ruled out as, for example, sodium atom with only one outer-shell electron could not be expected to form covalent bonds with 8 nearest neighbouring atoms in its crystal. **The peculiar type of bonding which holds the atoms together in metal crystal is called the Metallic Bonding.**

Many theories have been proposed to explain the metallic bonding. Here we will discuss the simplest of these : The Electron Sea Model.

THE ELECTRON SEA MODEL

Metal atoms are characterised by :

(1) **Low ionization energies** which imply that the valence electrons in metal atoms can easily be separated.

(2) **A number of vacant electron orbitals in their outermost shell.** For example, the magnesium atom with the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^0$ has three vacant 3*p* orbitals in its outer electron shell.

There is considerable overlapping of vacant orbitals on one atom with similar orbitals of adjacent atoms, throughout the metal crystal. Thus it is possible for an electron to be delocalized and move freely in the vacant molecular orbital encompassing the entire metal crystal. The delocalized electrons no longer belong to individual metal atoms but rather to the crystal as a whole.

As a result of the delocalization of valence electrons, the positive metal ions that are produced, remain fixed in the crystal lattice while the delocalized electrons are free to move about in the vacant space in between. The metal is thus pictured as a network or lattice of positive ions of the metal immersed in a 'sea of electrons' or 'gas of electrons'. This relatively simple model of metallic bonding is referred to as the **Electron Sea model** or the **Electron Gas model** (Fig. 5.10.)

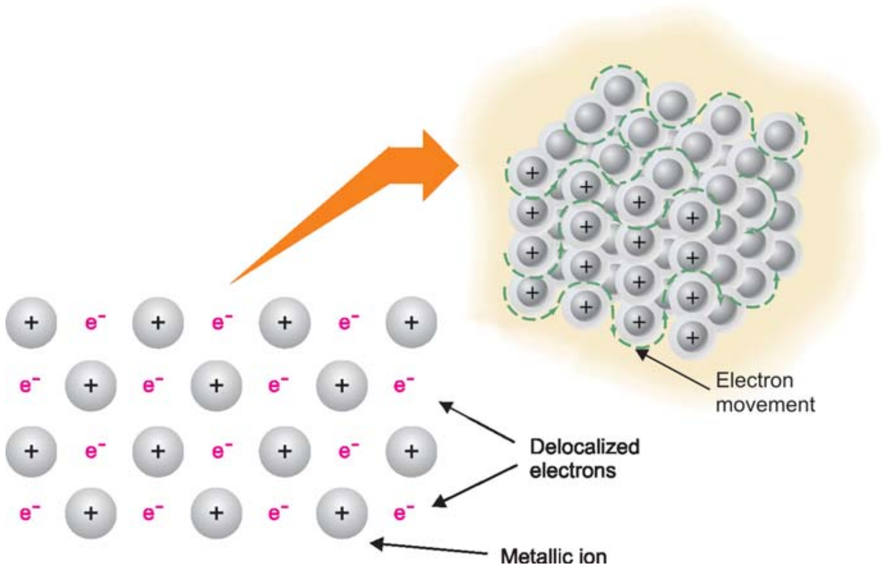
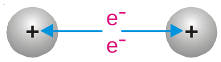


Figure 5.10
The Electron Sea model of metallic bonding.

A metallic bond is the electrostatic force of attraction that the neighbour positive metallic ions have for the delocalized electrons.



The electron sea model of metallic bonding explains fairly well the most characteristic physical properties of metals.

(1) **Luster or Reflectivity.** The delocalized mobile electrons of the 'electron sea' account for this property. Light energy is absorbed by these electrons which jump into higher energy levels and return immediately to the ground level. In doing so, the electrons emit electromagnetic radiation (light) of the same frequency. Since the radiated energy is of same frequency as the incident light, we see it as a reflection of the original light.

(2) **Electric Conductivity.** Another characteristic of metals is that they are good conductors of electricity. According to the electron sea model, the mobile electrons are free to move through the vacant space between metal ions. When electric voltage is applied at the two ends of a metal wire, it causes the electrons to be displaced in a given direction. The best conductors are the metals which attract their outer electrons the least (low ionization energy) and thus allow them the greatest freedom of movement.

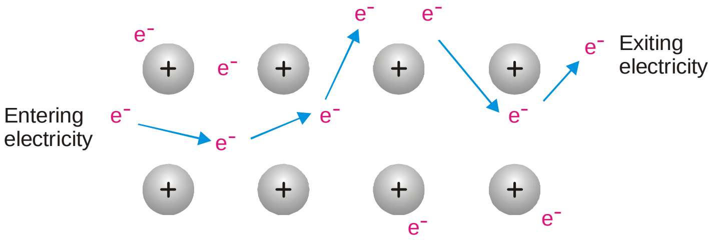


Figure 5.11
Electrical conductivity by flow of electrons based on Electron Sea model.

(3) **Heat Conductivity.** If a metal is heated at one end, the heat is carried to the other end. The mobile electrons in the area of the 'electron sea' around one end of the metal easily absorb heat energy and increase their vibrational motion. They collide with adjacent electrons and transfer the added energy to them. Thus the mobility of the electrons allows heat transfer to the other end (Fig. 5.12).

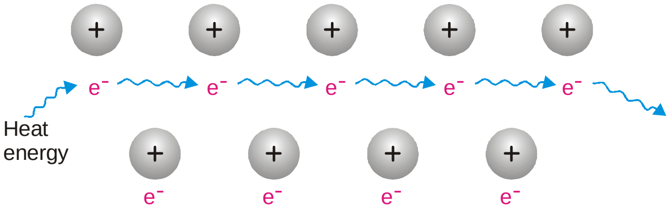


Figure 5.12
Heat conduction through a metal.

