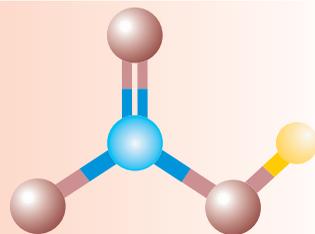


UNIT 3



Chemical Bonding and Structure

Unit Outcomes

At the end of this unit, you should be able to:

- *understand that a chemical bond is an attractive force between particles;*
- *demonstrate an understanding of the formation and general properties of substances containing ionic, covalent and metallic bonds;*
- *draw Lewis structures for simple ionic and covalent compounds;*
- *understand the origin of polarity within molecules;*
- *describe the formation and nature of hydrogen bonds, dipole-dipole forces and London forces;*
- *know the three different but related bonding models (Lewis model, Valence bond model and Molecular orbital model) and recognize the usefulness of the bonding theories in explaining and predicting molecular properties (bond angle, bond length, bond energy, etc);*
- *explain how the properties of a substance (solid or liquid) depends on the nature of the particles present and the type of intermolecular forces;*
- *appreciate the importance of intermolecular forces in plant and animal life;*

- *explain how the Valence Shell Electron Pair Repulsion (VSEPR) model can be used to predict molecular shape;*
- *Know the types of crystalline solid (ionic, molecular, covalent network, or metallic) formed by a substance and describe their properties;*
- *conduct experiments to observe and analyze the physical properties of different substances to determine the type of bonding present; and*
- *describe scientific enquiry skills along this unit: observing, inferring, predicting, classifying, comparing and contrasting, making models, communicating, asking questions, applying concepts, relating cause and effect and making generalizations.*

MAIN CONTENTS

- 3.1 Introduction
- 3.2 Ionic Bonding
- 3.3 Covalent Bonding and Molecular Geometry
 - Covalent Bonding
 - Molecular Geometry
 - Intermolecular Forces in Covalent Compounds
- 3.4 Metallic Bonding
- 3.5 Chemical Bonding theories
 - Valence Bond Theory
 - Molecular Orbital Theory
- 3.6 Types of crystals

3.1 INTRODUCTION

At the end of this section, you should be able to:

- describe the reason why atoms form chemical bonds;
- state octet rule;
- define chemical bonding; and
- describe the types of chemical bonding and their mechanisms of the bonding process.

Almost everything a person sees or touches in daily life, like the air we breathe, the food we eat, the clothes we wear, are the result of chemical bonds. The concept of chemical bonding lies at the very core of chemistry; it is what enables about little over one hundred elements to form millions of known chemical substances that make up our physical world.

In Grade 9, you have learned about chemical bonding and its types such as ionic, covalent and metallic bonding and their characteristics. In this unit, we will discuss some new concepts about chemical bonding, like molecular geometry, theories of chemical bonding and much more.

Activity 3.1



Form a group and discuss the following questions:

1. Why do atoms readily combine to form molecules?
2. Why molecules are more stable than free atoms?
3. What keeps the atoms together in a molecule?
4. Why do elements combine in certain fixed ratio?
5. The following diagram shows how energy varies as two H atoms approach each other to form H_2 . Interpret the diagram to show the decrease in potential energy favouring bonding.

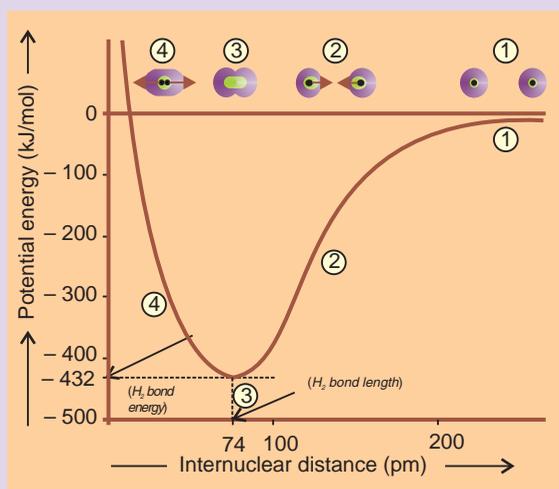


Figure 3.1 Energy diagram for hydrogen molecule.

3.1.1 Octet Rule

Activity 3.2



Form a group and discuss the following:

1. Why some atoms are very reluctant to combine with other atoms and exist as single atoms?
2. Is there any thing common amongst these atoms?
3. What is special about these atoms with respect to their electronic configuration?
4. What is the common name for this group of elements?
5. What is the reason for their stability?
6. Atoms lose or gain electrons not merely to satisfy the octet rule but to reach a lower energy state in an ionic compound. But it is in reaching this lower energy state that they often tend to follow the octet rule. Explain.

Share your ideas with the rest of the class.

You have studied in your earlier classes that **noble gases** have very stable electron arrangements such as 2; 2, 8; 2, 8, 8 and their outer shells are fully saturated. The

first three are shown in **Figure 3.2** and explains why noble gases are so reluctant to form compounds with other elements.

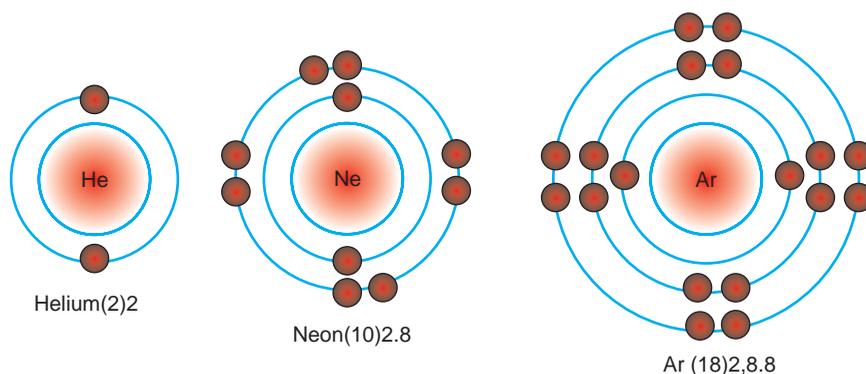


Figure 3.2 First three noble gases.

The noble gases have very stable electron configuration, as reflected by their high ionization energies, low electron affinity and general lack of reactivity. Because all noble gases (except He) have eight valence electrons, many atoms undergoing reaction also attain eight valence electrons. The ns^2np^6 electron configuration of the valence shell of all noble gas (except Helium) atoms, is commonly called an **octet** of electrons. The octet rule, a useful generalization that applies to all types of bonding which states that when atoms bond, they lose, gain or share electrons to attain the electronic configuration ns^2np^6 of the nearest noble gas. Nearly every main-group monoatomic ion has a filled outer level of electrons (*either two or eight*), the same number as in the nearest noble gas.

Compounds such as CH_4 and NH_3 obey octet rule, whereas others like BeCl_2 , BF_3 , SF_6 and PCl_5 though stable, but do not obey octet rule. Such compounds are exceptions to the octet rule. In such compounds the central atom is either short of electrons or has excess of electrons as compared to the octet. These are discussed later in this unit. Though there are certain exceptions to the octet rule, yet it provides us a useful framework for introducing many important concepts of bonding.

Note! Octet rule states that during the formation of a chemical compound, each atom has an octet (8) electrons in its highest occupied energy level by gaining, losing, or sharing electrons.

3.1.2 Types of Chemical Bonding

In Grade 9 you have learnt in details what exactly is a chemical bond? The forces of attraction that hold atoms together are called chemical bonds. Broadly these forces of attraction can be categorised as intramolecular forces, which affect the chemical properties of the species.

There are three main types of chemical bonds – covalent, ionic and metallic bonds. In general, there is a gradual change from more metallic to more non-metallic property when moving from left to right across a period and when moving from bottom to top within a group. Three types of bonding can result from the manner in which the atoms can combine:

Ionic Bonding is formed by electron transfer from a **metal to a non-metal** with different electronegativity values.

Covalent Bonding is formed as a result of electron sharing between two **non-metals**. If the electronegativity values are very similar then it is **non-polar covalent bonding** but if the electronegativity values are much different, then it is a **polar covalent bonding**.

Metallic Bonding refers to the interaction between the delocalised electrons and the metal nuclei.

Activity 3.3



Form a group and:

1. Illustrate the formation of ionic bond between the elements from Group IA, period 2 and Group VIIA and period 3. Correlate this bonding with the electronic configuration.
2. Indicate whether each of the following formulas is a likely formula for a stable ionic compound, and give explanation for your answer:

a Rb_2O b BaCl c MgF_3 d ScBr_3 e Na_3N

Share your ideas with the rest of the class.

3.2 IONIC BONDING

At the end of this section, you should be able to:

- define ionic bonding;
- use Lewis electron dot symbols to depict main group elements;

- describe ionic bonding using Lewis electron dot symbols;
- list the favourable conditions for the formation of ionic bond;
- explain the formation of ionic bonding;
- give examples of ionic compounds;
- define Lattice energy;
- calculate lattice energy of ionic crystal from a given data using the Born-Haber cycle;
- discuss the exceptions to octet rule;
- describe the properties of ionic bonding;
- carry an activity to demonstrate the effect of electricity on ionic compounds (PbI_2 and NaCl); and
- carry an activity to investigate the melting point and solubility of some ionic compounds (NaCl and CuCl_2).

Activity 3.4

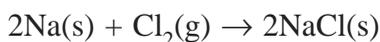


Form a group and discuss the following questions:

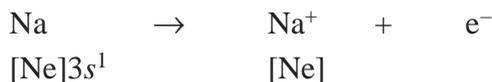
1. What types of elements are involved in ionic bonding?
2. What is ionization energy?
3. What role does electron affinity play in the formation of an ionic bond?
4. How many ionic bonds will result from the combination of magnesium and chlorine?
5. What type of bond will be formed between a metal and a non-metal?

Share your ideas with the rest of the class.

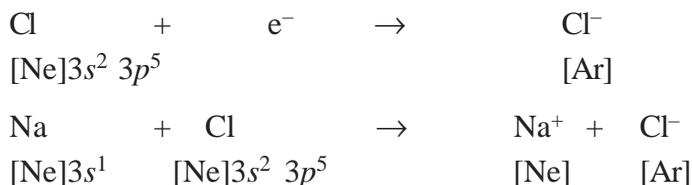
You are familiar with how sodium metal reacts with chlorine gas, Cl_2 , to form sodium chloride, NaCl , a substance composed of Na^+ and Cl^- ions.



Let us look at the electronic configurations of sodium and chlorine atoms for a possible interpretation of the reaction between them. A sodium atom, Na , by losing an electron, forms a sodium ion, Na^+ , which has the same electron configuration as the noble gas neon.



A chlorine atom, **Cl**, by gaining an electron, forms a chloride ion, **Cl⁻**, which has the same electron configuration as the noble gas argon.



When particles have opposite electric charges, a force of attraction exists between them; known as **electrostatic force of attraction**. In sodium chloride, the sodium ions and the chloride ions are held together by electrostatic force of attraction, thus forming an **ionic bond** or **electrovalent bond**.

Exercise 3.1

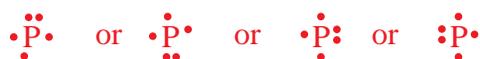
- Explain the formation of bonds in the following pairs of elements:
 - potassium and chlorine,
 - magnesium and oxygen and
 - sodium and oxygen.
- Which of the following elements will form a ionic bond with chlorine and why? Calcium, Carbon, Oxygen and Silicon
- Why ionic bond is also known as electrovalent bond?
- How many types of chemical bonding you are familiar with?
- State and explain the formation of ionic, covalent and metallic bonds. Use diagrams wherever required.
- List four important characteristics of ionic compounds.
- What observable properties can you use to distinguish one kind of bond from another?

Note! Ionic compounds are usually formed when metal cations bond with non-metal anions. The only common exception is ammonium ion which is not a metal, but it forms ionic compounds.

3.2.1 Lewis Electron-Dot Symbols

In grade 9, you practiced how to write the Lewis formula for sodium and chlorine. Do their electron configurations change when these atoms form ions?

The American Chemist Gilbert N. Lewis (1875–1946) created a simple shorthand system for depicting the electrons involved in bonding and the sequence of atoms in a molecule. In a Lewis electron-dot symbol of an atom, the element symbol represents the nucleus and inner electrons, (core electrons), and it is surrounded by a number of dots equal to the number of valence electrons. You can write the Lewis symbol of any main group element from its group number (IA to VIIIA), which gives the number of valence electrons. These are placed one at a time on the four sides of the element symbol and then paired up until all are used. For example, the Lewis electron-dot symbol for phosphorus can be written as:



The Lewis electron-dot symbols for elements of period 2 may be written as:



Activity 3.5



Form a group and:

- Use *s p d f* notation and Lewis symbols to represent the electron configuration of each of the following:
 - K^+
 - S^{2-}
 - F^-
 - Al^{3+}
- Explain how Lewis symbols and *spdf* notation differ in their representation of electron spin.

Share your ideas with the rest of the class.

Exercise 3.2

- Use Lewis electron-dot symbols to depict the formation of sodium and bromide ions from the atoms and determine the formula of the compound.

2. Use Lewis electron-dot symbols to show the transfer of electrons from magnesium atoms to nitrogen atoms to form ions with noble gas electron configurations. What is the formula and name of the product?
3. Use Lewis electron-dot symbol to show the transfer of electron from aluminium to oxygen atoms to form ions with noble gas electron configurations. What is the formula and name of the product?

3.2.2 Formation of Ionic Bonding

The formation of ionic compounds is not merely the result of low ionization energies and high affinities for electrons, although these factors are very important. It is always an exothermic process; the compound is formed because it is more stable (lower in energy) than its elements. Much of the stability of ionic compounds result from the packing of the oppositely charged **positive** and **negative** ions together. A measure of just how much stabilization results from this packing is given by the **lattice energy** (U). This quantity is the energy change occurring when gaseous ions come together to form one mole of a solid ionic compound, or the enthalpy change required for one mole of the solid ionic substance to be separated completely into ions far removed from one another.

The lattice energy is an important indication of the strength of ionic interactions and is a major factor influencing melting points, hardness, and solubility of ionic compounds. The lattice energy plays a crucial role in ionic compound formation, but it is difficult to measure it directly. Nevertheless, the lattice energies of many compounds have been determined using Hess's law of heat summation, which states that an overall reaction's enthalpy change is the sum of the enthalpy changes for the individual reactions that make it up:

$$\Delta H_{\text{total}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots$$

Lattice energies can be calculated through a Born-Haber cycle, in which a series of steps from elements to ionic compounds for which all the change in enthalpies are known except the lattice energy. This general approach to describing the energetics of ionic compound formation is applied to sodium fluoride in the steps outlined below and illustrated in **Figure 3.3**.

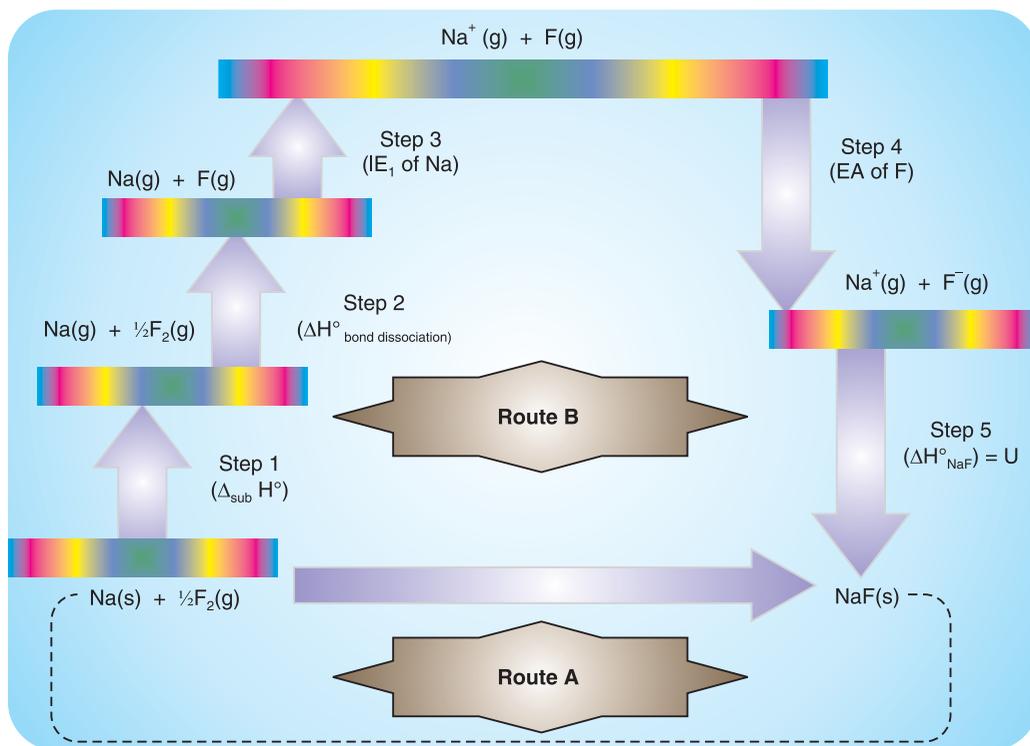


Figure 3.3 The Born-Haber cycle for NaF(s).

Consider the Born-Haber cycle for the formation of sodium fluoride. We choose steps that we can measure to depict the energy components of ionic compound formation, from which we calculate the lattice energy. We begin with the elements in their standard states, metallic sodium and gaseous diatomic fluorine. There are two routes to follow: either the direct combination reaction (**Route A**) or the multi-step cycle (**Route B**), one step of which is the unknown lattice energy. From Hess's law, it is known that both routes involve the same overall enthalpy change.

The formation of NaF(s) from its elements is shown as happening either in one overall reaction (**Route A**) or in five steps, each with its own enthalpy change (**Route B**). The overall enthalpy change for the process ($\Delta_f H^\circ$) is calculated as the sum of the enthalpy changes $\Delta H^\circ_{\text{step1}}$, through $\Delta H^\circ_{\text{step4}}$. Therefore, $\Delta H^\circ_{\text{step5}}$, the lattice energy (U_{NaF}), can be calculated.

$$\Delta_f H^\circ \text{ of NaF(s) (Route A) = sum of } \Delta H^\circ \text{ for steps in cycle (Route B)}$$

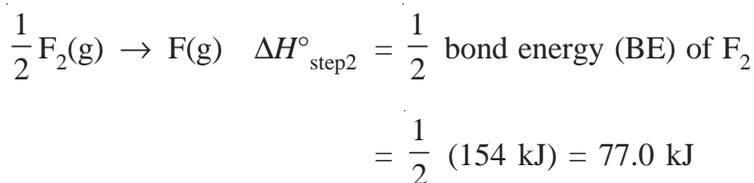
To preview **Route B**, the elements are converted to individual gaseous atoms (**Step 1** and **Step 2**), the electron transfer steps form gaseous ions (**Step 3** and **Step 4**), and the ions form a solid (**Step 5**). We identify each ΔH° by its step number:

Step 1: Converting solid sodium to separate gaseous sodium atoms involves breaking the metallic bonds that hold atoms in the sample, so it requires energy:



(This process is called atomization, and the enthalpy change is $\Delta_{\text{at}}H^\circ$.)

Step 2: Converting fluorine molecule to fluorine atoms involves breaking the covalent bond in F_2 , so it requires energy. One mole of **F** atoms are needed to form one mole of **NaF**, so start with $\frac{1}{2}$ mol F_2 :



Step 3: Removing the 3s electron from Na to form Na^+ requires energy:



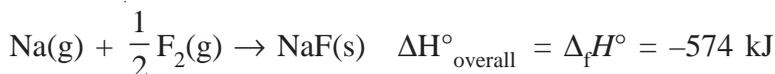
Step 4: Adding an electron to F to form F^- releases energy:



Step 5: Forming the crystalline ionic solid from the gaseous ions is the step whose enthalpy changes (**the lattice energy**) is unknown:



We know the enthalpy change of the formation reaction (**Route A**),



Therefore, we calculate the lattice energy using **Hess's Law**:

Solving for U_{NaF} gives

$$\begin{aligned} U_{\text{NaF}} &= \Delta_{\text{f}}H^\circ - (\Delta H^\circ_{\text{step1}} + \Delta H^\circ_{\text{step2}} + \Delta H^\circ_{\text{step3}} + \Delta H^\circ_{\text{step4}}) \\ &= -574 \text{ kJ mol}^{-1} - [108 \text{ kJ mol}^{-1} + 77 \text{ kJ mol}^{-1} \\ &\quad + 495 \text{ kJ mol}^{-1} + (-328 \text{ kJ mol}^{-1})] \\ &= -926 \text{ kJ mol}^{-1} \end{aligned}$$

Note that the magnitude of the lattice energy dominates the multistep process.

Exercise 3.3

- Write the formulas and names of the compounds formed from the following ionic interactions: (use periodic table)
 - The $2+$ ion and $1-$ ion are both isoelectronic with the atoms of a chemically unreactive period 4 element.
 - The $2+$ ion and the $2-$ ion are both isoelectronic with the period 3 noble gas.
 - The ions formed are the largest and smallest ionizable atoms in period 2.
- In each of the following ionic compounds identify the main group to which X belongs:
 - XF_2
 - MgX
 - X_2O_3
 - Na_2X

- For lithium, the enthalpy of sublimation is $+161 \text{ kJ mol}^{-1}$, and the first ionization energy is $+520 \text{ kJ mol}^{-1}$. The dissociation energy of fluorine is $+154 \text{ kJ mol}^{-1}$, and the electron affinity of fluorine is -328 kJ mol^{-1} . The lattice energy of LiF is $-1047 \text{ kJ mol}^{-1}$. Calculate the overall enthalpy change for the reaction?

$$\text{Li(s)} + \frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{LiF(s)} \quad \Delta H^\circ = ?$$

- The enthalpy of formation of caesium chloride is

$$\text{Cs(s)} + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{CsCl(s)} \quad \Delta H^\circ = -44.28 \text{ kJ mol}^{-1}$$

The enthalpy of sublimation of caesium is



Use these data, with other data from other sources, to calculate the lattice energy of CsCl(s)

- Using the following data:

Enthalpy of sublimation of $\text{Ca} = +178.2 \text{ kJ mol}^{-1}$
 Enthalpy of dissociation of $\text{Cl}_2 = +243.4 \text{ kJ mol}^{-1}$
 Enthalpy of formation of $\text{CaCl}_2 = -795.8 \text{ kJ mol}^{-1}$
 First and second Ionization energies for Ca are $+590 \text{ kJ mol}^{-1}$ and $+1145 \text{ kJ mol}^{-1}$ respectively.
 The electron affinity of $\text{Cl} = -348.7 \text{ kJ mol}^{-1}$
 Determine the lattice energy of CaCl_2

Factors Affecting Formation of Ionic Bonding

Activity 3.6



Form a group and discuss the following questions:

- In general, how does the lattice energy of an ionic compound depend on the charges and sizes of the ions?
- For each pair, choose the compound with the higher lattice energy, and explain your choice.
 - LiCl or CsCl
 - NaF or MgO
 - BaS or CsCl

Share your ideas with the rest of the class.

The formation of ionic bonding is influenced by various factors. Some of the major factors are presented below.

Ionization energy (IE): Elements having low IE have a more favourable chance to form a cation, thereby having a greater tendency to form ionic bonds. Thus, low ionization energy of metallic elements favours the formation of an ionic bond. That is why alkali and alkaline earth metals form ionic compounds.

Electron affinity (EA): The other atom participating in the formation of an ionic compound must form an anion by gaining electron(s) and losing energy. Higher electron affinity favours the formation of an anion. Generally, the elements having higher electron affinity favour the formation of an ionic bond. Halogens have high electron affinities, and therefore halogens generally form ionic compounds when they react with metals.

Lattice energy: When a cation and an anion come closer, they get attracted to each other due to the electrostatic (coulombic) force of attraction. The electrostatic force of attraction between oppositely-charged ions release a certain amount of energy and an ionic bond is formed. If the coulombic attraction forces are stronger, then more energy gets released and a more stable or a stronger ionic bond is formed. Larger lattice energy would favour the formation of an ionic bond. Lattice energy thus is a measure of coulombic attractive force between the combining ions. The lattice energy (U) of

an ionic compound depends directly on the product of the ionic charges ($q_1 \times q_2$), and inversely on the distance (r) between them.

$$U \propto \frac{q_1 \times q_2}{r}$$

where q_1 and q_2 are the charges on +ve and -ve ions respectively, and r is the distance between the charges q_1 and q_2 . Thus, small ions having higher ionic charge shall have larger lattice energy. If the total energy released is more than that which is absorbed, then the formation of ionic compound is favoured.

3.2.3 Exceptions to Octet Rule in Ionic Compounds

Activity 3.7



Form a group and discuss the following:

- The principal exceptions to the octet rule are found in ionic compounds in which the cations do not acquire noble gas electron configuration. Identify the cations that obey or violate the octet rule.

a FeCl_3 b CuO c NaCl d LiF

- Draw Lewis structure for CH_4 , BF_3 and SF_6 .

How many electrons are present around the central atoms, C, B and S, respectively?

What is the difference between the central atoms in terms of number of electrons?

Are these in conformity with the Octet rule?

Can you name some more examples similar to these?

Share your ideas with the rest of the class.

As you have studied in grade 9, the octet rule works well for the representative metals (Group IA, IIA) and the nonmetals, but not for the transition elements and post-transition elements. This is because they have d and f subshell orbitals.

There are certain exceptions to octet rule. We will discuss it here in context with the ionic compounds.

Less than Octet (Central Atom is Deficient of Electrons):

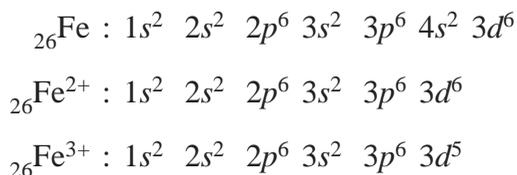
Ions of some elements which are near to helium in the periodic table do not obey the octet rule. The tendency of these atoms (H, Li, Be and B) is to attain an arrangement of two electrons like the noble gas He (duplet configuration), which is also a stable configuration. Hydride ion (H^-), lithium ion (Li^+), beryllium ion (Be^{2+}) and boron ion (B^{3+}) are isoelectronic with He. Therefore, compounds like LiH , BeCl_2 and BF_3 are stable in spite of short of electrons around the central atom than the octet. In these cases the number of electrons around Li, Be and B is 2, 4 and 6 respectively. Although atoms with less than an octet may be stable, they will usually attempt to form a fourth bond to get eight electrons. BF_3 is stable, but it will form BF_4 when possible.

More than Octet (18-Electron Rule):

The ions of some transition elements and post-transition elements do not usually obey the octet rule. For transition metals, the 18-electron rule replaces the octet rule, due to the involvement of d orbitals of these atoms. The atoms of these elements would have to lose a large number of electrons to achieve the noble-gas configurations. This will require enormous amount of ionization energy, which cannot be available easily. Nevertheless, these elements also form positive ions. But these ions do not have the usual noble gas valance shell electron configurations of ns^2np^6 and are not isoelectronic with any of the noble gases. It is important to note that when these atoms form positive ions, electrons are always lost first from the shells with the highest value of the principal quantum number (n).

Consider the electron configurations of the ions of the transition elements iron and zinc and the post-transition elements gallium and tin.

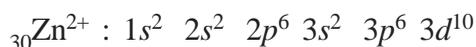
Electron Configurations of Iron:



A stable ion of iron with valence shell electron configuration is $3s^2 3p^6 3d^5$ which is not isoelectronic with a noble gas. Fe^{2+} is a well-known stable ion with a valence shell electron configuration $3s^2 3p^6 3d^6$ which is not isoelectronic with any of the noble gases.

Electron configurations of zinc:

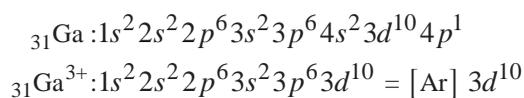
Also,



is not isoelectronic with any of the noble gases.

Electron configurations of gallium:

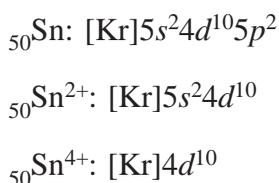
The post-transition element gallium (Ga) loses electrons first from the 4p orbital and then from the 4s orbital to form a Ga^{3+} ion as



On closely examining the electron configurations of Zn^{2+} and Ga^{3+} , we will realize that ions have completely-filled outer subshells and a noble gas core. Their valence electron configuration can be generally represented as $ns^2 np^6 nd^{10}$.

Electron configurations of tin:

The heavier post-transition elements like Pb and Sn lose the p electrons or both the p and s electrons from the valence shell.



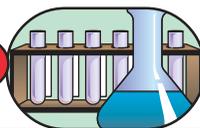
Generally, these properties are exhibited by ions of elements from

- i)* Group IB and Group IIB (*transition elements*) and
- ii)* Group IIIA and Group IVA (*heavier post-transition elements*)

Neither of these configurations are noble gas configurations.

3.2.4 Properties of Ionic Compounds

Experiment 3.1



Investigation of Solubility of Ionic Compounds

Objective: To investigate the solubility of NaCl and CuCl_2

Apparatus and Chemicals: Test tube, water bath, Bunsen burner, NaCl , CuCl_2 , ethanol, hexane and benzene

Procedure:

1. Place about 0.5 g each of NaCl and CuCl_2 in three separate test tubes and add about 2.5 mL of water and shake well.
2. If some residue is there in the test tube/s, heat it on Bunsen burner.
3. Repeat step 1 afresh using ethanol, hexane and benzene.

(If the salt is soluble at room temperature, do not heat it.)

Observations and analysis:

Prepare an observation table in your notebook for the solubility of NaCl and CuCl_2 in all the three solvents at room temperature and on heating (wherever required) and record the observations.

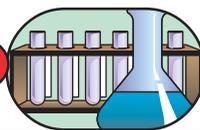
| Solvent | NaCl | CuCl_2 |
|---------|---------------|-----------------|
| Water | | |
| Ethanol | | |
| Hexane | | |
| Benzene | | |

Inference/Conclusion

Interpret the observation table and give results.

Make a generalised statement about the solubility of ionic compounds in polar and non-polar solvents.

Experiment 3.2



Thermal behaviour of ionic compounds

Objective: To study the effect of heat on ionic compounds.

Apparatus and chemicals: Test tubes, test tubes holders, sodium chloride, and copper (II) chloride.

Procedure:

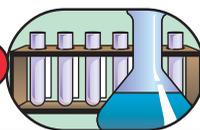
1. Take two hard glass test tubes and label them as A and B.
2. Add 0.5 g each of dry sodium chloride crystals and copper (II) chloride in test tubes A and B respectively.
3. Hold these test tubes with the help of test tube holders.
4. Heat the tubes simultaneously on the Bunsen burner flame first slowly and then strongly while shaking intermittently.

Caution: Take care not to inhale any fumes/vapours formed during heating.

Observations and analysis:

1. Do the crystals melt?
2. Do they have high or low melting points?

Experiment 3.3



Electrical Conductivity of Ionic Compounds

Objective: To test the electrical conductivity of molten compounds

Apparatus and chemicals: 9-volt battery, 6-watt bulb with a bulb holder, conducting wires, two carbon rods, lead (II) iodide or lead (II) bromide.

Procedure A:

1. Connect the circuit as shown in **Figure 3.3** in which a 9 volt DC is connected via a bulb.
2. Using about 2 cm depth of PbI_2 in a small beaker, test the conductivity of the lead iodide crystals. Do not throw away the PbI_2 and be careful not to contaminate the sample because you will reuse it later. (Note: it could be

argued that a fairer test of the solid compound would be to use a lump of the compound rather than its powder).

3. Test the conductivity of large crystals of copper (II) sulphate and sodium chloride if any of them are available in your laboratory.

Procedure B:

1. Now heat the same lead (II) iodide or Lead (II) bromide (used in the above experiment) in a beaker on a tripod and wire gauze or in a boiling tube supported by a clamp and stand until it melts;
2. Test the conductivity of the molten compound by dipping the carbon electrodes (carbon rods) into the molten compound as shown in the figure below:

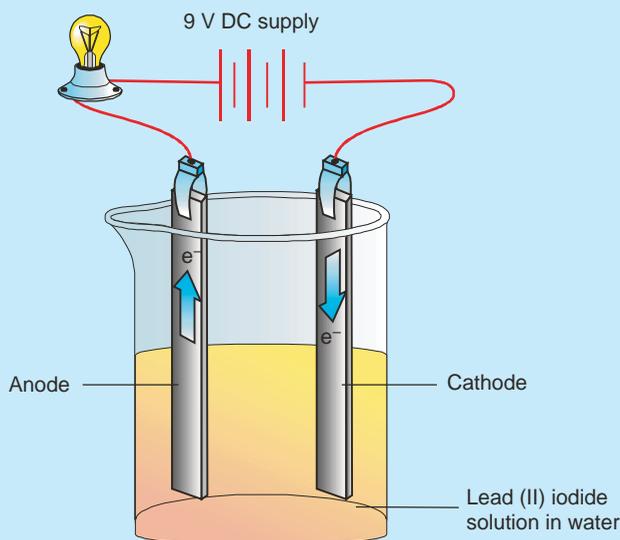
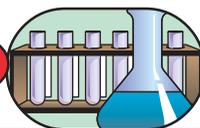


Figure 3.4 Conductivity of electrolytes.