(4) **Ductility and Malleability.** The ductility and malleability of metals can also be explained by the electron sea model. In metals the positive ions are surrounded by the sea of electrons that 'flows' around them. If one layer of metal ions is forced across another, say by hammering, the internal structure remains essentially unchanged (Fig. 5.13). The sea of electrons adjusts positions rapidly and the crystal lattice is restored. This allows metals to be ductile and malleable. However, in ionic crystals of salts *e.g.*, sodium chloride, displacement of one layer of ions with respect to another brings like charged ions near to each other. The strong repulsive forces set up between them can cause the ionic crystals to cleave or shatter. **Thus ionic crystals are brittle.**

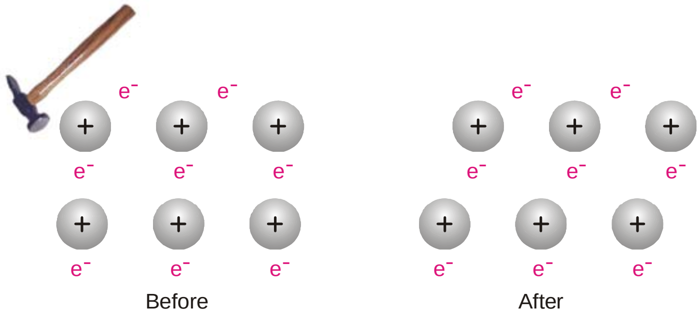


Figure 5.13
When force is applied to the upper layer of cations it slips to the right without changing the environments. illustration of malleability and ductility.

(5) **Electron Emission.** When enough heat energy is applied to a metal to overcome the attraction between the positive metal ions and an outer electron, the electron is emitted from the metallic atom. When the frequency and, therefore, the energy of the light that strikes the metal is great enough to overcome the attractive forces, the electron escapes from the metal with a resultant decrease in the energy of the incident photon (**Photoelectric effect**).

GEOMETRIES OF MOLECULES

So far we have depicted molecules by Lewis structures in the flat plane of paper. But **all molecules containing three or more atoms are three-dimensional.** The shape of a particular molecule is determined by the specific arrangement of atoms in it and the bond angles. Molecular shapes may be linear, bent (or angular), trigonal planar, pyramidal or tetrahedral.

The shapes of molecules can be determined in the laboratory by modern methods such as X-ray and electron diffraction techniques. Molecular shapes are important because they are helpful in the investigation of molecular polarity, molecular symmetry or asymmetry. Physical and chemical properties of compounds depend on these factors. VSEPR theory throws light on the three dimensional shapes of molecules.

VSEPR THEORY

The Lewis structure of a molecule tells us the number of pairs of electrons in the valence shell of the central atom. These electron pairs are subject to electrostatic attractions between them. On this basis, R.G.Gillespie (1970) proposed a theory called the **Valence-Shell Electron Pair Repulsion or VSEPR (pronounced as 'Vesper') theory.** It states that : **The electron pairs (both lone pairs and shared pairs, surrounding the central atom will be arranged in space as far apart as possible to minimise the electrostatic repulsion between them.**

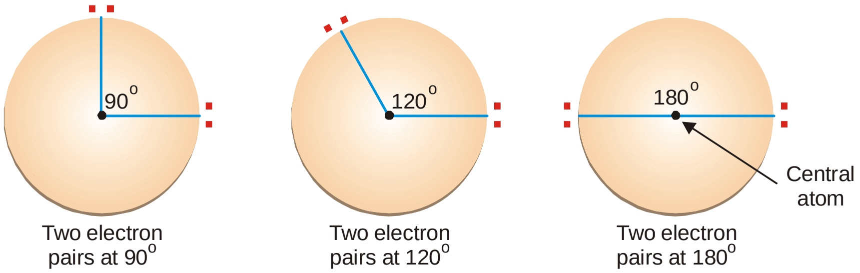


Figure 5.14

Arrangement of two electron pairs on circle at 90°, 120° and at 180°. Placement of electron pairs at 180° puts them the farthest apart, thereby minimising the electrostatic repulsion.

Let us consider the simplest case of an atom with two electron pairs. We wish to place the electron pairs on the surface of a sphere such that they will be as far apart as possible so as to minimise repulsion between them. Fig. 5.14 illustrates it by showing some possible placements of the two electron pairs. The arrangement in which the electron pair-central atom-electron pair angles is 180°, makes the electron pairs farthest apart. **This arrangement is called linear because the electron pairs and the central atom are in a straight line.**

VSEPR theory is simple but remarkably powerful model for predicting molecular geometries and bond angles. While working out the shapes of molecules from this theory, it must be remembered :

(1) **Multiple bonds behave as a single electron-pair bond** for the purpose of VSEPR. They represent a single group of electrons.

(2) **Order of repulsions** between lone pair and lone pair (*lp-lp*), lone pair and bonding pair (*lp-bp*), and bonding pair and bonding pair (*bp-bp*) is

$$lp - lp >> lp - bp > bp - bp$$

When a molecule has lone pairs of electrons, the bonding electron pairs are pushed closer and thus the bond angle is decreased.

Now we proceed to work out the shapes of some common molecules with the help of VSEPR theory.

(1) Linear Molecules

(*a*) **Beryllium chloride, $BeCl_2$.** It has the Lewis structure

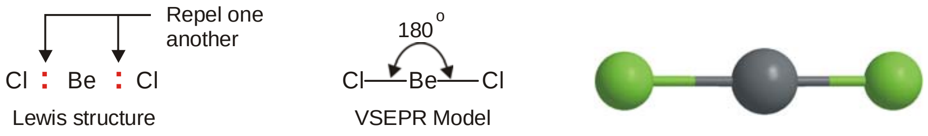


Figure 5.15
Geometry of $BeCl_2$ molecule.

The central atom Be has two bonding electron pairs and no unshared electron. According to VSEPR theory, the bonding pairs will occupy positions on opposite sides of Be forming an angle of 180º. An angle of 180º gives a straight line. Therefore, $BeCl_2$ molecule is linear. In general, **all molecules as A–B–A which have only two bonds and no unshared electrons are linear.**

(*b*) **Carbon dioxide, CO_2.** It has the structure

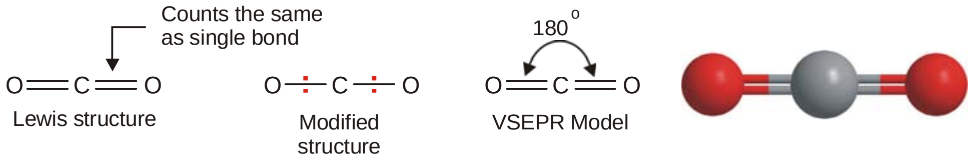
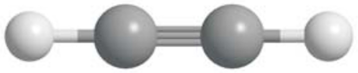


Figure 5.16
Geometry of CO_2 molecule.