Observations and analysis:

1. What did you observe?
2. Which of the compounds (molten or solid) conduct electricity? Why?
3. All compounds contain at least two elements. Examine the names of those compounds which conduct electricity when in molten state and decide to which classes of elements the components of these compounds belong. Name the type of bonding that exists in the compounds used.

Experiment 3.4



Electrical Conductivity of Ionic compounds

Objective: To test the electrical conductivity of the aqueous solutions of some common ionic compounds.

Apparatus and chemicals: 9-volt battery, 6-watt bulb with a bulb holder, conducting wires, two carbon rods, H_2O , lead (II) iodide, NaCl .

Procedure:

1. Dissolve the compound in 50 mL of water in two separate beakers.
2. Connect the same circuit you used above and test the conductivity of each aqueous solution.

Observations and analysis:

- a Predict what happens at the electrodes based on the type of the compound used for the experiment.
- b Do you expect the same product(s) at the respective electrodes when electricity passes through molten and aqueous solutions of the compounds?

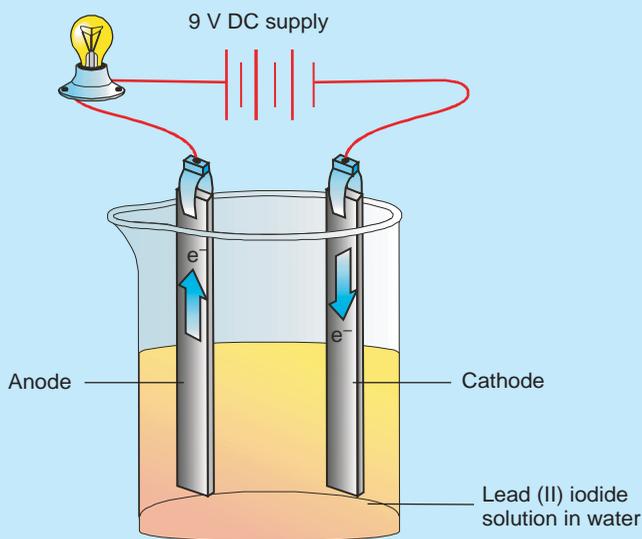


Figure 3.5 Electrochemical cell showing the conductivity of an aqueous solution.

Let us Summarise

Ionic compounds are crystalline solids at room temperature. The fundamental units of ionic solid are positive and negative ions. Crystalline ionic solids are usually brittle and non-conductors of electricity, although molten crystals may be good conductors. They usually have high melting and boiling points.

Ionic compounds are nonvolatile.

Ionic compounds are usually soluble in inorganic solvents (water is the most common solvent for ionic compounds) but insoluble in organic solvents like benzene, ethanol and carbon tetrachloride.

Note! Ionic compounds are very resistant to heat but many will be easily broken by water.

3.3 COVALENT BONDING AND MOLECULAR GEOMETRY

At the end of this section, you should be able to:

- define covalent bonding;
- explain the formation of covalent bonding;
- give examples of covalent molecules;
- draw Lewis structures or electron dot formulas of some covalent molecules;
- illustrate the formation of coordinate covalent bonding using examples;
- define resonance structures;
- draw resonance structures of some covalent molecules and polyatomic ions;
- discuss the exceptions to the octet rule in covalent bonding;
- distinguish between polar and non polar covalent molecules;
- describe the properties of covalent molecules;
- carryout an activity to investigate the effects of heat, electricity and some solvents on covalent compounds (naphthalene, graphite, iodine and ethanol);
- describe the valence shell electron pair repulsion theory (VSEPR);
- distinguish between the bonding pairs and non bonding pairs of electrons;
- describe how electron pair arrangements and shapes of molecules can be predicted from the number of electron pairs;
- explain why double bonds and lone pairs cause deviations from ideal bond angles;

- explain the term dipole moment with the help of a diagram;
- describe the relationship between dipole moment and molecular geometry;
- describe how bond polarities and molecular shapes combine to give molecular polarity;
- predict the geometrical shapes of some simple molecules;
- construct models to represent shapes of some simple molecules;
- define intermolecular forces;
- name the different types of intermolecular forces;
- explain dipole dipole interactions;
- give examples of dipole dipole interaction;
- define hydrogen bonding;
- explain the effect of hydrogen bond on the properties of substances;
- give reason why H bonding is stronger than ordinary dipole dipole interaction;
- explain dispersion (London) forces;
- give examples of dispersion forces; and
- predict the strength of intermolecular forces for a given pair of molecules;

Formation of Covalent Bonding

Activity 3.8



Form a group and attempt the following as per the instructions:

1. Give one main difference between ionic and covalent bond.
2. What happens to the valence electrons when a covalent bond is formed between two atoms?
3. Explain the formation of polar covalent and coordinate covalent bond.
4. Draw Lewis dot structures for AlCl_4^- and BH_4^- .
5. Arrange single, double and triple bonds in ascending order of their bond strength and bond lengths. Justify your answer.
6. Describe the interactions that occur between individual chlorine atoms as they approach each other to form chlorine molecules (Cl_2). What combination of forces gives rise to the energy holding the atoms together and to the final internuclear distance.

Share your ideas with the rest of the class.

When elements from group IA (period 2 onwards), VIA or VIIA combine together, an ionic bond is formed. What will happen if two atoms of the same element or the elements from any of these groups combine together?

Consider the formation of hydrogen molecule (H_2). When two hydrogen atoms are far apart, each behaves as though the other were not present. As they approach each other and the distance between the two nuclei decreases, each nucleus starts to attract the other atom's electron, which lowers the potential energy of the system. Attractions continue to draw the atoms closer, and the system becomes progressively lower in energy. As attractions increase, repulsions between the nuclei and the electrons will also increase. At some internuclear distance, maximum attraction is achieved in the face of the increasing repulsion, as the system has its minimum energy. Any shorter distance would increase repulsions and cause a rise in potential energy (see **Figure 3.1**). Thus, a covalent bond, such as the one that holds the hydrogen atoms together, arises from the balance between nucleus-electron attractions and electron-electron and nucleus-nucleus repulsions. Therefore, a covalent bond is formed when a pair of electrons is shared between two atoms. Some examples of covalent molecules are HCl , H_2S , C_2H_4 , N_2 , CCl_4 , BCl_3 , H_2O , NH_3 , SO_2 , PCl_5 , O_3 , etc. Generally, substances that contain covalent bonds are called molecules.

Note: Ionization energy of hydrogen ($IE_1 = 1312 \text{ kJ mol}^{-1}$) is very high making it difficult to lose electron.

Representation of Covalent Bond (Drawing Lewis Structures)

The representation of covalent bonding through Lewis symbols and shared electron-pairs is called a **Lewis structure**. Lewis structure for hydrogen molecule formed from hydrogen atoms is



If we “double count” the shared electrons each **H** atom appear to have two electrons in its valence shell analogous to the electron configuration of helium.

Similarly, consider fluorine, which also exists in the diatomic form, F_2 . Fluorine atoms are also joined by a covalent bond.



Each fluorine atom in the fluorine molecule has eight valence electrons, an arrangement similar to that of the noble gas argon. The fluorine atoms obey the octet rule. The shared pairs of electrons in a molecule are called **bonding pairs**. The other electron pairs that stay with one atom and are not shared are called non-bonding pairs or lone pairs.

We can write the Lewis formula for a covalent compound of known geometry by using the following rules.

- Determine the total number of valence electrons. It is this number of electrons that must appear in the final Lewis structure. The total number of electrons for a molecule is the sum of the valence electrons for each atom. For a polyatomic anion, which has one or more extra electrons, add one electron for each unit of negative charge. For a polyatomic cation, which is missing one or more electrons, subtract one electron for each unit of positive charge.

Exercise 3.4

Determine the total number of valence electrons for the following species:

- | | | | |
|---|--------------------|---|------------------------|
| a | CO_2 | c | NH_4^+ |
| b | SO_4^{2-} | d | N_2O_4 |

- Write the skeletal structure. The most electropositive atom usually occupies the central position. Connect bonded atoms with an electron-pair bond (a dash). Hydrogen is an exception; it is always a terminal atom, even when bonded to a more electronegative atom.
- Place electron pairs around terminal atoms so that each (except hydrogen) has an octet.
- Assign any remaining electrons as lone-pairs around the central atom.
- If at this stage, a central atom has fewer than eight electrons, a multiple bond(s) is likely. Move one or more lone-pair of electrons from a terminal atom(s) to a region between it and the central atom to form a double or a triple bond.

Exercise 3.5

- Write a plausible Lewis structure of:

| | | | |
|---|--------------------------------------|---|--------------------------------|
| a | nitrogen trichloride, NCl_3 | b | chlorate ion, ClO_3^- |
| c | phosphonium ion, PH_4^+ | d | phosgene, COCl_2 |
- Draw a Lewis structure for CO_3^{2-} , SF_4 and HCOOH (formic acid).
- Which of the following atoms cannot serve as a central atom in a Lewis structure O, He, F, H, P? Explain.
- Write a plausible Lewis structure for carbonyl sulphide, COS .

Coordinate-Covalent Bonding

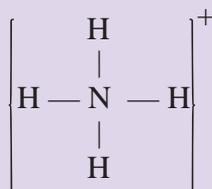
What is a coordinate covalent bond?

Activity 3.9



Form a group and discuss the following:

1. Why (a) the ammonia molecule, (b) the oxygen atom can participate readily in coordinate covalent bonding.
2. Use Lewis structures to show the formation of coordinate covalent linkage between (a) phosphorus trichloride and oxygen (b) boron trifluoride and ammonia.
3. In the following structure of ammonium ion, can you identify the coordinate covalent bond?



Share your ideas with the rest of the class.

Covalent bonds are formed through the contribution of one electron each by atoms involved in an electron-pair bond. There is another possibility in which one atom can “donate” two of its electrons to provide the shared pair between itself and an “acceptor” atom. When one atom provides both the electrons for a shared pair, the bond is called a **coordinate-covalent bond**.

Some examples of molecules which contain coordinate-covalent bond include O_3 , NH_3BF_3 and POCl_3 .

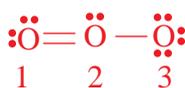
Resonance Structures

Discuss the concept of resonance. What is the difference between a resonance structure and a resonance hybrid?

For some molecules, there is no best choice between a number of equally acceptable Lewis structures. Consider the simple example of ozone, O_3 , in which the arrangement of nuclei is $\text{O}-\text{O}-\text{O}$. This molecule has $6 \times 3 = 18$ valence electrons, and it is possible to draw two possible structures for O_3 :

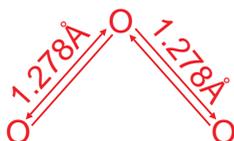


(I)

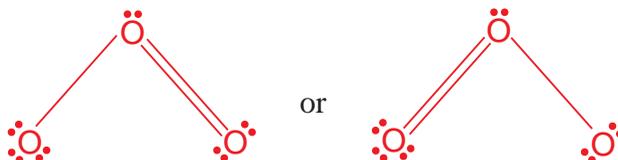


(II)

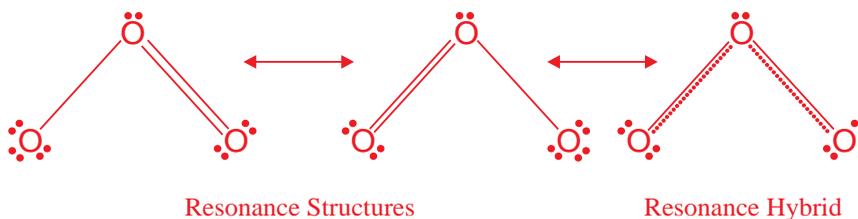
Both the structures satisfy octet rule. The two structures for O_3 suggest that the bond between O^1 and O^2 differs from that between O^2 and O^3 one single bond and one double bond. Therefore, in each of the two structures one bond should be a single bond while the other a double bond. If it is so then one bond (double bond) should be shorter than the other bond (single bond). But experimental evidences show that both the bonds are exactly equivalent having same bond lengths and bond strengths.



Since both the bonds are identical which one is a double bond?



The Lewis structure is equivalent except for the placement of the electrons (i.e., the location of the double bond). In such a situation, the correct way to describe ozone molecule as Lewis structures would be:



This indicates that the ozone molecule is described by an average of two Lewis structures (i.e. the resonance forms). The bond-lengths between the oxygens are intermediate between characteristic single and double bond-lengths between a pair of oxygen.

This description of O_3 is called **resonance**, a circumstance in which two or more possible Lewis structures can be written and the true structure is a composite or hybrid of them. The different structures used to represent the molecule or ion are called **contributing structures** or **resonance structures**, and we write them linked by double-headed arrows. The actual species that exists is called a **resonance hybrid**. The resonance structures differ only in the distribution of electrons.

Known misconceptions about the structure of ozone:

- The bond lengths between the central oxygen and the other two oxygen atoms are identical.
- It may be expected that if one bond is a double bond, then it should be shorter than the other (single) bond.

In molecules such as CH_4 , H_2S , NF_3 , PF_5 , SF_6 etc in which resonance is not involved, bonding electron pairs can be described as existing in fairly well-defined regions between the two atoms. These electrons are localized. In O_3 , to produce O-to-O bonds that are intermediate between single and double bonds, we need to think of some of the electrons in the resonance hybrid as being delocalized. Delocalized electrons are bonding electrons that are spread over several atoms.

Activity 3.10



Form a group and discuss the concept of resonance. When is this concept applied to depict adequately the bonding in a molecule; explain using suitable examples.

Share your ideas with the rest of the class.

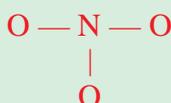
Example 3.1

Write three equivalent Lewis structures for the nitrate ion, NO_3^- . Describe its resonance hybrid structure.

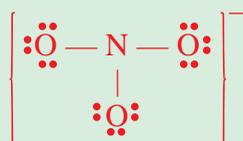
Solution:

a There are $5 + (3 \times 6) + 1 = 24$ electrons

b The skeletal structures is:

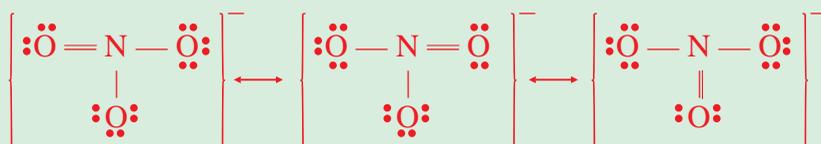


c Place three lone pairs of electrons on each O atom.



d All 24 electrons have been assigned.

e The central N atom has only six valence electrons as shown. Move a lone pair of electrons from one of the terminal oxygen atom to form a double bond to the central N atom. Because the double bond can go to any one of the three O atoms, we get three structures that differ only in the position of the double bond.



The resonance hybrid, which involves equal contributions from these three equivalent resonance structures, has N-to-O bonds with bond length and bond energies intermediate between single and double bonds.

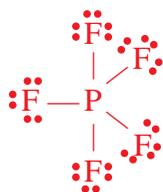
Exercise 3.6

- Write three equivalent structures for the SO_3 molecule that obey the octet rule.
- Draw Lewis structures of all the important resonance forms of each of the following:

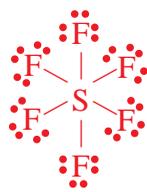
a NO_2F (N central) b HNO_3 c NO_2^-

More than octet (central atom has excess of electrons):

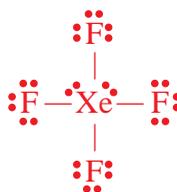
Molecules whose central atoms have more than eight electrons (Expanded octet). This group consists of molecules containing central atoms from periods 3, 4, 5, and 6. PF_5 , SF_6 and XeF_4 are typical examples of this type;



10 electrons around P



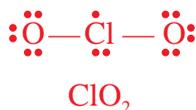
12 electrons around S



12 electrons around Xe

Molecules containing an odd number of electrons:

Even if stable molecules of this kind are rare, they do exist. Some examples are ClO_2 , NO and NO_2 having 19, 11 and 17 valence electrons respectively. The best way to suggest the Lewis-like structure for these molecules is:

**Exercise 3.7**

- Suggest the Lewis-like structure for NO and NO_2 molecules.
- The following species do not obey the octet rule. Draw a Lewis structure for each one and state the type of octet rule exception:

| | | | |
|------------------|--------------------|-------------------|-------------------|
| a BH_3 | b AsF_4^- | c SeCl_4 | d PF_6^- |
| e ClO_3 | f BrF_3 | g BeF_2 | h XeF_2 |

Polar and Non-Polar Covalent Molecules

Activity 3.12



From a group and collect the following substances. Divide them in two groups. Group A consists of:

- a Naphthalene
- b Sodium chloride
- c Iodine
- d Wax

and group B consists of the following solvents

- i Carbon tetrachloride
- ii Water
- iii Methylbenzene

Each solid in group A dissolves best in at least one solvent in group B. Point out the solid and the solvent it dissolves in and give reasons for your choice.

When bonding electron-pairs in a covalent bond are shared equally, the result is a nonpolar covalent bond. When the atoms are alike in a covalent bond, the two atoms with equal electronegativities will exhibit equal sharing of an electron pair, and the electrons are not drawn closer to one atom than to the other. The **H–H** and **Cl–Cl** bonds are nonpolar. In a covalent bond between atoms of different electronegativities, there is an unequal sharing of an electron pair and the electrons spend more of their time around the more electronegative atom. Such a bond is said to be polar covalent bond. The **H–Cl** bond is a polar bond. This is because chlorine is more electronegative than the hydrogen atom and represented as



to indicate the polar nature of a bond. In the representation the $\delta+$ and $\delta-$ (read “delta plus” and “delta minus”) signify that one end (**H**) is partially positive and the other end (**Cl**) is partially negative. The term partial charge signifies something less than the full charges of the ions that would result from complete electron transfer.

For a diatomic molecule having a polar covalent bond, such as **HCl**, we can describe a quantity called the **dipole moment**, which is a vector sum of the bond moments in a

molecule. Bond moment is a measure of polarity of a diatomic covalent bond. The **dipole moment** (μ) is defined as the product of the magnitude of the charge (δ) at either end of the dipole multiplied by the distance (d) that separates the charge.

$$\mu = \delta \times d$$

The SI-unit of dipole moment is coulomb-metre (C.m). Dipole moments are often expressed in the non-SI unit debye (D), where $1\text{D} = 3.33564 \times 10^{-30} \text{ Cm}$.

Note! For a diatomic molecule, the bond moment is the dipole moment. The dipole moment of a polyatomic molecule (three or more atoms) depends on the geometry of the molecule. If the bond moments are equal in magnitude but opposite in direction, then they will cancel each other and the resultant dipole moment will be zero, provided that the vector sum of the bond moments is zero.

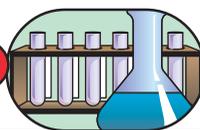
Exercise 3.8

Both CO_2 and BCl_3 have zero dipole moments, but the $\text{C} = \text{O}$ and $\text{B} - \text{Cl}$ bond moments are not zero. Explain.

Properties of Covalent Compounds

Tetrachloromethane (carbon tetrachloride) is a covalent compound. Would you expect it to be a conductor of electricity?

Experiment 3.5



Investigating the effect of heat on covalent compounds

Objective: To determine the melting points of naphthalene.

Apparatus and chemicals: Thermometer, stirrer, beaker, melting point tube, naphthalene, glycerine, Bunsen burner.

Procedure:

Set up the apparatus shown in **Figure 3.6**. Place a small amount of naphthalene in melting point tube. Attach the tube to the side of the thermometer (the liquid in the beaker will hold the tube in position). Heat the beaker slowly. When the naphthalene melts, record the reading on the thermometer. Determine the melting point of iodine and graphite similarly.

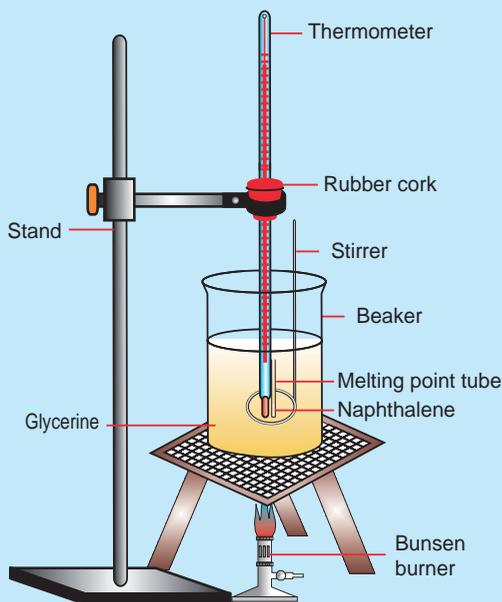
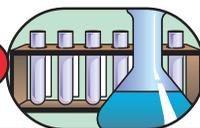


Figure 3.6 Determination of melting point of naphthalene.

Observations and analysis:

Check your result by referring to standard melting point values. Discuss on possible reasons for the differences in melting point compared to the standard melting point.

Experiment 3.6



The effects of heat, electricity and some solvents on covalent compounds

Objective: To test the effects of heat, electricity and some solvents on covalent compounds.

Apparatus and chemicals: Beakers, stirrer, test tubes, water, alcohol, naphthalene, iodine crystals, and graphite.

Procedure:

You are provided with four substances, namely naphthalene, graphite, iodine and ethanol. Investigate the effect of heat and electricity on these substances as well as their solubility in water and other non-polar (organic) solvent.

Observations and analysis:

Record your observations in the following table by drawing on your note book.

| Substance → | Naphthalene | Graphite | Iodine | Ethanol |
|---------------------------------|-------------|----------|--------|---------|
| Property ↓ | | | | |
| Effect of Heat | | | | |
| Effect of Electricity | | | | |
| Solubility in water | | | | |
| Solubility in non-polar solvent | | | | |

Results and Discussion:

1. Draw your conclusion from the above observations.
2. Do these substances conduct electricity either in the solid state or in the molten (liquid) state?
3. Is there any chemical reaction that takes place at the electrodes?

Activity 3.13



Form a group and discuss the following question:

Why does ammonia, NH_3 , dissolve in water but methane, CH_4 does not?

Share your ideas with the rest of the class.

Unlike any ionic compound, many of the covalent compounds are found in gaseous state at room temperature. Consider methane (CH_4), the simplest compound between carbon and hydrogen, which have comparable, intermediate electronegativities. It is a gas at room temperature. Cooling methane to a low temperature condenses it first to a liquid and then to a solid. Unlike melted ionic compounds, liquid covalent compounds do not conduct electricity. Therefore, liquid methane does not conduct electricity. Covalent compounds are molecular substances. They have low melting and boiling points. Most covalent compounds are soluble in non-polar solvents. Generally,

- Covalent compounds exist as separate molecules because electrically neutral atoms form them and the forces of attraction between these molecules are relatively weak.
- Due to weak intermolecular forces, many covalent molecules or covalent compounds are liquids or gases at room temperature. However, some covalent molecules like iodine are solids at room temperature.

Liquid — H_2O , Br_2 ,

Gas — CO_2 , H_2 , Cl_2 , NH_3 .

- Covalent compounds are volatile.
- Generally they have low melting points and boiling points.
- Covalent compounds are generally insoluble in water. Most covalent compounds are soluble in nonpolar solvents.
- Nonpolar covalent compounds are non-electrolytes because they do not conduct electricity.

3.3.1 Molecular Geometry

Valence Shell Electron Pair Repulsion (VSEPR) Theory

A molecule is an independent, minute architecture extending in three dimensions throughout its tiny volume of space. Let us discuss the shapes of molecules and their effect on the properties of a molecule. We start by describing the Valence Shell Electron Pair Repulsion (VSEPR) model, which allows us to convert two-dimensional Lewis structure into three-dimensional (3D) geometry.

The basic principle of VSEPR theory is that the pair of valence shell electrons around the central atom stays as far apart from each other as possible to minimize repulsion among them. For simplicity, a set of electrons is defined as any number of electron-pairs that occupies a localized region around a central atom. This set may consist of a single bond (–), a double bond (=), a triple bond (\equiv), lone-pair(s) or in some cases even a lone (single) electron. Each of these is a separate set of electrons that repels the other groups and occupies as much space as possible around the central atom - one set of electrons repels the other sets to maximize the angles between them. The three-dimensional arrangement of these sets gives rise to the shape of the molecule.

Electron Pair Arrangement and Molecular Shape

The electron pair arrangement is defined by the sets of electrons, both bonding and nonbonding (lone-pair), around the central atom. On the other hand the molecular shape is defined by the relative positions of the atomic nuclei. Molecular shapes that occur when all the surrounding electron sets are bonding sets differ from molecular shapes when some of the electron sets are non-bonding sets. Thus, the same electron set arrangement can give rise to different molecular shapes. To classify molecular

shapes, the AX_mE_n designation is assigned, where A is the central atom, X is the terminal atom, E is lone-pair (nonbonding) electron sets, m and n are positive integers.

The arrangements that best minimize repulsions naturally depend on the number of electron sets. Repulsive forces among valence pairs diminish in the following order:

Lone pair vs lone pair > lone pair vs bonding pair > bonding pair vs bonding pair.

In this section, you will see electrons set ranging from two to six around the central atom. Two electron sets locate themselves on opposite sides of the atom in a **linear arrangement**, three sets form a **trigonal planar** structure, four sets arrange themselves at the corners of a **tetrahedron**, five sets define a **trigonal bipyramid**, and six sets form an **octahedron**.

In the case of multiple (*double or triple*) bonds the counting is not different, because you are already informed that a double bond is considered as one set and a triple bond as another set of electrons. For example, in the case of CO_2 , $\text{O}=\text{C}=\text{O}$, there are two sets of electrons around the central atom, acetylene, C_2H_2 , $\text{H}-\text{C}\equiv\text{C}-\text{H}$, two sets of electrons around each of the central atoms.

Guidelines for Applying VSEPR Model

The VSEPR model is an approach of using the number of electrons surrounding a central atom to study the molecular structures, based on the theory that the structure around a given atom is determined principally by minimizing electron-pair repulsion. Here are some guidelines for applying the VSEPR model:

1. First, write the Lewis structure of the molecule, in this model, consider only the electron sets (pairs) of the central atom.
2. Count the total number of electron sets around the central atom, including both the bonding pairs and lone pairs. Usually a lone pair, a single unpaired electron and any bond: single, double or triple, each count as one area of electron density. For species with more than one central atom, treat each central atom separately.
3. Use the VSEPR geometry to predict the shape of the molecule.
4. In predicting bond angles, bear in mind that the repulsion of the lone pairs is stronger than between those of the bonding pairs. VSEPR theory is best used as a tool to explain why a given structure is distorted rather than as a predictive tool.

In explaining why the distortion occurs you need to balance three competing influences:

- lone pairs take up more space than bonding pairs. Repulsions between electrons in a lone-pair and the other electrons (in either bonds or other lone pairs) may cause distortions in the structure.
- triple bonds are fatter than double bonds, which are fatter than single bonds. The amount of electron-electron repulsion experienced between a bond and lone pairs or other bonding pairs decreases in the order: triple > double > single. Therefore, we expect that a triple bond may cause more distortions in the structure than either a double or single bond and that a double bond will cause more distortion when compared to a single bond.
- bonds which involve a significant difference in electronegativity between the atoms in the bond will have the electrons in the bond distorted toward the more electronegative atom. This will decrease electron density near the central atom and lessen the repulsion between this bonding-pair and other electron-pairs in the molecule.

Molecular Shape and Molecular Polarity

Activity 3.14



Form a group and discuss the following:

Water has a resultant dipole moment of 6.23×10^{-30} C m (1.87D). Explain why this fact proves that the H_2O molecule must have a bent shape.

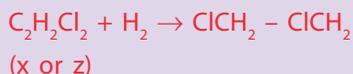
Share your ideas with the rest of the class.

Many aspects of molecule's chemical behaviour can be understood if one knows the geometry (*shape*) of a substance. Molecular shape affects many properties of the molecule like molecular polarity, which in turn influence melting and boiling points, solubility, and even reactivity. Molecular polarity is created by molecules with a net imbalance of charge. In molecules with more than two atoms, both shape and bond polarity determines the molecular polarity.

*Bond Polarity and Dipole Moment***Activity 3.15**

Form a group and discuss the following questions:

There are three different dichloroethenes, $C_2H_2Cl_2$, which we can designate x , y and z . Compound x has no dipole moment, but compound z does. Compound z and x each combine with hydrogen to give the same product:



What are the structures of x , y and z ? Would you expect compound y to have a nonzero dipole moment?

Share your ideas with the rest of the class.

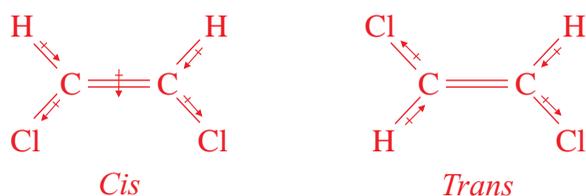
Polar bonds do not necessarily lead to polar molecules. For example, the large electronegativity difference between C and oxygen makes each C-O bond quite polar. However, because carbon dioxide (CO_2) is a AX_2 type molecule with two sets of electrons around the central atom, and its shape is **linear**, and its bonds are directed 180° from each other, so there is no net dipole moment (μ); $\mu = 0$ D

Another molecule with identical atoms bonded to the central atom is water. Unlike carbon dioxide, water has a significant dipole moment ($\mu = 1.87$ D). Both water and carbon dioxide are triatomic molecules and you may expect them to exhibit similar shape and polarity. Due to the effect of the lone pairs of electrons on its shape, water is a polar molecule. In each O-H bond, electron density is pulled toward the more electronegative O atom, but the bond polarities do not counterbalance each other, because the water molecule is V-shaped. Instead, the bond polarities partially reinforce each other, and the oxygen end of the molecule is considerably more negative than the other end.

Carbon dioxide and water demonstrate how molecular shape influences polarity. When two or more different molecules have the same shape, the nature of the atoms surrounding the central atom can have a major effect on the polarity of a molecule. Consider tetrachloromethane (CCl_4) and trichloromethane ($CHCl_3$), two AX_4 type molecules - tetrahedral shape with different polarities. In CCl_4 , the surrounding atoms are all Cl atoms. Although each C-Cl bond is polar, the molecule is nonpolar because the individual bond polarities counterbalance each other. In $CHCl_3$, an H atom substitutes for one of the Cl atoms, disturbing the balance and giving chloroform a significant dipole moment.



If you consider the two constitutional isomers of dichloroethane ($\text{C}_2\text{H}_2\text{Cl}_2$), they have the same molecular formula. However, they have different physical and chemical properties. VSEPR theory predicts that all the nuclei lie in the same plane with a trigonal planar molecular shape around each carbon atom.



The trans isomer has no dipole moment ($\mu = 0 \text{ D}$) because the C – Cl bond polarities balance each other. In contrast, the cis-isomer is polar ($\mu = 1.90 \text{ D}$) because the bond dipoles partially reinforce each other, with the molecular dipole pointing between the Cl atoms.

Bond Angle

Bond angle is the angle formed by two surrounding atoms with the central atom at the vertex. Ideal bond angles are observed when all the bonds around a central atom are identical and connected to the same type of atom. When this is not the case, such as when lone pairs, multiple bonds, or different surrounding atoms are present, the bond angles deviate from the ideal angles.

Predicting the Shapes of Molecules

The geometrical shapes of some simple molecules can be predicted based on the following general patterns:

Molecular Shapes with Two Electron Sets (Linear Arrangement- AX_2 type)

The repulsion of two electron groups with each other results in the assignment on opposite sides of the central atom in a straight line. The linear arrangement of electron sets results in a linear molecular shape and bond angle of 180° . All AX_2 type

molecules or ions are linear in geometry. The examples of the molecules of this type are CO_2 , BeCl_2 , CS_2 , HCN , etc.

Molecular shapes with three electron sets (Trigonal Planar Arrangement, AX_3 type)

Three electron sets around the central atom repel each other to lie at the corners of an equilateral triangle. This is the trigonal planar arrangement and the ideal bond angle is 120° : Example: BF_3 , NO_3^- , HCHO (formaldehyde) etc. Another molecular shape is possible within this electron set arrangement, with two bonding and one lone pair (AX_2E type). The examples of this type include PbCl_2 , SnBr_2 , SO_2 , O_3 , etc. They have bent (*V-shaped or angular*) geometry. This is the first example of the effect of a lone-pair on adjacent bonding-pairs. Since a lone-pair is held on the central atom, it exerts a stronger repulsion than bonding pair.