The central C atom has no unshared electron. We know that a double bond counts the same as a single bond in VSEPR model. Thus CO_2 is a linear molecule.

Similarly, it can be shown that hydrogen cyanide ($H - C \equiv N$) and acetylene ($H - C \equiv C - H$) are linear molecules.


Hydrogen cyanide


Acetylene

(2) Trigonal Planar Molecules

(*a*) **Boron trifluoride, BF_3.** Its Lewis structure shown that the central atom B has three bonding electron pairs and no unshared electrons. VSEPR theory says that the three bonding electron pairs will be as far apart as possible. This can be so if these electron pairs are directed to the corners of an equilateral triangle. Thus VSEPR model of BF_3 molecule has three F atoms at the corners of the triangle with B atom at its centre. All the four atoms (three *F* and one B) lie in the same plane. Therefore, the shape of such a molecule is called **trigonal planar.** The bond angle is 120º.

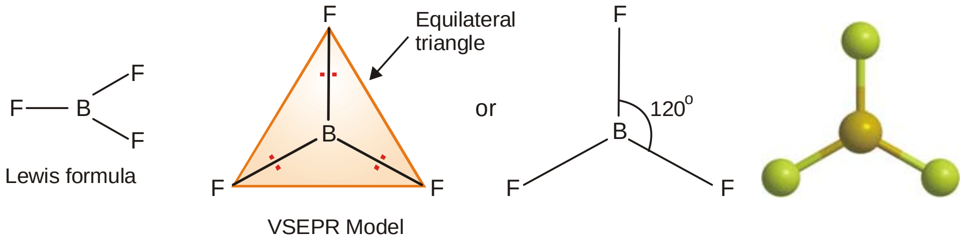


Figure 5.17
Geometry of BF_3 molecule.

(*b*) **Sulphur trioxide, SO_3.** In the Lewis structure of SO_3, the central S atom is joined with two O atoms by covalent bonds. The third O atom is joined with S by a double bond. But a double bond is counted as a single electron pair for the purpose of VSEPR model. Therefore, in effect, S has three electron pairs around it. Thus like BF_3, SO_3 has trigonal planar geometry.

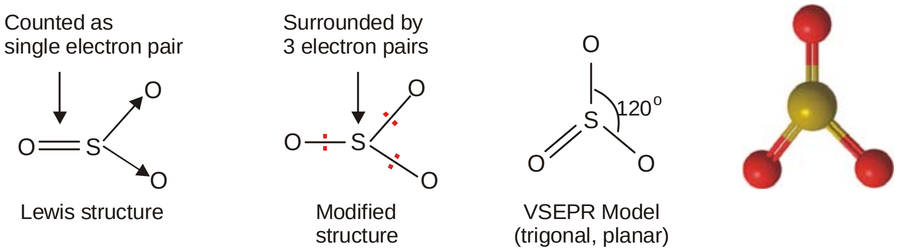


Figure 5.18
Geometry of SO_3 molecule.

(3) Tetrahedral Molecules

(*a*) **Methane, CH_4.** Lewis structure of methane shows that the central C atom has four bonding electron pairs. These electron pairs repel each other and are thus directed to the four corners of a regular tetrahedron. A regular tetrahedron is a solid figure with four faces which are equilateral triangles. All bond angles are 109.5°.

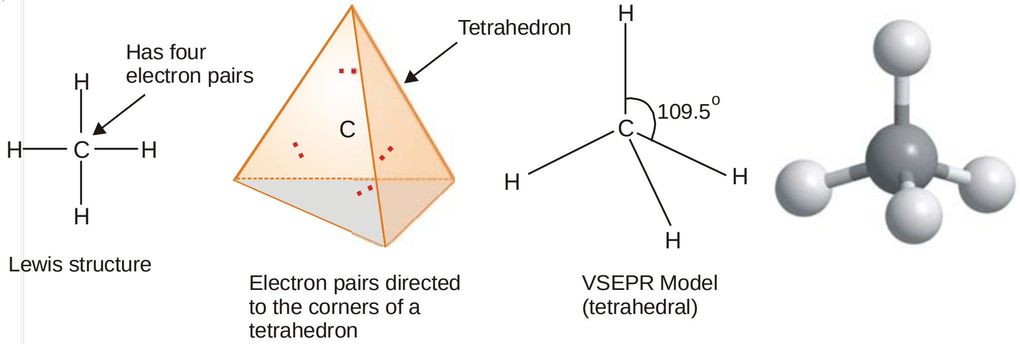
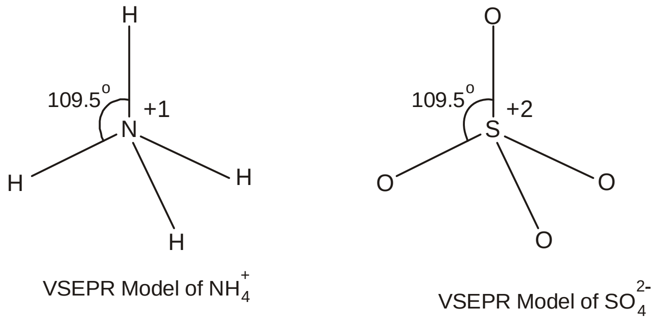


Figure 5.19
Geometry of CH_4 molecule.

Similarly, CCl_4 in which the central C atom is bonded to four other atoms by covalent bonds has tetrahedral shape.

(*b*) **Ammonium ion, NH_4^+, and Sulphate ion, SO_4^{2-}.** The N atom in NH_4^+ and S atom in SO_4^{2-} have four electron pairs in the valence shell. These are directed to the corners of a tetrahedron for maximum separation from each other. Thus both NH_4^+ and SO_4^{2-} have tetrahedral shape.