Thus, in AX_2E type species a lone-pair repels bonding-pairs more strongly than bonding-pairs repel each other. The repulsion increases the angle between lone-pair and bonding-pair, which decreases the angle between bonding-pairs. Note the large decrease from the ideal 120° angle in AX_2E type molecules. (Example $\text{SnCl}_2 = 95^\circ$).

Molecular Shapes with Four Electrons Sets (Tetrahedral Arrangement, AX_4 Type)

Note that AX_3E and AX_2E_2 types are with four electron sets like AX_4 type but differ in shape and bond angle because of the presence of lone pair(s) on the central atom.

In three dimensions, the four electron sets can move farther apart and point to the corners of a tetrahedron, giving a bond angle of 109.5° . Therefore, all molecules or ions with four electron sets around the central atom adopt the tetrahedral arrangement.

Some of the examples of this type are CH_4 , NH_4^+ , SO_4^{2-} . When one of the four electron sets in the tetrahedral arrangement is a lone pair, the molecular shape is that of a **triangular pyramid** (AX_3E type). The measured bond angle is slightly less than the ideal 109.5° . In ammonia (NH_3), for example, the lone pair forces the N–H bonding pairs together, and the H–N–H bond angle is 107.3° . When the four sets of electrons around the central atom include two bonding and two non-bonding sets, the molecular shape is bent, V-shaped or angular (AX_2E_2 type). Recall that one of the shapes in the trigonal planar arrangement - that with two bonding sets and one lone pair-is also

called **angular** or bent or **V-shaped** (AX_2E type), but its ideal bond angle is 120° , not 109.5° . Water is the most important V-shaped molecule in the tetrahedral arrangement of electrons. We would expect the repulsions between its two lone-pairs to have a greater effect on bond angle than the repulsions from the single lone pair in NH_3 , and observation confirms this: two lone-pairs on the central O atom compress the H–O–H bond angle to 104.5° .

Thus, for similar molecules within a given tetrahedral electron set arrangement, electron pair repulsions cause deviation from ideal bond angles.

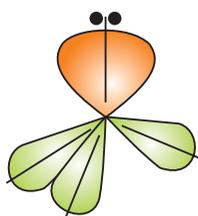


Figure 3.7 Molecular shape of ammonia.

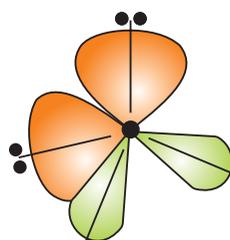


Figure 3.8 Molecular shape of water.

Example 3.2

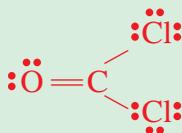
Determine the molecular shape of and ideal bond angles in:



Solution:



a Write the Lewis Structure



b Assign the electron set arrangement: There are three sets of electrons around carbon (*two single and one double bond*) gives AX_3 type molecule with a trigonal planar arrangement of electron sets.

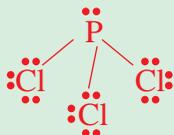
c The ideal bond angle is 120° .

d The shape is trigonal planar.

The correct Lewis structures determine the other steps. Therefore, you have to be sure when you sketch the structure.

2. For PCl_3

a Write the Lewis structure:



b Assign the electron set arrangement. There are four electron sets around phosphorus (three bonding and one lone pair) gives AX_3E type, a molecule with tetrahedral arrangement of electron sets.

c The ideal bond angle is 109.5° . Since there is one lone pair, the actual bond angle should be less than 109.5° .

d PCl_3 has a trigonal pyramidal shape.

3. For SF_2

a Write the Lewis structure:



b Assign the electron set arrangement:

There are four electron sets around sulphur (two bonding and two lone pair) give AX_2E_2 type, a molecule with tetrahedral arrangement of electron sets.

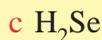
c The ideal bond angle is 109.5° . Since there are two lone-pairs, the actual bond angle should be less than a tetrahedral arrangement of electron sets with one lone-pair.

d SF_2 has angular (*bent*) or V-shape.



Exercise 3.9

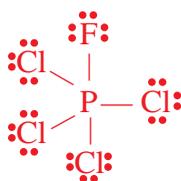
Determine the molecular shape and ideal bond angles in



Molecular Shapes with Five Electron Sets (Trigonal Bipyramidal Arrangements, AX_5 Type)

AX_4E , AX_3E_2 and AX_2E_3 types are with five electron sets around the central atom like AX_5 type but differ in shape and bond angle because of the presence of one or more lone-pairs on the central atom. Therefore, we dare to predict that the electron set geometry is trigonal bipyramidal.

Molecules with five or six electron sets must have a central atom from **period 3** or higher with *d*-orbitals available to expand its valence shell beyond eight electrons. When five electron sets maximize their separation, they form the trigonal bipyramidal arrangement with all five positions occupied by bonded atoms, the molecule has a trigonal bipyramidal shape (AX_5 type). Phosphorus pentachloride (PCl_5) is an example:



Lone-pairs exert stronger repulsive forces than bond pairs. With one lone-pair present (AX_4E type), the molecule has a **Seesaw shape**. For example, SF_4 , XeO_2F_2 , IF_4^+ , $IO_2F_2^-$. With two lone pairs present (AX_3E_2 type), the molecule has a **T-Shape**. Some of the examples of this type include ClF_3 , BrF_3 , and ICl_3 .

Molecules with two bonding and three lone pair sets are linear in shape (AX_2E_3 type). The examples of this type are XeF_2 , I_3^- , IF_2^- .

Molecular Shapes with Six Sets of Electrons (Octahedral Arrangement, AX_6 Type)

AX_5E and AX_4E_2 are the two common shapes under consideration. They are with six sets of electrons like AX_6 type and exhibit similar electron arrangement around the central atom but different molecular shapes.

With six bonding groups, the molecular shapes are **octahedral** (AX_6 type). For example, SF_6 , IOF_5 . Five bonded atoms and one lone pair (AX_5E type) define the **square pyramidal** shape. The examples of this type are BrF_5 , TeF_5^- , $XeOF_4$.

When a molecule has two lone pairs and four bonding set (AX_4E_2 type) the positioning gives rise to the **square-planar shape**. The examples of this type are XeF_4 , ICl_4^-

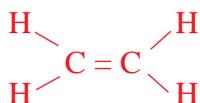
Exercise 3.10

- In which situation/s the molecular shape and the electron-set arrangement is/are same?
- Arrange the following AF_n species in order of increasing F–A–F bond angles. BF_3 , BeF_2 , CF_4 , NF_3 , OF_2
- In the gas-phase, phosphorus pentachloride exists as separate molecules. In the solid phase, however, the compound is composed of alternating PCl_4^+ and PCl_6^- ions. What change(s) in molecular shape occur(s) as PCl_5 solidifies? How does the angle change?
- For molecules of general formula AX_n (where $n > 2$), how do you determine if a molecule is polar?
- For each of the following molecular formula (AX_mE_n), A is the central atom, X is the terminal atom, m is the number of terminal atoms bonded to the central atom; E is the lone-pair of electrons and n is the number of lone-pairs possessed by the central atom. The first item has been completed as an example. Fill the rest of the table after drawing in your note book.

| Number of e-pairs | Molecular formula | Molecular geometry | Electron set geometry | Sketch | Examples |
|-------------------|---|--------------------|-----------------------|--------|----------|
| 2 | AX_2 | linear | linear | X–A–X | Cl–Be–Cl |
| 3 | AX_2E AX_3 | | | | |
| 4 | AX_4 AX_3E AX_2E_2 | | | | |
| 5 | AX_5 AX_4E AX_3E_2 AX_2E_3 | | | | |
| 6 | AX_6 AX_5E AX_4E_2 | | | | |

6. Determine the molecular shape and predict the bond angles (relative to the ideal angles) in
- a SbF_5 b BrF_5
7. Predict the geometry of and bond angles (relative to the ideal angles) in the following molecules and ions.
- a ClO_3^+ b ClO_2^+ c ICl_2^- d SOF_4 e ClF_3
8. Draw molecular shapes for the molecules/ions in question number 8.

The molecular shape of molecules with more than one central atom are different in different parts of the molecule. Consider ethene (C_2H_4). Three bonding sets and no lone pair are around each of the two central carbon atoms, so ethene is shaped like two trigonal planar geometries that share a point.



Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) has three central atoms. The CH_3 group is tetrahedrally shaped and the CH_2 group has four bonding groups around its central C atom, so it is also tetrahedrally shaped. The O atom has four sets of electrons, but the two lone pairs give it a **V-shape** (AX_2E_2 type). For these types of molecules, it is easiest to find the molecular shape around one central atom at a time. **Figure 3.8** is another example for the molecular shape of molecules with more than one central atom.

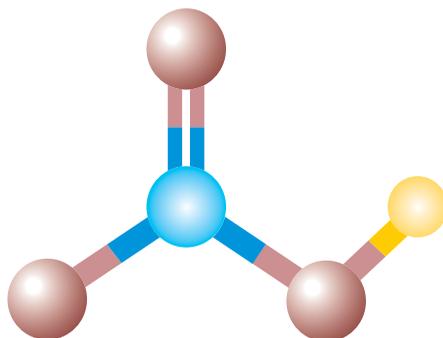


Figure 3.9 Predicted geometrical shape of the HNO_3 molecule by the VSEPR theory.

3.3.2 Intermolecular Forces in Covalent Compounds

Activity 3.16



Form a group and discuss the following questions:

1. Why does a polar liquid generally have a higher normal boiling point than a nonpolar liquid of the same molecular mass?
2. State the principal reasons why CH_4 is a gas at room temperature whereas H_2O is a liquid.
3. Only one of these substances is a solid at STP: $\text{C}_6\text{H}_5\text{COOH}$, $\text{CH}_3(\text{CH}_2)_8\text{CH}_3$, CH_3OH , $(\text{CH}_3\text{CH}_2)_2\text{O}$. Which do you think it is and why?
4. Only one of these substances is a gas at STP: NI_3 , BF_3 , PCl_3 , and CH_3COOH . Which do you think it is and why?

Share your ideas with the rest of the class.

There are two types of electrostatic forces at work in any sample of matter. These are: intramolecular and intermolecular forces. Intramolecular force which is a chemical bond (ionic, covalent or metallic) is a force that exists within a particle (molecule or polyatomic ion) and affects the chemical property of the species. Whereas, intermolecular forces exist between particles and influence physical properties of the species

Intermolecular forces are due to the attraction between ions and molecules. Intermolecular forces are relatively weak as compared to intramolecular forces, because they typically involve lower charges that are farther apart. The charges that give rise to intermolecular forces are farther apart because they exist between non-bonded atoms in adjacent molecules.

Activity 3.17



Form a group and discuss the following:

1. Name some intermolecular forces.
2. Cis-1,2-dichloroethene shows higher boiling point than trans-1,2 dichloroethene. Explain.
3. Which type of compounds exhibit hydrogen bonding?
4. Name the factors on which the strength of dispersion forces of the particles depend?
5. 'Ice is lighter than water.' Comment

Share your views with rest of the class.

Though there are several important types of intermolecular forces, only **dipole-dipole, hydrogen bonding, and, London (Dispersion) forces**, will be discussed.

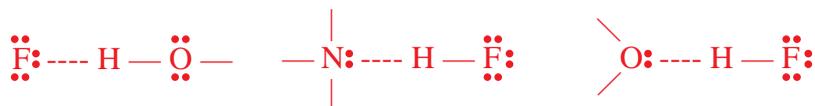
Dipole-Dipole forces

When polar molecules are brought near one another, their partial charges act as tiny electric fields that orient them and give rise to dipole-dipole forces; the partially positive end of one molecule attracts the partially negative end of another.

For compounds of approximately the same mass and size, greater is the dipole moment, greater is the dipole-dipole forces between their molecules, so greater is the energy required to separate their particles. These can be manifested in several of its physical properties. For instance, both methyl chloride (CH_3Cl) and ethanal (CH_3CHO) have comparable mass and size, but CH_3Cl has a smaller dipole moment than CH_3CHO ; therefore less energy is needed to overcome the dipole-dipole forces between its molecules and it boils at a lower temperature. Dipole-dipole forces give polar cis-1,2-dichloroethene a higher boiling point than nonpolar trans-1, 2-dichloroethene.

Hydrogen Bonding

Hydrogen bonding is a special type of dipole-dipole forces that arise between molecules that have a hydrogen atom bound to a smaller sized, most electronegative atoms. These atoms are: Fluorine, Oxygen and Nitrogen. The bond formed between hydrogen and such an atom is highly polar. The partially positive (δ^+) H of one molecule is attracted to the partially negative (δ^-) lone pair on the F, O or N of the same or another molecule. As a result a hydrogen bond result. The atom sequence that leads to an H bond (*dotted line*) is indicated below. The following three examples illustrate the sequence.



Hydrogen bonds hold water molecules in a rigid but open structure. When ice melts, some of the hydrogen bonds break. Water molecules move into the holes that are in the ice structures. The molecules are therefore closer together in liquid water than in ice. This means that liquid water at 0°C is denser than ice. Water is most unusual in this regard. When water on the surface of lakes and other areas freezes, the ice floats on the liquid water. If the solid were denser than the liquid as is true for nearly every other substance, the surface of the lake would freeze and sink until the entire lake was solid; aquatic plants and animals would be endangered.

Dispersion or London Forces

Intermolecular forces in which non-polar atoms or molecules interact by inducing dipoles in each other are known as dispersion or London Forces. These classes of intermolecular forces cause substances like CO_2 , Cl_2 , noble gases, etc, to condense and solidify. An attractive force must be acting between these non-polar molecules and atoms, or they would remain gaseous under any conditions. In fact, bond dipoles exert some weak attraction but the intermolecular forces are mainly responsible for the condensed state of non-polar substance. These forces are known as **London forces** or **dispersion forces**, named after **Fritz London**, the physicist who explained the quantum mechanical basis of the attractive forces.

Dispersion forces are very weak and are caused by a sudden shift of electron density to one side of the nucleus than the other. So the molecule has an instantaneous dipole. These instantaneous dipole will induce the neighbouring non-polar molecule. As a result, an induced-dipole is created. This process occurs throughout the sample and keeps the particles together. These dipoles are collectively known as dispersion forces or London forces. They are present between all particles (atoms, ions, and molecules.)

For substance with the same molar masses, the strength of the dispersion forces is often influenced by molecular geometry (*shape*). Shapes that allow more points of contact have more area over which electron clouds can be distorted, so stronger attractions result. This is probably the reason why n-pentane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) exhibits higher boiling point than its isomer 2,2-dimethyl propane.

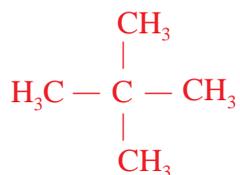
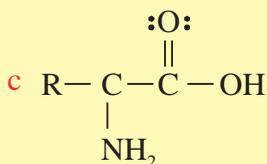
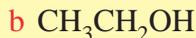


Table 3.1 Strength and polarity of intermolecular forces

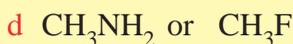
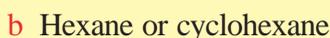
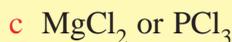
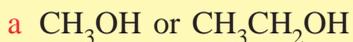
| Intermolecular force | Strength | Polarity |
|--------------------------|---------------|-----------|
| Hydrogen Bonding | The Strongest | Polar |
| Dipole-dipole Forces | Moderate | Polar |
| London Dispersion Forces | The Weakest | Non-polar |

Exercise 3.11

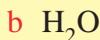
1. In which of the following substances do hydrogen bonds occur? Explain with the help of diagrams.



2. Identify the dominant intermolecular force that is present in each of the following substance and select the substance with the higher boiling point in each pair:



3. Which type of intermolecular force is dominant in the following substances?



4. Compare intermolecular forces with that of intramolecular bonding.

3.4 METALLIC BONDING

At the end of this section, you should be able to:

- explain how metallic bond is formed;
- explain the properties of metals related to the concept of bonding; and
- carryout an activity to investigate the conductivity, malleability and ductility of some metals and non-metals (Al, Cu, Fe, Sn, Zn, S, C charcoal, C graphite and Si).

3.4.1 Formation of Metallic Bonding

Activity 3.18



Form a group and discuss the following:

1. Two characteristics that lead to an element being classified as a metal.
2. Type of bond existing in solid copper.
3. What is delocalisation of electrons?

4. Electron sea model.
5. Even though so much energy is required to form a metal cation with a 2+ charge, the alkaline earth metals form halides with general formula MX_2 rather than MX . Explain.

Share your ideas with the rest of the class.