VSEPR Model of NH_4^+

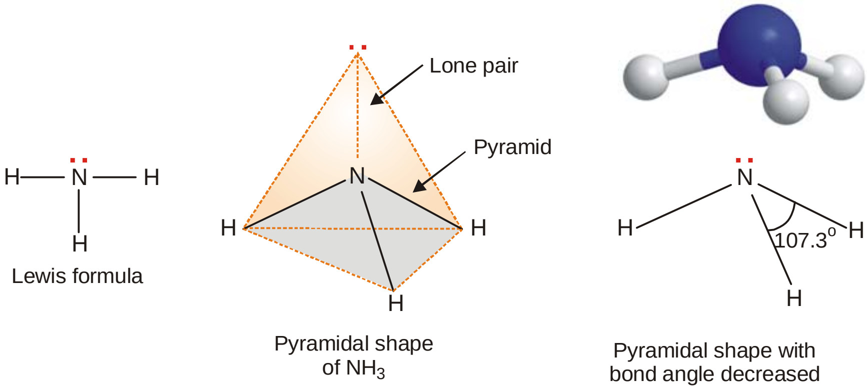
VSEPR Model of SO_4^{2-}

Figure 5.20
Geometry of NH_4^+ ion and SO_4^{2-} ion.

(4) Pyramidal Molecules

(*a*) **Ammonia molecule.** The Lewis structure of NH_3 shows that the central N atom has three bonding electrons and one lone electron pair. The VSEPR theory says that these electron pairs are directed to the corners of a tetrahedron. Thus we predict that H–N–H bond angle should be 109.5º. But the shape of a molecule is determined by the arrangement of atoms and not the unshared electrons. Thus, if we see only at the atoms, we can visualise NH_3 molecule as a pyramid with the N atom located at the apex and H atoms at the three corners of the triangular base.

According to VSEPR theory, **a lone pair exerts greater repulsion on the bonding electron pairs than the bonding pairs do on each other.** As a result, the bonds of NH_3 molecule are pushed slightly closer. This explains why the observed bond angle H–N–H is found to be 107.3º instead of 109.5º predicted from tetrahedral geometry.



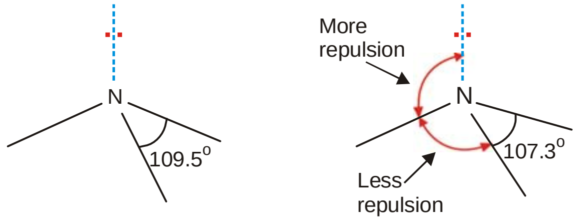
Lewis formula

Pyramidal shape of NH_3

Pyramidal shape with bond angle decreased to 107.3°

Figure 5.21
Geometry of NH_3 molecule.

All molecules in which the N atom is joined to three other atoms by covalent bonds, have pyramidal shape. For example, amines RNH_2, R_2NH and R_3N have pyramidal shape.



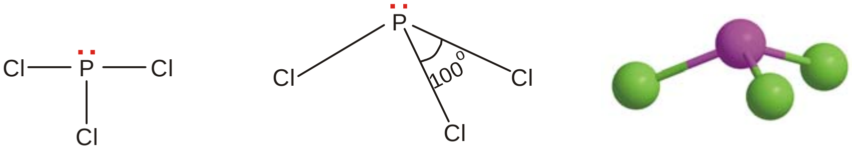
Tetrahedral geometry predicts H—N—H angle of 109.5°

The bond angle decreases because of greater repulsion of lone electron pair

Figure 5.22

Why the angle H—N—H in NH_3 molecule is 107.3° while the tetrahedral angle is 109.5°?

(*b*) **Phosphorus trichloride, PCl_3.** The structural formula indicates that the central phosphorus atom has three bonding electron pairs and one lone electron pair. Thus, like NH_3 it has pyramidal shape and the observed bond angle Cl–P–Cl is 100º.



Lewis formula

Pyramidal PCl_3 molecule

Figure 5.23

Geometry of PCl_3 molecule.

(5) Bent or Angular Molecules

(*a*) **Water, H_2O.** In the structural formula of H_2O, the O atom is bonded to two H atoms by covalent bonds and has two lone pairs. Thus O is surrounded by two bonding electron pairs and two unshared electron pairs. VSEPR theory says that in order to secure maximum separation between them, the four electron pairs are directed to the corners of a tetrahedron. If we look at the three atoms (and ignore the unshared pairs), the atoms HOH lie in the same plane and the predicted bond angle is 109.5º. But with two unshared pairs repelling the bonding pairs, the bond angle is compressed to 105º, the experimental value. Thus the H_2O molecule is flat and bent at an angle at the O atom. Such a molecule is called a **bent molecule** or **angular molecule.**

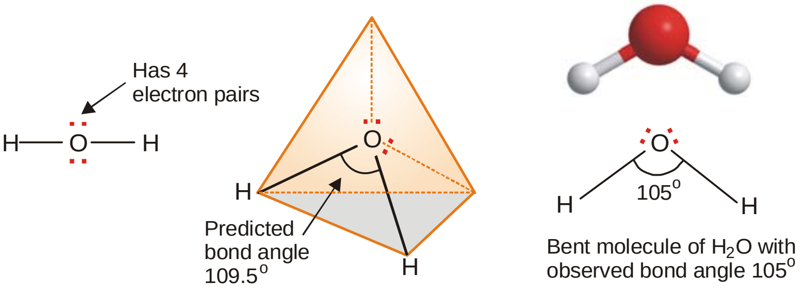


Figure 5.24

Geometry of H_2O molecule.

(*b*) **Sulphur dioxide, SO_2.** The Lewis structure of SO_2 is given below. The S atom is bonded to one O by a double bond and to the other O by a single bond. It has an unshared electron pair. In VSEPR model a double bond is counted as a single electron pair. That way, the S atom is surrounded by three electron pairs, two bonding pairs and one unshared pair. For maximum separation the three electron pairs are directed to the corners of an equilateral triangle. The predicted bond angle is 120º. But with the unshared electron pair repelling the bonding electron pairs, the bond angle is actually reduced somewhat. Thus SO_2 has a planar bent molecule with the observed bond angle 119.5º.

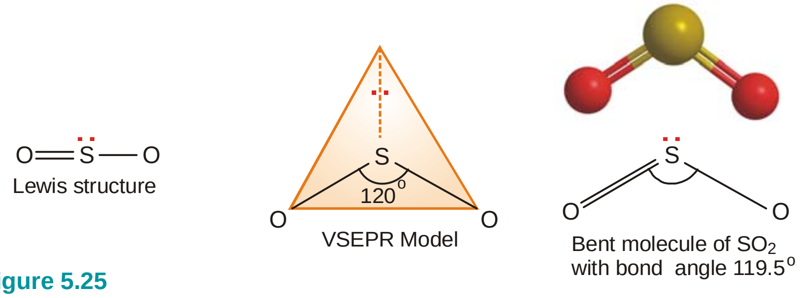
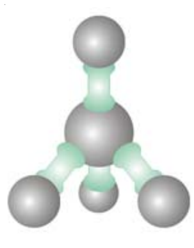
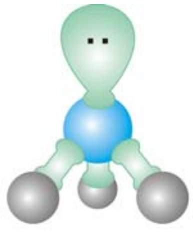
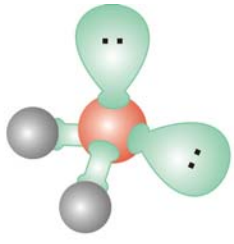


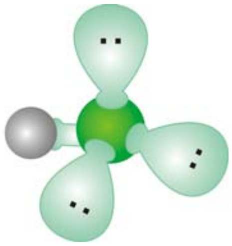
Figure 5.25
Geometry of SO_2 molecule.

SUMMARY : SHAPES OF MOLECULES


Methane (CH_4)


Ammonia (NH_3)


Water (H_2O)


Hydrogen fluoride (HF)

The directional nature of covalent bonds is shown in the diagrams of molecules above. The shape of the methane molecule is tetrahedral because the four bonding pairs of electrons repel each other equally, and the equilibrium position of all four bonding electron pairs is tetrahedral.

HOW TO WORK OUT THE SHAPE OF A MOLECULE

It is possible to work out the shape of a small molecule that has a formula XY_n by applying a few simple rules. We will use ammonia as an example to illustrate the idea.

Rule 1 First find the number of bonding pairs of electrons in the molecule. The number of bonding pairs of electrons in the molecule NH_3 can be seen in the formula. There must be three bonding pairs of electrons holding the three hydrogens onto the nitrogen.

Rule 2 Find the number of valence electrons (electrons in the outer energy level) on an atom of the central atom (The one of which there is only one.) Nitrogen is in group V, so the nitrogen has five electrons in the outer energy level.

Rule 3 Find the number of lone pairs on the central atom by subtracting the number of bonding pairs (3) from the valence electrons (5) to find the number of electrons (2) that will make up lone pairs of electrons. Divide this number by 2 to find the number of lone pairs, 2/2 = 1.

Rule 4 Distribute all the electron pairs around the central atom and learn the angles they will make from molecules with no lone pairs.

Rule 5 Learn that the repulsion between lone pairs of electrons is greater than the repulsion between bonding pairs, and subtract 2º from the bond angles for every lone pair.

Rule 6 Learn the names of the shapes. The shapes are named from the position of the atoms and not the position of the orbitals.

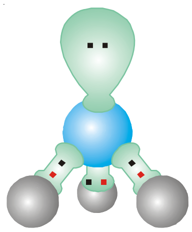
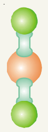
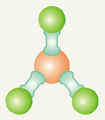
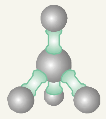
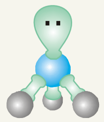
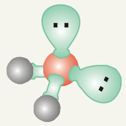


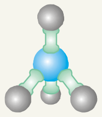
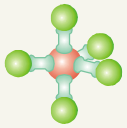
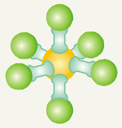
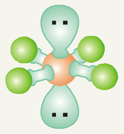
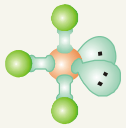
TABLE OF SHAPES

Formula	**$BeCl_2$** **Beryllium chloride**	**BCl_3** **Boron trichloride**	**CH_4** **Methane**	**NH_3** **Ammonia**	**H_2O** **Water**
Bonding Pairs	2	3	4	3	2
Valence Electrons	2	3	4	5	6
Lone Pairs	0	0	0	1	2
Angles between bonding pairs	180°	120°	109.5°	107°	105°
Name of shape	Linear	Trigonal Planar	Tetrahedral	Trigonal Pyramid	Bent
					

There is one more rule to learn, and it concerns the shape of polyatomic ions.

Rule 2(a) If the molecule is an ion, e.g. ammonium (NH_4^+), subtract 1 from the number of valence electrons for every + charge on the ion and add 1 to the valence number for every - charge, then proceed as before.

SOME MORE EXAMPLES

Formula	**NH_4^+**	**PCl_5**	**SF_6**	**XeF_4**	**ICl_3**
Bonding Pairs	4	5	6	4	3
Valence Electrons	5	5	6	8	7
Rule 2(a)	5 – 1 = 4				
Lone Pairs	0	0	0	2	2
Angles between bonding pairs	109.5°	90° & 120°	90°	90°	90°
Name of shape	Tetrahedral	Trigonal Bipyrimid	Octahedron	Square	T shape
					

EXAMINATION QUESTIONS

1. Define or explain the following terms :
- (*a*) Octet rule
- (*b*) Ionic bond
- (*c*) Covalent bond
- (*d*) Co-ordinate covalent bond
- (*e*) Polar covalent bond
- (*f*) Hydrogen bonding
- (*g*) Intermolecular H-bonding
- (*h*) Intramolecular H-bonding
- (*i*) VSEPR theory

2. (*a*) Compare the properties of ionic and covalent compounds.
(*b*) State whether the following compounds are ionic or covalent.
- (*i*) $AlCl_3$
- (*ii*) HgF_2

3. (*a*) Draw the structure of NaCl crystal and give the co-ordination number of Na^+.
(*b*) Which of the two is more covalent and why in the following pairs
- (*i*) AgCl and AgI
- (*ii*) LiCl and KCl

4. In methane, ammonia and water molecule the bond angle is decreasing. Explain giving reasons.

5. (*a*) Explain the formation of covalent bond between two atoms of chlorine in a chlorine molecule on the basis of octet rule.
(*b*) Define (*i*) Ionic bond; (*ii*) Co-ordinate bond; and (*iii*) Metallic bond

6. (*a*) What do you understand by 'Stable configuration'? What are the ways by which an atom can attain stable configuration?
(*b*) Write the electronic configuration of any two of the following compounds :
- (*i*) Phosphorus pentachloride
- (*ii*) Sulphuric acid
- (*iii*) Lithium fluoride

7. What type of bonds do you expect in the following cases? Give reasons :
- (*i*) between a very small cation and a large anion.
- (*ii*) between atoms having a very large difference in electronegativities,
- (*iii*) between atoms of the same element.