In simple terms, metallic bonding is referred to as bonding in metal atoms. It is also defined as interaction between metal nuclei and the delocalized electrons. Delocalized electrons are also called as conduction electrons. Metals nuclei are the positive ions and so metallic bonding can be imagined as **sea of electrons** in which positive metal ions are embedded. Positive metal ions are called **Kernels**. Thus metallic bonding can be summarized as: The force of attraction which binds together the positive metal ions or Kernels with the electrons within its sphere of influence.

Is a metal made up of atoms or ions?

The strength of the metallic bond depends on the:

1. number of electrons in the delocalised 'sea' of electrons. (More delocalised electrons results in a stronger bond and a higher melting point.)
2. packing arrangement of the metal atoms.

(The more closely packed the atoms are the stronger the bond is and the higher the melting point.)

3.4.2 Electron-Sea Model

The **electron-sea model** of metallic bonding proposes that all the metal atoms in the sample contribute their valence electrons to form "sea" of electrons, which is not localized for a particular atom. The metal ions (*the nuclei with their core electrons*) are submerged within this electron sea in an orderly array. See Figure 3.10.

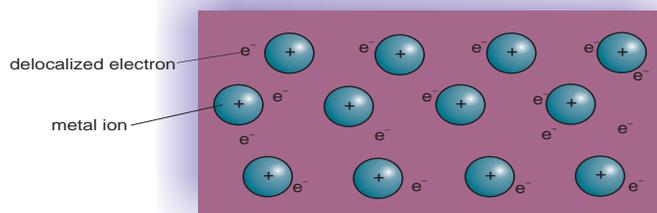


Figure 3.10 Schematic illustrations of electron-sea model for the electronic structure of metals.

In contrast to ionic bonding, the metal ions are not held in place as rigidly as in ionic solid. In contrast to covalent bonding, no particular pair of metal atoms is bonded through any localized pair of electrons. Rather, the valence electrons are shared among all the atoms in the substance, which is held together by the mutual attraction of the metal cations for the mobile, highly delocalized electrons. An electron-pair in a covalent resonance hybrid is delocalized over only a few atoms, but the extent of delocalization in metal is much greater. The bonding-electrons are free to move throughout the three dimensional structure.

3.4.3 Properties of Metals Related to the Concept of Bonding

Activity 3.19



Form a group and perform the following activity:

1. Take a piece of metal and a piece of wood of the same size.
2. Let these remain on a table so that both attain room temperature.
3. Place your left hand on the metal and right one on the wood.

What do you observe? Which hand feels colder? Why?

Discuss and share your findings with rest of the class..

The general properties of metals include malleability and ductility and most are strong and durable. They are good conductors of heat and electricity. Their strength indicates that the atoms are difficult to separate, but malleability and ductility suggest that the atoms are relatively easy to move in various directions. These properties suggest the nature of the metallic bonding between atoms.

Metallic bonds show typical metallic properties such as high electrical conductivity, lustre, and high heat conductivity. Metals are good conductors of electricity and heat because of their mobile electrons. They are strong and opaque in nature.

Most metals are malleable, which means that they can be hammered into thin sheets, and ductile, which means that they can be drawn into wires. These properties indicate that the atoms of the metallic lattice are capable of slipping with respect to one another. When a piece of metal is struck by a hammer, the metal ions move to a new lattice positions, sliding past each other through intervening electrons.

Most metals are solids with high melting and much higher boiling points; because the atoms of metals have strong attractive forces between them and much energy is required to overcome this force. For instance, the increase in melting point between the alkali metals [Group IA] and the alkaline earth metals [Group IIA] can be explained by the IIA metals having two valence electrons, available for metallic bonding, whereas the IA metals have only one. The greater attraction between the M^{2+} ions and twice the number of mobile electrons mean that higher temperatures are needed to melt such solid. The metals have a wide range of melting points, (from -39°C (mercury) to 3410°C (tungsten).

The properties of metals suggest that their atoms possess strong bonds, yet the ease of conduction of heat and electricity suggest that electrons can move freely in all directions in a metal. The general observations give rise to a picture of "positive ions in a sea of electrons" to describe metallic bonding.

Activity 3.20



Form a group and discuss the following questions:

- Use the periodic table to arrange the following in order of increasing melting point K, Br_2 , Mg and O_2 . Explain the reason for the order you choose.
- List four physical characteristics of a solid metal .
- Briefly account for the following relative values:
 - Lithium boils at 1317°C and melts at 179°C . The boiling point is about 1138°C higher than its melting point.
 - The melting point of Li and Be are 180°C and 1287°C , respectively.
 - The melting point of sodium is 89°C , where as that of potassium is 63°C .
- For each of the following pairs, which element will have the greater metallic character:

| | | | |
|------------|------------|------------|------------|
| a Li or Be | b Li or Na | c Sn or Pb | d B or Al? |
|------------|------------|------------|------------|

Explain briefly. Share your ideas with the rest of the class.

Group Assignment



Form a group and do as directed:

- You have been provided with aluminium, copper, iron, tin, zinc, charcoal, graphite and silicon. Complete the following table on your notebook. Perform experiment if required.

| Sample | Conductivity | Malleability | Ductility |
|-----------|--------------|--------------|-----------|
| Aluminium | | | |
| Copper | | | |
| Iron | | | |
| Tin | | | |
| Zinc | | | |
| Charcoal | | | |
| Graphite | | | |
| Silicon | | | |

- Can you classify the samples as metal or non-metal?
- Prepare another table and tabulate more properties of metals.

3.5 CHEMICAL BONDING THEORIES

At the end of this section, you should be able to:

- name two chemical bond theories;
- explain the valence bond theory;
- distinguish the Lewis model and the valence bond model;
- discuss the overlapping of orbitals in covalent bond formation;
- explain hybridization;
- show the process of hybridization involved in some covalent molecules;
- draw hybridization diagram for the formation of sp , sp^2 , sp^3 , sp^3d and sp^3d^2 hybrids;
- suggest the kind of hybrid orbitals on the basis of the electron structure of the central atom;
- predict the geometrical shapes of some simple molecules on the basis of hybridization and the nature of electron pairs.

- discuss the hybridization involved in compounds containing multiple bonds;
- explain bond length and bond strength;
- explain molecular orbital theory;
- describe molecular orbital-using atomic orbitals;
- describe bonding and anti bonding molecular orbitals;
- draw molecular orbital energy level diagrams for homonuclear diatomic molecules;
- write the electron configuration of simple molecules using the molecular orbital model;
- define bond order and determine the bond order of some simple molecules and molecule-ions;
- determine the stability of a molecule or an ion using its bond order; and predict magnetic properties of molecules.

The two modern chemical bonding theories which use quantum mechanics are the **Valence Bond Theory** (VBT) and the **Molecular Orbital Theory** (MOT).

3.5.1 Valence Bond Theory (VBT)

Lewis theory provides a simple, qualitative way to describe covalent bonding, and VSEPR theory allows us to carry the description further. Probable molecular shapes were predicted by VSEPR theory. Now consider a quantum mechanical approach to covalent bonding that confirms much of what is described through VSEPR theory, but which allows extending that description still further. The valence-bond approach is the most useful approach to answer questions like: what is a covalent bond? And how can we explain molecular shapes from the interaction of atomic orbitals?

The basic principle of valence bond theory is that a covalent bond forms when orbitals of two atoms overlap and the overlap region, which is between the nuclei, is occupied by a pair of electrons.

For instance, form an image in your mind of two hydrogen atoms approaching one another. The moment they get closer, their electron-charge clouds begin to combine into a whole. This intermingling is described as the overlap of the 1s orbitals of the two atoms. The overlap results in an increased electron charge-density in the region between the atomic nuclei. The increased density of negative charge serves to hold the positively-charged atomic nuclei together. In the valence bond (VB) method, a covalent bond is a region of high electron charge-density that results from the overlap of atomic orbitals between two atoms.

The strength of the bond between any two atoms generally depends on the extent of the overlap between the two orbitals. As the two atoms are brought more closely together, however, the repulsion of the atomic nuclei becomes more important than the electron-nucleus attraction and the bond becomes unstable. For each bond, then, there is a condition of optimal orbital overlap that leads to a maximum bond strength (bond energy) at a particular internuclear distance (*bond length*). The valence bond method attempts to find the best approximation to this condition for all the bonds in a molecule.

The bonding of two hydrogen atoms into a hydrogen molecule through the overlap of their 1s orbitals is pictured in **Figure 3.11**.

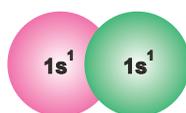


Figure 3.11 Atomic orbital overlap and bonding in H_2 .

Note! The *s* orbital is spherical, but *p* and *d* orbitals have particular orientations - more electron density in one direction than in another - so a bond involving *p* or *d* orbitals will tend to be oriented in the direction that maximizes overlap.

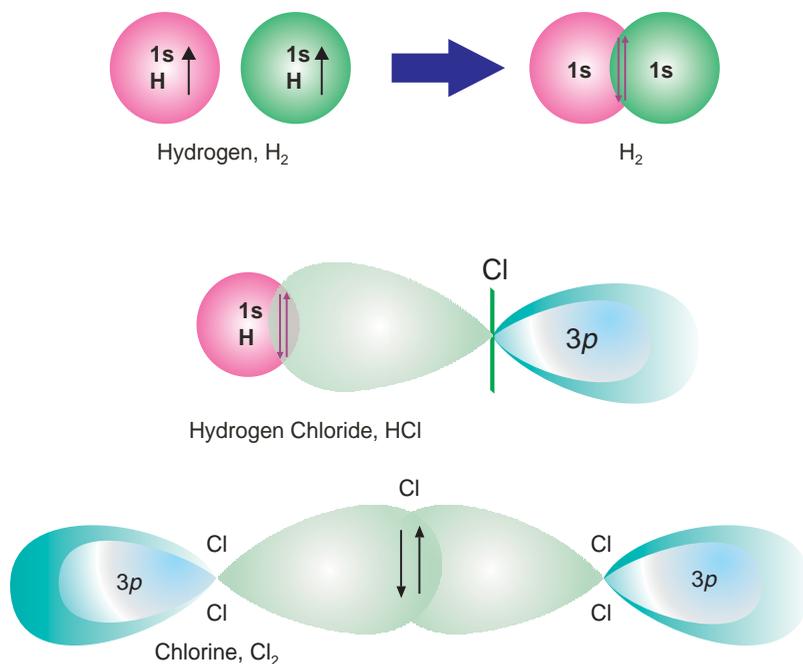


Figure 3.12 Orbital and spin pairing in three diatomic molecules.

In the HCl bond, for example, the $1s$ orbital of hydrogen overlaps the half-filled $3p$ orbital of Cl along the axis of that orbital. In **Figure 3.11B** any other direction would result in less overlap and, thus, a weaker bond. Similarly, in the Cl–Cl bond of Cl_2 , the two $3p$ orbitals interact end-to-end, that is along the orbital axes, to attain maximum overlap (**Figure 3.11C**).

VSEPR theory predicts a tetrahedral bond angle (109.5°) in H_2S . However, if we take in to account the strong repulsions between the lone pairs of electrons on the S atom and the bond pairs, bonds are expected to be forced into a smaller angle. The measured bond angle in the H_2S molecule is 92.1° , suggesting that the valence bond method describes the covalent bonding in H_2S better than the VSEPR theory does (see **Figure 3.12**). There are not many cases, however, where the VB method produces superior results. A combination of VSEPR theory and the VB method are used in describing the shape of the molecules.

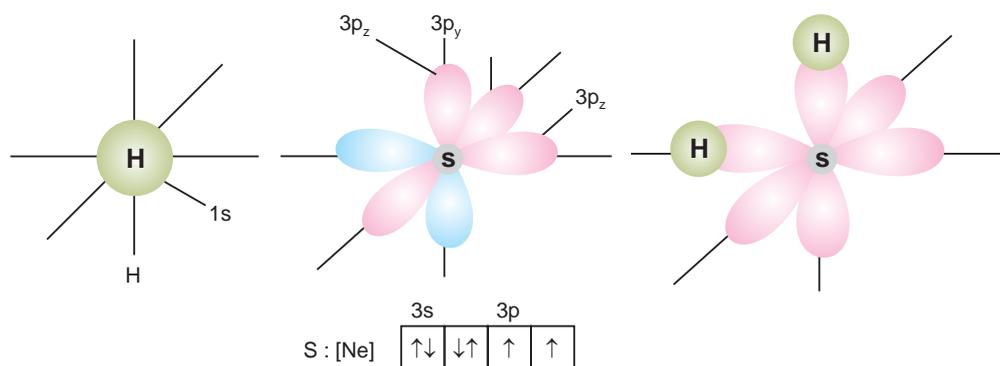
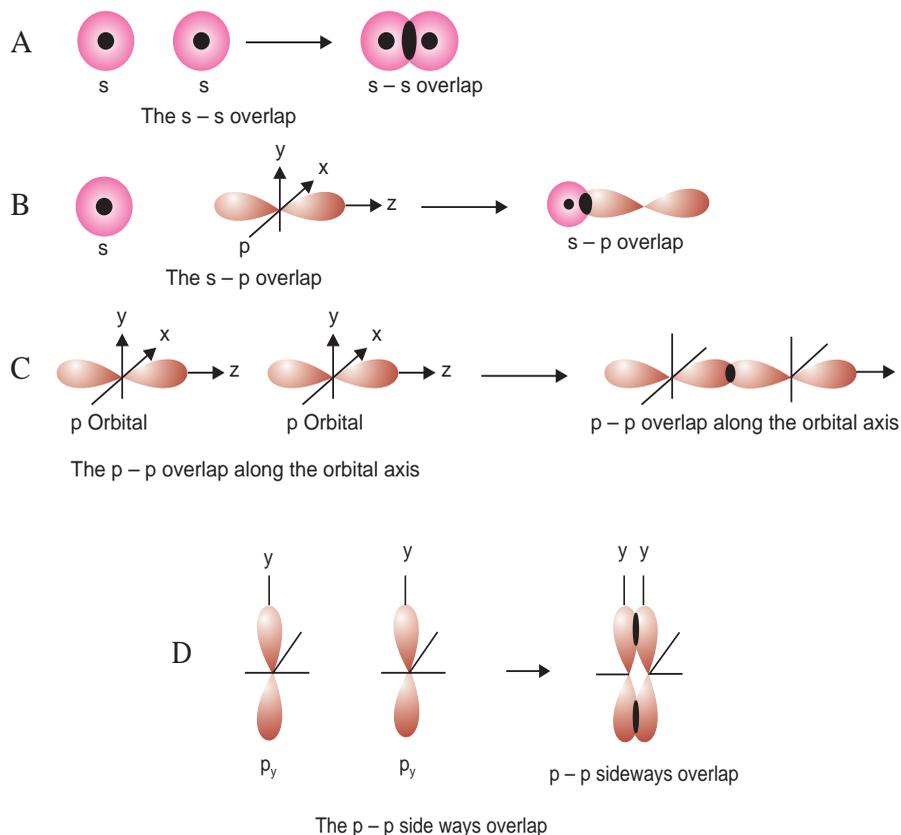


Figure 3.13 Atomic orbital overlap and bonding in H_2S .

Overlap of Atomic Orbitals (Sigma and Pi Bonds)

To see the detailed makeup of covalent bonds, it is essential to focus on the mode by which orbitals overlap because orbital overlap is necessary for sharing of electrons and bond formation. Various type of atomic orbital overlap leads to covalent bond formation. Three simple basic ones are s - s , s - p and p - p shown in **Figure 3.13**.

1. s - s overlap in which half filled s orbitals overlap,
2. s - p overlap where half filled s orbital of one atom overlaps with one of the p orbital having one electron only and

3. p - p overlap in which two half filled p orbitals overlap.**Figure 3.14 Atomic orbital overlap.**

(A) s-s overlap, (B) s-p overlap, (C) p-p overlap along the orbital axis and (D) p-p sideways overlap.

Because of the directional nature of p orbital, the overlap may take place in two ways: (i) the half filled p orbitals along the line joining the two nuclei. This is called as head on, end-to-end, end on or linear overlap and (ii) the half filled p orbitals overlap along the line perpendicular to the nuclear axis. This overlapping of p orbitals is parallel to each other, hence is called lateral or sideways overlapping. These two modes give rise to the two types of covalent bonds, namely, sigma (σ) and pi (π) bond respectively. Valence bond theory is used to describe the two types here, but they are essential features of molecular orbital theory as well. $s - s$ and $s - p$ will always overlap along the nuclear axis, hence results only in sigma bonds.

Sigma bond has its highest electron density along the bond axis (an imaginary line joining the nuclei) in between the bonded nuclei. All single bonds have their electron density concentrated along the bond axis, and thus are sigma bonds.

A side - to - side or parallel overlap forms another type of covalent bond called a pi (π) bond. It has two regions of electron density. One above and one below the sigma bond axis. One π -bond holds two electrons that occupy both regions of the bond. A double-bond always consists of one σ and one π bond. The double-bond increases electron density between the nuclei. A triple bond consists of one σ and two π bonds.

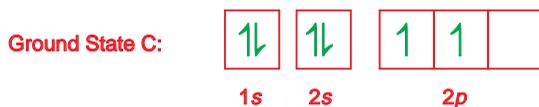
Now it can be seen clearly why a double and triple bonds were considered as one electron set in the discussion of VSEPR. The reason is that each electron pair occupies a distinct orbital, a specific region of electron density, so repulsions are reduced.

The extent of overlap influences bond strength, however, many factors, such as lone - pair repulsions, bond polarities, and other electrostatic contributions affect overlap and the relative strength of σ and π bonds between other pairs of atoms. Thus as a rough approximation, a double bond is about twice as strong as a single bond, and a triple bond is about three times as strong.

Hybridization of Orbitals

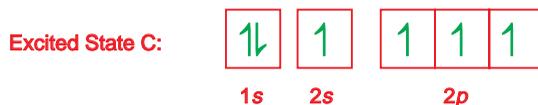
Valence bond theory employs the concept of hybridization. It is the overlap or blending of s , p and d orbitals to explain bond formation.

In applying the valence bond method to the ground state electron configuration of carbon you can assume that the filled $1s$ orbital will not be involved in the bonding and focus your attention on the valence-shell orbitals.



From its ground state configuration, two unpaired electrons in the $2p$ subshell are observed. One can predict the simplest hydrocarbon molecule to be CH_2 , by overlapping the two unpaired electrons from two H atoms with the two unpaired electrons of carbon. However, you might question the existence of this molecule because it does not follow the octet rule. In fact, experiment shows that CH_2 is not a stable molecule. The simplest stable hydrocarbon is methane, CH_4 . To account for this, you need an orbital diagram that shows four unpaired electrons in the valence shell of carbon, requiring four bonds (and therefore four atoms of hydrogen). To get such a diagram imagine that one of the $2s$ electrons is promoted to the empty $2p$ orbital. To excite the $2s$ electron to a higher energy sublevel, energy must be absorbed. The resulting electron configuration is that of an excited state having energy

greater than the configuration in the ground state.



Valence bond theory proposes that the one $2s$ and all three $2p$ orbitals of the carbon atom 'mix' to produce four new orbitals that are equivalent to each other in energy and in shape and pointing in different directions with equal H–C–H bond angles. This blending is called **hybridization** and the resultant orbital as **hybrid orbitals**. It is a hypothetical process (not an observed one) that can be carried out as a quantum mechanical calculation. The symbols used for hybrid orbitals identify the kinds and numbers of atomic orbitals used to form the hybrids.

In hybridization scheme, *the number of new hybrid orbitals is equal to the total number of atomic orbitals that are combined.*

Hybridization provides a useful and convenient method of predicting the shapes of molecules. It must be noted that though it is valuable in predicting and describing the shape, it does not explain the reason for the shape.

Exercise 3.12

1. How do carbon and silicon differ with regard to the types of orbitals available for hybridization? Explain
2. Are these statements true or false? Correct any that is false.
 - a Two σ bonds comprise a double bond.
 - b A triple-bond consists of one π bond and two σ bonds.
 - c Bonds formed from atomic s orbitals are always σ bonds.
 - d A π -bond consists of two pairs of electrons
 - e End-to-end overlap results in a bond with electron density above and below the bond axis.

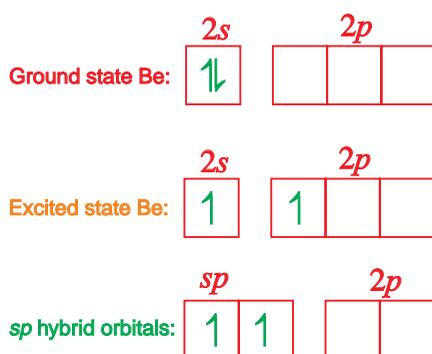
sp hybrid orbitals

When two electron sets surround the central atom, you observe a linear molecular shape. VB theory explains this by proposing that mixing two non-equivalent orbitals of

a central atom one s and one p , gives rise to two equivalent sp hybrid orbitals that lie 180° apart. Combination (mixing) of one s and one p orbital is called sp hybridization and the resultant orbitals are called sp hybrid orbitals.

For instance, the beryllium atom has two electrons and four orbitals in its valence shell. In the triatomic molecule BeCl_2 , which is present in gaseous BeCl_2 at high temperatures, the $2s$ and one of the $2p$ orbitals of the Be atom are hybridized into sp hybrid orbitals. The remaining two $2p$ orbitals are left unhybridized and unoccupied in the orbital diagram.

Since there are no unpaired electrons this atom cannot form any covalent bonds. It follows that in BeCl_2 , the Be atom is not in the ground state but it is in the excited state, with sufficient extra energy to unpair a $2s$ electron.



As shown in **Figure 3.15** the two sp hybrid orbitals are directed along a straight line, 180° apart. It is predicted that the BeCl_2 molecule should be linear, and this

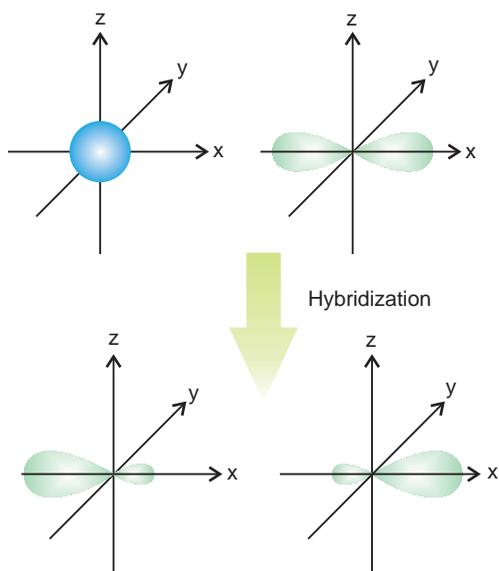


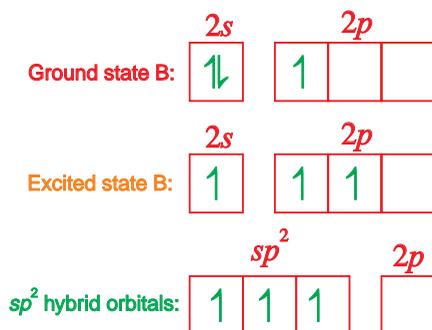
Figure 3.15 The sp -hybridization scheme illustrated.

prediction is confirmed by experimental evidence. Most examples of sp hybridization are found in organic molecules, especially those with triple bonds.

sp^2 hybrid orbitals

Now turn your attention to boron, a Group IIIA element. The boron atom has four orbitals but only three electrons in its valence shell. In most boron compounds the hybridization scheme combines one $2s$ and two $2p$ orbitals into three sp^2 hybrid orbitals. Using orbital diagrams to represent this hybridization, we have

sp^2 hybridization for B



The atom in its ground state has only one unpaired electron, so that it can form only one covalent bond, but in the excited state there are three unpaired electrons, hence three bonds can be formed.

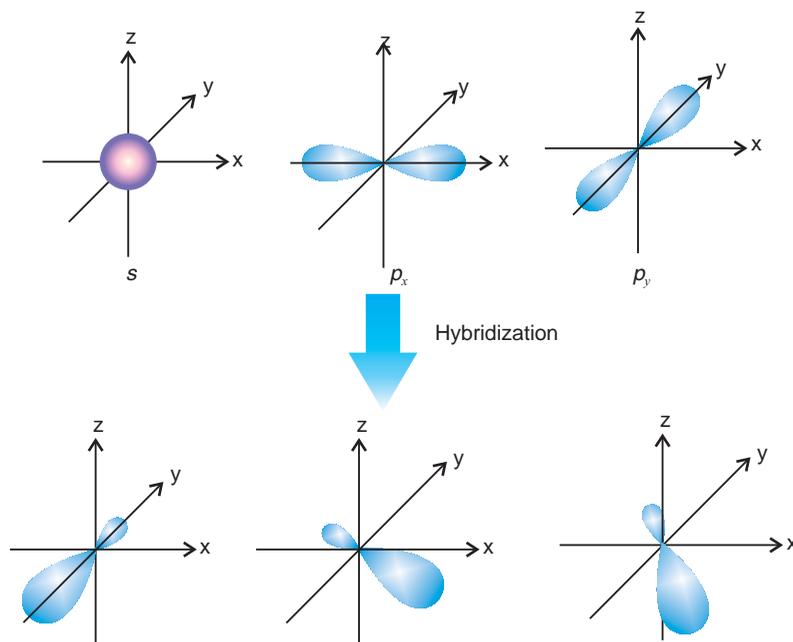


Figure 3.16 The sp^2 hybridization scheme illustrated.

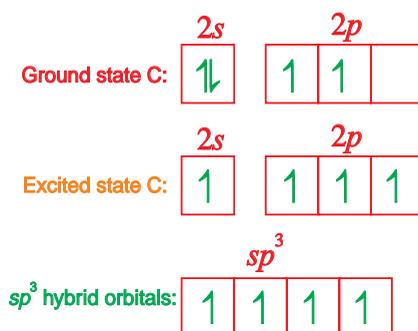
As shown in [Figure 3.15](#) the sp^2 hybrid orbitals are distributed geometrically within a plane at 120° angles. The valence bond method predicts that BCl_3 is a trigonal planar molecule with 120° Cl-B-Cl bond angle. This indeed is what is observed experimentally.

By far the most common examples of sp^2 hybridization are found in organic molecules with double bonds.

sp^3 hybridization

Carbon, the central atom in a molecule of methane CH_4 has only two unpaired electrons in the ground state. The two electrons in the $2p$ level are not paired, *i.e.*, put into the same box, in accordance with Hund's rule. Carbon in its excited state can form four bonds. The one $2s$ and three $2p$ -orbitals of carbon are mixed to produce four new orbitals that are equivalent to each other in energy and in shape, but pointing in different directions, as shown in [Figure 3.17](#).

sp^3 hybridization for carbon



The four sp^3 hybrid orbitals point to the corners of a regular tetrahedron, and make a bond angle of 109.50° in CH_4 ([Figure 3.17](#)).

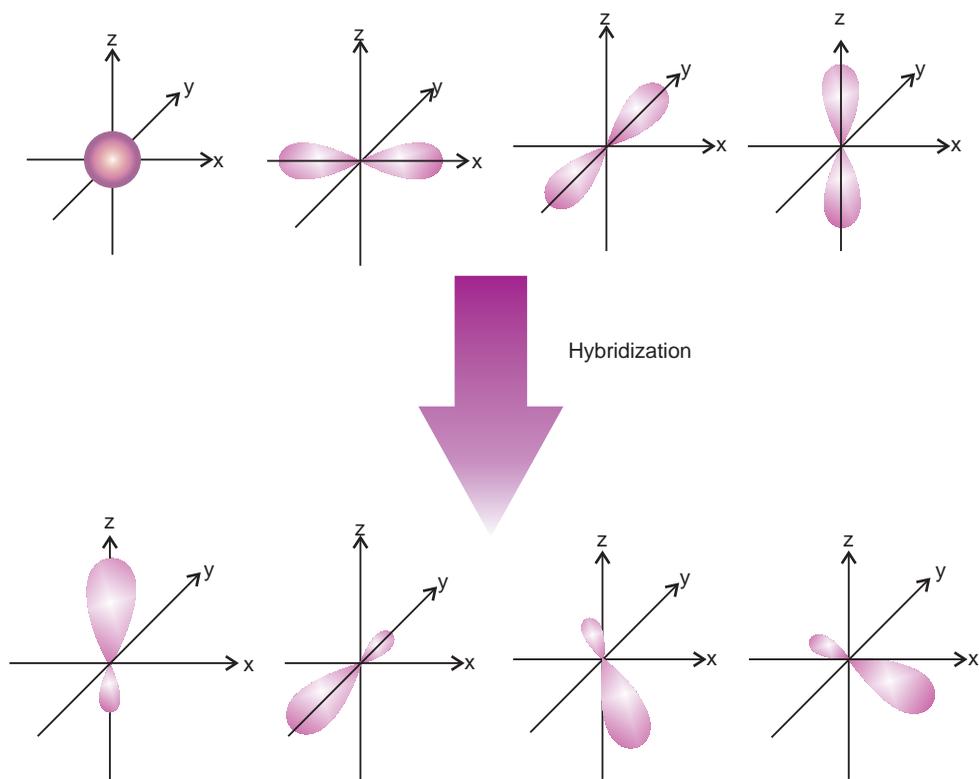


Figure 3.17 The sp^3 hybridization.

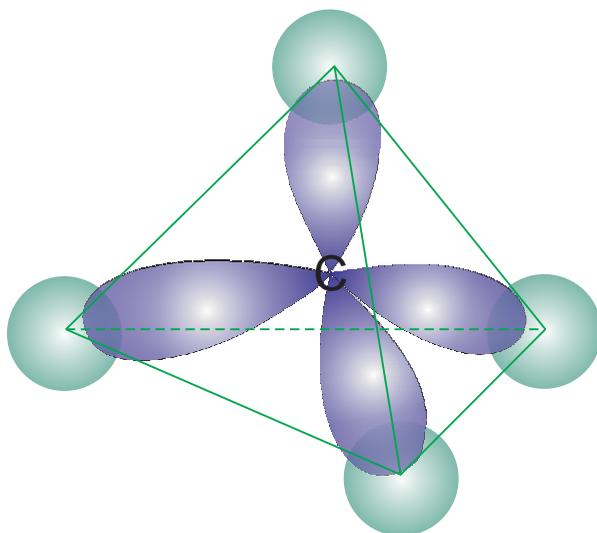
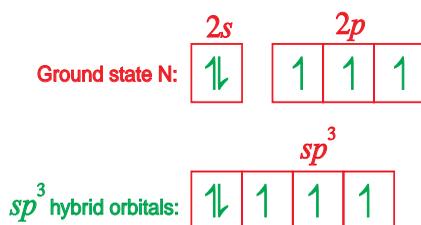


Figure 3.18 sp^3 Hybrid orbitals and bonding in methane scheme illustrated.

We might also expect to use sp^3 hybridization not only for structures of the type AX_4 type (as in CH_4), but also for AX_3E type (as in NH_3) and AX_2E_2 type (as in H_2O). Nitrogen has three unpaired electrons in its ground state, sufficient to form three bonds; so it is not necessary to excite the atom. sp^3 hybridization of the central atom N in NH_3



accounts for the formation of three N–H bonds and a lone-pair of electrons on the N atom (Figure 3.19). The predicted H–N–H bond angles of 109.5° are close to the experimentally observed angles of 107° .

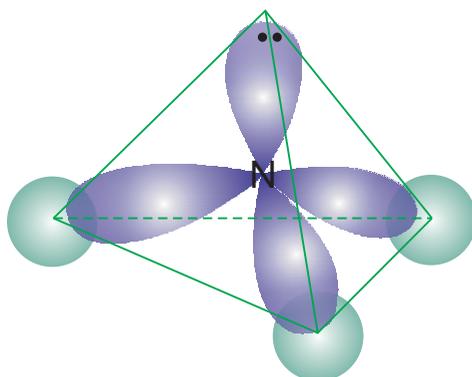
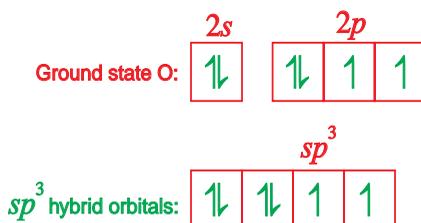


Figure 3.19 sp^3 hybrid orbitals and bonding in NH_3 .

A similar scheme for H_2O accounts for the formation of two O–H bonds and two lone-pairs of electrons on the oxygen atom.



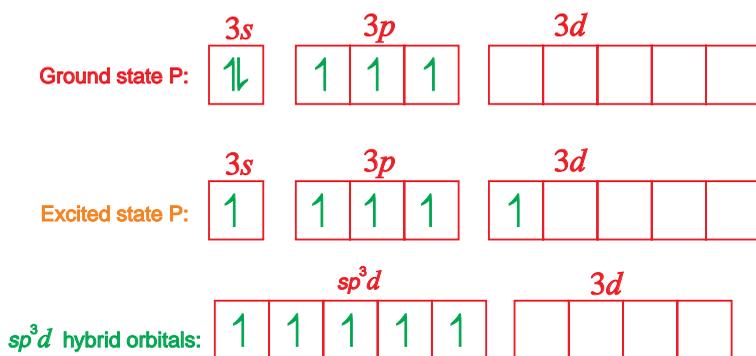
The predicted H–O–H bond angle of 109.5° is also reasonably close to the observed angle of 104.5° . As in our discussion of the VSEPR theory, we can explain somewhat

smaller than tetrahedral bond angles in NH_3 and H_2O in terms of repulsions involving lone-pair electrons.

sp³d hybridization

A maximum of eight valence electrons can be accommodated by any hybridization scheme involving only *s* and *p* orbitals. Hybridization schemes for structures involving expanded octets must include additional orbitals and these extra orbitals can come from a *d*-subshell.