8. Explain qualitatively the valence bond theory with reference to Hydrogen molecule.

9. Compare the properties of ionic and covalent compounds. Give two examples of each type of compounds.

10. Indicate the type of bonding that exists in the following solids :
- (*i*) Ice
- (*ii*) Naphthalene
- (*iii*) Diamond
- (*iv*) Potassium chloride

11. Write Lewis dot formulae of : (*a*) HOCl (*b*) BF_3 (*c*) NH_4^+.

12. Show the formation of a co-ordinate bond in ozone molecule and discuss briefly the electron gas model of the metallic bond and how it explains the electrical conductivity of metals.

13. What is electronegativity? How is the concept of electronegativity used to predict the bond types between hetero atoms?

14. Account for the variation of bond angles between the pairs (*i*) H_2O and H_2S (104.5° and 92°) and (*ii*) H_2O and OF_2 (104.5° and 101.1°).

15. Describe the structures of water, ammonia and methane molecules in terms of the electron pair repulsion theory. Explain why the bond angles are different in the three molecules.

16. What is a co-ordinate covalent bond? How does it differ from a normal covalent bond?

17. Discuss the shape of the following molecules on the basis of VSEPR theory :

$$NH_3, \quad CH_4, \quad PCl_3$$

18. Explain the formation of NH_3 molecule if no hybridization of *s* and *p*-orbitals of nitrogen is assumed.

Give diagrammatic representation also.

19. Explain :

(*a*) The structure of H_2 molecule according to V.B. theory.

(*b*) Ionic bond and Metallic bond.

20. Two elements *X* and *Y* occur in the same period and their atoms have two and seven valence electrons respectively. Write down the electronic structure of the most probable compound between *X* and *Y*. Will the bond between *X* and *Y* be predominantly ionic or covalent?

Answer. XY_2; Ionic

21. Using VSEPR theory, identify the type of hybridisation and draw the structure of OF_2. What are the oxidation states of O and F?

22. Account for : The experimentally found N——F bond length in NF_3 is greater than the sum of single covalent radii of N and F.

23. Which of the following compounds contain bonds that are predominantly ionic in character : MgO, Ca_3P_2, $AlCl_3$, Mg_2Si and CsF.

Answer. CsF, Mg_2Si and MgO

24. Classify the bonds in the following as ionic, polar covalent or covalent : (*a*) HCl (*b*) NaCl and (*c*) NCl_3.

Answer. HCl - Polar covalent, NaCl - Ionic and NCl_3 - Covalent

25. Predict the geometry of the following molecules using VSEPR theory.

(*a*) CCl_4 (*b*) $AlCl_3$

(*c*) H_2Se

Answer. (*a*)Tetrahedral (*b*) Trigonal planar (*c*) Bent

26. Predict the geometry of the following ions having VSEPR model.

(*a*) H_3O^+ (*b*) NO_2^-

(*c*) ClO_2^-

Answer. (*a*) Pyramidal (*b*) Bent (*c*) Bent

27. Calculate the percentage ionic character of C—Cl bond in CCl_4, if the electronegativities of C and Cl are 3.5 and 3.0 respectively.

Answer. 8.875%

28. The experimentally determined dipole moment, *m*, of KF is 2.87×10^{-29} coulomb meter. The distance, *d*, separating the centers of charge in a KF dipole is 2.66×10^{-3} m. Calculate the percent ionic character of KF.

Answer. 67.4%

29. The dipole moment of KCl is 3.336×10^{-29} coulomb meter which indicates that it is highly polar molecule. The interionic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit localised at each nucleus. Calculate the percentage ionic character of KCl.

Answer. 80%

30. What is meant by an ionic bond? What are the conditions necessary for the formation of an ionic bond? (*Agra BSc, 2000*)

31. Describe the basic ideas of the VSEPR theory. Explain the application of the theory for predicting the shapes of the molecules, BCl_3, NH_3, H_2O and SF_6. (*Delhi BSc, 2001*)

32. (*a*) What are electrovalent compounds? Discuss various factors which affect the formation of these compounds.

(*b*) What do you understand by hydrogen bonds? Classify them with examples. Explain why water has abnormally high boiling point. (*Baroda BSc, 2002*)

33. Why bond angles of H_2O and NH_3 are 104.5° and 107° respectively although central atoms are sp^3 hybridized. (*Aligarh BSc, 2002*)

34. Define Lattice energy. Discuss the factors on which it depends.

35. (*a*) Why melting and boiling points of ionic compounds are usually higher than covalent compounds?

(*b*) Discuss the geometry and shape of PF_5 molecule.

(*c*) Write a short note on hydrogen bonding. (*Arunachal BSc, 2003*)

36. Each of the concepts of covalency and electrovalency relates to an idealised state of chemical bonding which often does not exist in real compounds. Discuss how far this statement is valid and give two examples with suitable explanation of cases where such non-ideality infact arises. (*Delhi BSc, 2003*)

37. Strength of hydrogen bond in H–F is more than in H_2O but still HF is a gas and H_2O is a liquid at room temperature. Explain. (*Delhi BSc, 2004*)

38. (*a*) The bond angle $\angle \text{HNH}$ in ammonia is 107° while bond angle $\angle \text{HOH}$ in water is about 104°. Why?

(*b*) A covalent bond is stronger than a metallic bond. Why? (*Sambalpur BSc, 2004*)

39. Explain intermolecular and intramolecular hydrogen bonding with one example for each.

(*Agra BSc, 2005*)

40. Based on metallic bond, explain why metals are :

(*a*) good conductors of electricity (*b*) malleable and ductile

(*c*) having characteristic lustre (*Mysore BSc, 2006*)

MULTIPLE CHOICE QUESTIONS

1. The valency of an element is
(*a*) the combining capacity of one atom of it
(*b*) the number of bonds formed by its one atom
(*c*) the number of hydrogen atoms that combine with one atom of it
(*d*) all the above

Answer. (*d*)

2. The octet rule is
(*a*) the tendency of atoms to have eight electrons in the outermost shell
(*b*) the tendency of atoms to have eight pairs of electrons in the valency shell
(*c*) the tendency of the molecule to have a total of eight electrons
(*d*) the tendency of atoms to have eight non-bonding electrons

Answer. (*a*)

3. An ionic bond is formed between
(*a*) two metal atoms (*b*) two non-metal atoms
(*c*) one metal atom and one non-metal atom (*d*) one metal atom and one metalloid atom

Answer. (*c*)

4. Factors governing the formation of an ionic bond are
(*a*) low ionisation energy of metal and high electron affinity of non-metal atom
(*b*) high ionisation energy of metal and high electron affinity of non-metal atom
(*c*) low ionisation energy of metal atom and low electron affinity of non-metal atom
(*d*) high ionisation energy of metal and low electron affinity of non-metal atom

Answer. (*a*)

5. The lattice energy is the amount of energy that
(*a*) is released when one cation combines with one anion
(*b*) is released when one mole of cations combine with one mole of anions
(*c*) is released when one mole of an ionic compound is formed from its cations and anions

(*d*) is absorbed when one mole of an ionic compound is formed from its cation and anions

Answer. (*c*)

6. The most favourable conditions for the formation of an ionic compound is

(*a*) low charge on ions, small cation and small anion

(*b*) high charge on ions, large cation and large anion

(*c*) high charge on ions, small cation and large anion

(*d*) low charge on ions, large cation and small anion

Answer. (*c*)

7. Ionic compounds are generally

(*a*) solids having large melting points and good conductors of electricity

(*b*) gases having low melting points and poor conductors of electricity

(*c*) solids having low melting points and good conductors of electricity

(*d*) solids having high melting points and bad conductors of electricity

Answer. (*a*)

8. A covalent bond involves

(*a*) sharing of electrons between a metal and a non-metal atom

(*b*) sharing of electrons between two metal atoms

(*c*) sharing of electrons between two atoms having similar electronegativity

(*d*) sharing of electrons between two atoms having a large difference in electronegativity

Answer. (*c*)

9. The total number of electron pairs in a nitrogen molecule is

(*a*) 2 (*b*) 3 (*c*) 5 (*d*) 7

Answer. (*d*)

10. The covalent compounds are soluble in

(*a*) all acids (*b*) all bases (*c*) all solvents (*d*) non-polar solvents

Answer. (*d*)

11. The compounds which contain both ionic and covalent bonds are

(*a*) $CHCl_3$ and CCl_4 (*b*) KCl and $AlCl_3$ (*c*) KCN and NaOH (*d*) H_2 and CH_4

Answer. (*c*)

12. A co-ordinate bond is formed by

(*a*) complete transfer of electrons

(*b*) sharing of electrons contributed by both the atoms

(*c*) sharing of electrons contributed by one atom only

(*d*) none of these

Answer. (*c*)

13. The types of bonds present in sulphuric acid molecules are

(*a*) only covalent (*b*) ionic and covalent

(*c*) co-ordinate and covalent (*d*) co-ordinate, covalent and ionic

Answer. (*d*)

14. The common feature among the species O_3, SO_4^{2-}, H_3O^+ and $AlCl_3$ is that

(*a*) they contain only ionic bonds (*b*) they contain only covalent bonds

(*c*) they contain co-ordinate bond (*d*) they contain covalent and ionic bonds

Answer. (*c*)

15. The species CO, CN^- and N_2 are

(*a*) isoelectronic (*b*) having co-ordinate bond

(*c*) having low bond energies (*d*) having polar bonds

Answer. (*a*)

16. The polarity of a covalent bond is due to
(*a*) lesser electronegativity difference between two atoms
(*b*) greater electronegativity difference between two atoms
(*c*) lesser bond energy
(*d*) greater bond energy
Answer. (*b*)

17. A CO_2 molecule contains two polar bonds but the net dipole moment is zero. It is because
(*a*) the molecule has symmetrical linear geometry
(*b*) the molecule is non-linear
(*c*) the electronegativity difference between the two atoms is too large
(*d*) the electronegativity difference between the two atoms is too small
Answer. (*a*)

18. Among BeF_2, BF_3, NH_3 and CCl_4, the molecule with net dipole moment is
(*a*) BeF_2 (*b*) BF_3 (*c*) NH_3 (*d*) CCl_4
Answer. (*c*)

19. The common feature among the molecules HF, H_2O, HCl and NH_3 is
(*a*) intramolecular H-bonding (*b*) intermolecular H-bonding
(*c*) that they contain no polar bonds (*d*) that their dipole moment is zero
Answer. (*b*)

20. Methanol is soluble in water due to
(*a*) covalent bond nature (*b*) ionic bond nature
(*c*) hydrogen bonding (*d*) its poisonous nature
Answer. (*c*)

21. Among H_2O, H_2S, H_2Se and H_2Te, the substance with highest boiling point is
(*a*) H_2O; due to hydrogen bonding
(*b*) H_2S; due to large size of S atom
(*c*) H_2Se; due to large electronegativity difference
(*d*) H_2Te; due to largest size of Te atom
Answer. (*a*)

22. In ice crystal, the H_2O molecules are held together in a
(*a*) planar structure (*b*) linear structure
(*c*) tetrahedral three dimensional structure (*d*) none of these
Answer. (*c*)

23. The density of ice (solid) is lesser than that of water (liquid) because it has
(*a*) open cage like structure with no empty spaces
(*b*) open cage like structure with large empty spaces
(*c*) intermolecular H-bonding
(*d*) intramolecular H-bonding
Answer. (*b*)

24. The density of water is maximum at
(*a*) 273 K (*b*) 277 K (*c*) 281 K (*d*) 285 K
Answer. (*b*)

25. Among $BeCl_2$, $CHCl_3$, CCl_4 and PCl_5, the octet rule is not observed in
(*a*) $BeCl_2$ only (*b*) PCl_5 only (*c*) $BeCl_2$ and PCl_5 (*d*) $CHCl_3$ and CCl_4
Answer. (*c*)

26. An example of electron deficient compound among BF_3, CF_4, PF_5 and SF_6 is
(*a*) BF_3 (*b*) CF_4 (*c*) PF_5 (*d*) SF_6
Answer. (*a*)

27. The transition metals show variable valency because of

(*a*) the availability of vacant *d*-orbitals (*b*) their tendency to form complex ions

(*c*) their ability to form coloured ions (*d*) none of these

Answer. (*a*)

28. The electrical conductivity of metals is due to

(*a*) mobile protons is the nucleus (*b*) mobile nucleus in the nucleus

(*c*) mobile electrons in outer vacant spaces (*d*) none of these

Answer. (*c*)

29. According to VSEPR theory,

(*a*) the lone pairs only decide the structure of the molecule

(*b*) the bond pairs only decide the structure of the molecule

(*c*) the lone pairs and bond pairs both decide the structure of the molecule

(*d*) none of these

Answer. (*c*)

30. In which of the following, the central atom is surrounded by four electron pairs

(*a*) H_2O (*b*) NH_3 (*c*) CH_4 (*d*) All

Answer. (*d*)

31. The molecule among CCl_4, PCl_3, SF_4 and NH_3 that does not contain lone pairs of electrons around the central atom is

(*a*) CCl_4 (*b*) PCl_3 (*c*) SF_4 (*d*) NH_3

Answer. (*a*)

32. Which of the following are isostructural

(*a*) SO_2 and CO_2 (*b*) SO_2 and H_2O (*c*) BCl_3 and $CHCl_3$ (*d*) NH_3 and CH_4

Answer. (*b*)

33. The molecular shapes of H_2O, NH_3 and CH_4 are

(*a*) similar with 2, 1 and 0 lone pairs of electrons respectively

(*b*) similar with 0, 1 and 2 lone pairs of electrons respectively

(*c*) different with 0, 1 and 2 lone pairs of electrons respectively

(*d*) different with 2, 1 and 0 lone pairs of electrons respectively

Answer. (*d*)

34. The molecule of NH_3 is

(*a*) tetrahedral with bond angle 109° 28′ (*b*) pyramidal with bond angle 107° 20′

(*c*) trigonal with bond angle 120° (*d*) linear with bond angle 180°

Answer. (*b*)

35. The NH_4^+ and SO_4^{2-} ions have

(*a*) tetrahedral geometry (*b*) triangular geometry

(*c*) pyramidal geometry (*d*) square planar geometry

Answer. (*a*)

36. Which is incorrect?

(*a*) all molecules with polar bonds have dipole moment

(*b*) all molecules with polar bonds may or may not have dipole moment

(*c*) the greater the difference in electronegativity between two atoms, greater is the polarity

(*d*) if the electronegativity difference between two atoms is greater than 1.7, the bond will be ionic

Answer. (*a*)

37. The favourable conditions for the formation of H–bonding are

(*a*) high electronegativity and small size of the atom bonded to H–atom

(*b*) low electronegativity and large size of the atom bonded to H–atom

(*c*) high electronegativity and large size of the atom bonded to H–atom (*d*) low electronegativity and small size of the atom bonded to H–atom

Answer. (*a*)

38. The strength of hydrogen bonding lies in between

(*a*) covalent and ionic bond (*b*) metallic and covalent bond

(*c*) van der Waal's and covalent bond (*d*) metallic and ionic bond

Answer. (*d*)

39. The bond angles in a trigonal bipyramid molecules are

(*a*) 90° (*b*) 120° (*c*) 109.5° (*d*) 120°, 90°

Answer. (*d*)

40. CO_2 has zero dipole moment whereas H_2O has a dipole moment. It is because

(*a*) H_2O is linear while CO_2 is a bent molecule

(*b*) of intermolecular H–bonding in H_2O molecules

(*c*) CO_2 is linear while H_2O is a bent molecule

(*d*) CO_2 is a gas while H_2O is a liquid at room temperature

Answer. (*c*)

41. Which of the following does not obey the octet rule?

(*a*) PCl_5 (*b*) H_2O (*c*) NH_3 (*d*) CCl_4

Answer. (*a*)

42. The total number of electrons that take part in forming bonds in O_2 is

(*a*) 2 (*b*) 4 (*c*) 6 (*d*) 8

Answer. (*d*)

43. CO is isoelectronic with

(*a*) C_2H_2 (*b*) CN^- (*c*) O_2^+ (*d*) O_2^-

Answer. (*b*)

44. CO_2 is isostructural with

(*a*) H_2O (*b*) NO_2 (*c*) H_2S (*d*) C_2H_2

Answer. (*d*)

45. In a bond between two atoms X and Y, the shared electron pair does not lie in the centre. The bond is

(*a*) single bond (*b*) non-polar bond (*c*) polar bond (*d*) co-ordinate bond

Answer. (*c*)

46. The maximum number of Hydrogen bonds formed by a water molecule is

(*a*) 1 (*b*) 2 (*c*) 3 (*d*) 4

Answer. (*b*)

47. Out of the following, intramolecular Hydrogen bonding exists in

(*a*) water (*b*) H_2S (*c*) 2-nitrophenol (*d*) 4-nitrophenol

Answer. (*c*)

48. In a compound, hydrogen bonding exists but there is no effect on physical properties like m. pt., b. pt. etc. It shows the presence of

(*a*) weak van der Waal's forces (*b*) intramolecular hydrogen bonding

(*c*) intermolecular hydrogen bonding (*d*) resonance in the molecule

Answer. (*b*)

49. Which one of the following is the most polar

(*a*) H — F (*b*) H — Cl (*c*) H — Br (*d*) H — I

Answer. (*a*)

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