For example, we need five hybrid orbitals to describe bonding in PCl_5 . In a gaseous molecule of phosphorus pentachloride, PCl_5 , the central atom phosphorus has only three unpaired electrons in its ground state. Electrons must be unpaired to provide the correct number of unpaired electrons for bond formation.



Five orbitals are being used and sp^3d hybridization occurs, giving a trigonal bipyramidal structure. The sp^3d hybrid orbital and their trigonal bipyramidal structure is shown in Figure 3.20.

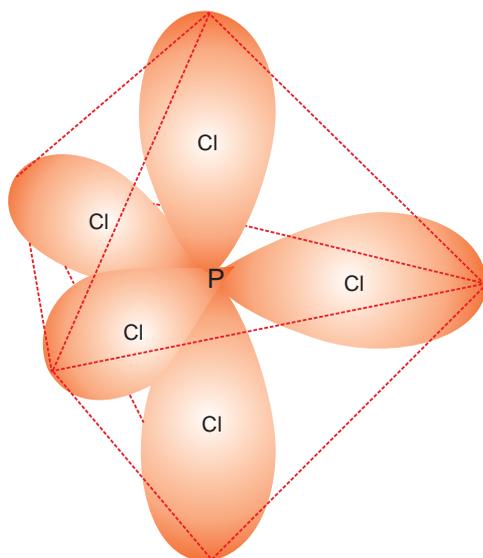


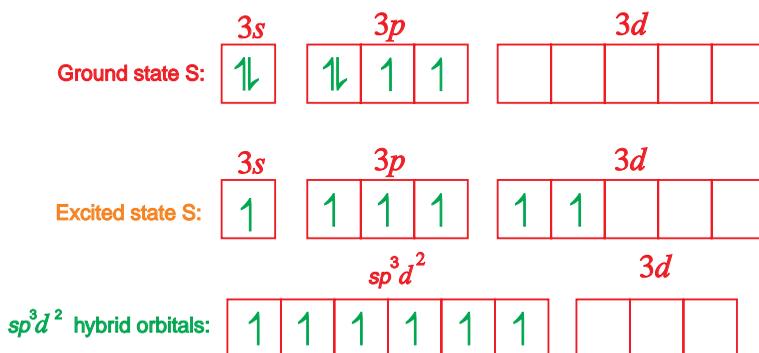
Figure 3.20 The sp^3d hybrid orbitals in the molecule of PCl_5 .

Like other hybrid orbitals we have considered, the five sp^3d hybrid orbitals are arranged in a symmetrical fashion, but unlike the other case, the five sp^3d orbitals are not all equivalent. Three of the orbitals are directed in the plane of the central atom at 120° angles with one another; the remaining two are perpendicular to the plane of the other three. The three positions in the central plane are called the **equatorial positions** and the two positions perpendicular to the plane are called **axial positions**.

Hybridization may take place only between orbitals of roughly the same energy. It follows that it is not possible to hybridize the $2s$ or $2p$ levels with the $3s$, or the $3s$ or $3p$ level with the $4s$. The d levels are intermediate in energy, and may in certain circumstance be used with the energy levels either below or above, that is $3s$ with $3d$, and $3d$ with $4s$ are both possible.

sp^3d^2 Hybridization

Another structure featuring an expanded octet is SF_6 . Here, six hybrid orbitals are required in order to describe bonding. These are obtained through the hybridization scheme sp^3d^2 , represented by the orbital diagrams.



The sp^3d^2 hybrid orbitals and their octahedral orientation are shown in Figure 3.21.

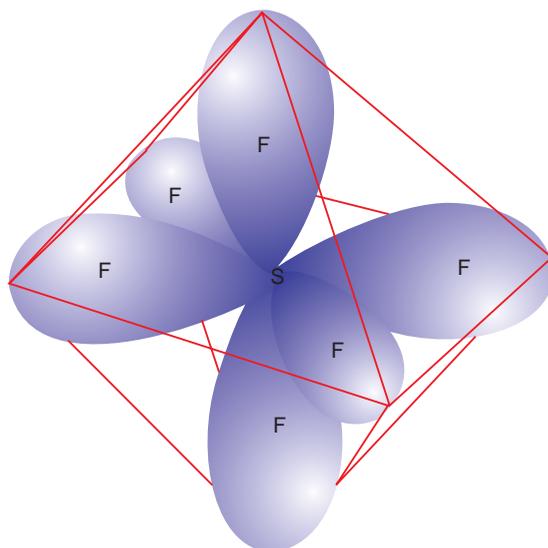


Figure 3.21 The sp^3d^2 hybrid orbitals SF_6 .

In hybridization schemes, one hybrid orbital is produced for every single atomic orbital involved. In a molecule, each of the hybrid orbitals of the central atom acquires an electron pair, either a bond-pair or a lone-pair. And the hybrid orbitals have the same orientation as the electron-set arrangement predicted by VSEPR theory.

When one describes the probable hybridization scheme for a structure, he/she must choose a scheme that conforms to experimental evidence. This can be done by mixing the VSEPR and valence bond approaches. The procedure is outlined in the following four steps and illustrated in **Example 3.4**.

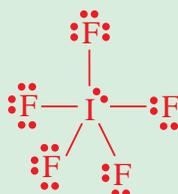
1. Write a reasonable Lewis structure for the species
2. Use VSEPR theory to predict the electron-set arrangement of the central atom
3. Select the hybridization scheme that correspond to the VSEPR prediction
4. Describe the orbital overlap

Example 3.3

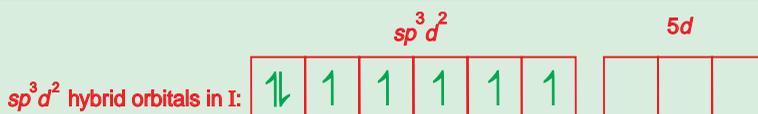
Describe a hybridization scheme for the central atom of iodine pentafluoride, IF_5 .

Solution:

- a The reasonable Lewis structure for IF_5 is



- b VSEPR predicts an octahedral electron-set arrangement for six electron pairs (AX_6 type)
- c The hybridization scheme corresponding to octahedral electron arrangement is sp^3d^2
- d The six sp^3d^2 hybrid orbitals are directed to the corners of an octahedron, but one of the orbitals is occupied by a lone pair of electrons (*shown in red below*).

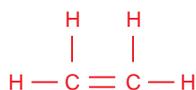


The resulting molecular shape is that of a square pyramid with bond angles of approximately 90° .

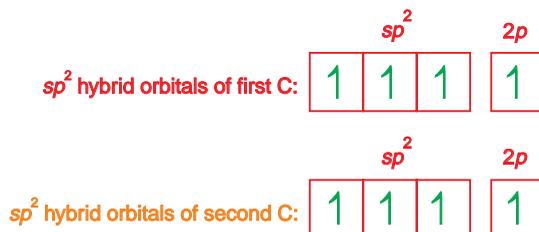
Exercise 3.13

1. Name the three types of hybrid orbitals that may be formed by an atom with only s and p orbitals in its valence shell. Draw the shapes of the hybrid orbitals so produced.
2. Describe a hybridization scheme for the central atom and molecular geometry of the triiodide ion, I_3^- .

The use of VSEPR theory to predict geometric structures of molecules and polyatomic ions with double and triple covalent bonds has already been described. When you combine this knowledge with the valence bond method, you gain additional insight. For example, the Lewis structure of ethene (*ethylene*) is depicted as



With VSEPR theory you predicted that the electron set geometry around each carbon atom is trigonal planar (AX_3 type). This corresponds to H–C–H bond angles of 120° . To account for these bond angles in the valence bond method, you assume that the $2s$ and two of the $2p$ orbitals of the valence shell combine to produce sp^2 hybridization of the two carbon atoms.



All the C–H bonds in C_2H_4 are formed by the overlap of sp^2 hybrid orbitals of the C atoms with $1s$ orbitals of the H atom, with these orbitals directed along hypothetical

lines joining the nuclei of the bonded atoms. A double covalent bond consists of one σ and one π bond. The features of a double bond described here are illustrated in Figure 3.22.

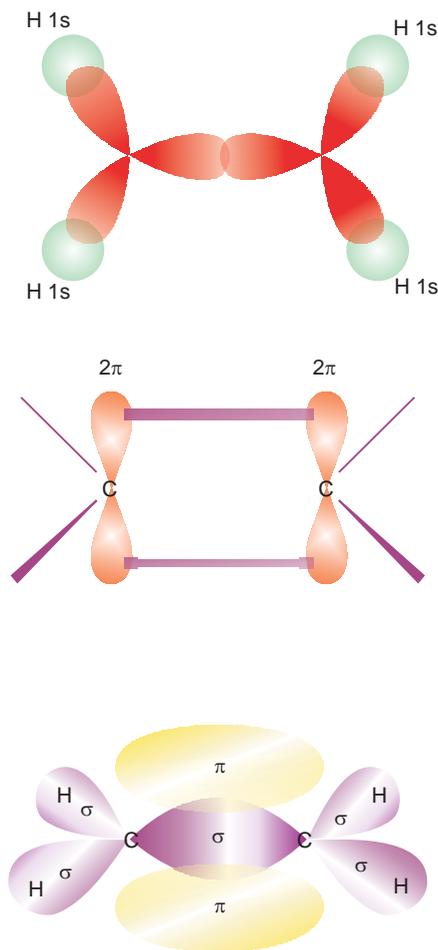


Figure 3.22 Bonding in ethylene, C_2H_4 .

VSEPR theory describes $H_2C = CH_2$ as consisting of two planar CH_2 groups, each with a 120° H–C–H bond angle. But it does not tell us how the two groups are oriented with respect to one another. Are they both in the same plane? Is one perpendicular to the other? The valence bond description of a double-bond gives the answer. The maximum sidewise overlap between the unhybridized $2p$ orbitals to form a π bond occurs when both CH_2 groups lie in the same plane. Ethene is a planar molecule. If one CH_2 group is twisted out of the plane of the other, the extent of overlap of the $2p$ orbitals is reduced, the π bond is weakened, and the molecule becomes less stable.

2. Describe a hybridization scheme for the central atom and the molecular geometry of CO_2 .
3. Discuss the bonding in nitrate ion, predict the ideal bond angles, bond length, shape of the ion, the number of sigma and pi bonds.

3.5.2 Molecular Orbital Theory (MOT)

Molecular orbital theory is a method of accounting for covalent bonds that depends on quantum theory and mathematical principles. This theory is based on the fact that electrons are not the substantive little dots as we portray in Lewis structures. We can speak only about energy levels/spatial probabilities when reckoning with them. We do this reckoning by thinking of quantized electron distribution as atomic orbitals (AOs) [pdf].

Combination of Atomic Orbitals

Atomic orbitals are capable of combining or overlapping, to produce new electron distributions called **molecular orbitals** (MOs) – one MO for every AO. The quantum mechanical treatment of electrons in atoms as matter waves yields atomic orbitals (AOs). A similar treatment applied to electrons in molecules yields molecular orbitals (MOs), which are mathematical descriptions of regions of high electron charge density in a molecule. It is easy to understand molecular orbital theory in principle; we seek an arrangement of appropriately placed atomic nuclei and electrons to produce an energetically favourable, stable molecule. The difficulty comes in practice, in trying to construct a wave equation for a system of several particles. The usual approach is to write approximate wave equations by relating them to atomic orbitals.

Bonding and Anti-Bonding Molecular Orbitals

Bonding molecular orbitals have a region of high electron density between the nuclei. Anti-bonding molecular orbitals have region of zero electron density (a node) between the nuclei. Typical results are like those shown for H_2 molecule in **Figure 3.23**. In place of atomic orbitals of the separated atoms, the molecular orbitals for the united atoms are obtained, and these are of two types. One type, a bonding molecular orbital, places a high electron charge density in between the two nuclei and the other type, an anti-bonding molecular orbital, places a high electron charge density away from the region between the two nuclei. Electrons in bonding orbitals contribute to bond formation and electrons in anti-bonding orbitals detract from bond formation.

When two atomic orbitals overlap end-to-end, they form two sigma-molecular orbitals (MOs). Consider the H_2 molecule, which has two H atoms and therefore two $1s$ AOs. The two $1s$ atomic orbitals combine (see Figure 3.23) to produce two σ MOs, which differ in energy and location. One of the σ MOs is a bonding orbital, denoted σ_{1s} , the other is an anti-bonding orbital denoted σ_{1s}^* .

The relative energy levels of these two MOs are different. The σ_{1s} MO has a lower energy than the original $1s$ AOs, while the σ_{1s}^* MO has a higher energy.

Electron Configuration of Diatomic Molecules

After applying two principles of filling orbitals

- The *aufbau* principle and
- The Pauli exclusion principle

we can predict that both electrons in H_2 will go into the lower energy orbital denoted by $(\sigma_{1s})^2$. A molecular-orbital diagram shows the relative energy and number of electrons in each MO, as well as the atomic orbitals from which they form. Figure 3.24 is the molecular orbital diagram for H_2 .

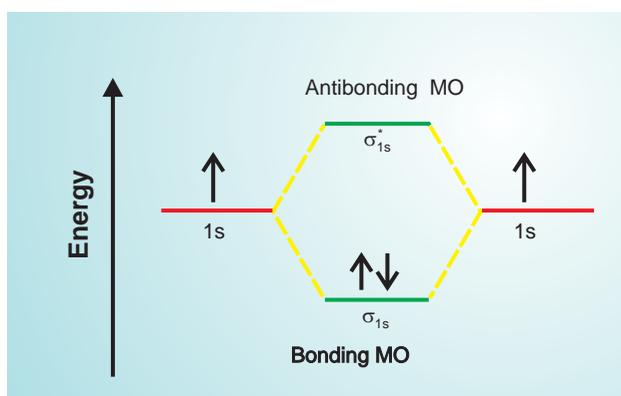


Figure 3.24 Molecular orbital diagram and bonding in the H_2 molecule.

There are no more electrons in H_2 so the σ_{1s}^* orbital remains empty in the ground state.

Note! The number of molecular orbitals formed must equal the number of atomic orbitals available for combination. Unfilled molecular orbitals are considered to be there, even when there are no electrons in them.

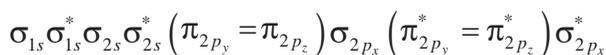
Exercise 3.15

Draw a molecular orbital energy diagrams for

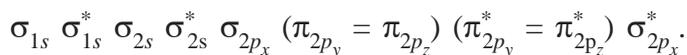
- a C_2^- b C_2 c C_2^+

The order of energy of molecular orbitals has been determined mainly from spectroscopic data.

- a In simple homonuclear diatomic molecules (total electrons = 14 or less) the order is:



- b For simple homonuclear diatomic molecules (total electrons greater than 14) the $(\pi_{2p_y} = \pi_{2p_z})$ comes after σ_{2p_x} and the order is:



Note that the $2p_y$ atomic orbital give π bonding and π antibonding (π^*) MOs of the same energy as those produced from $2p_z$ orbitals. The π_{2p_y} and π_{2p_z} orbitals are said to be double degenerate, and similarly $\pi_{2p_y}^*$ and $\pi_{2p_z}^*$ are double degenerate. A similar arrangement of MOs exists from σ_{3s} to $\sigma_{3p_x}^*$, but the energies are known with less certainty.

The Aufbau principle is used to derive the electronic structure of some simple diatomic molecules or molecule ions. The total number of electrons from the two atoms which make the molecule are filled into molecular orbitals. The MOs of lowest energy are filled first, each MO holds two electrons of opposite spins and when orbitals are degenerate, Hund's rule applies and electrons are not paired.

Example 3.4

Use the molecular orbital theory to derive the electron configuration of

- a H_2^+ b Li_2 c He_2^+ d O_2 . Which of these molecules or molecules ions exist?

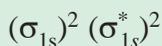
Solution:

- a H_2^+ molecule ion. This may be considered as a combination of H atom and a H^+ ion, giving one electron to be accommodated in a MO;
- b Li_2 molecule. Each Li atom has two electrons in its inner shell, and one in its

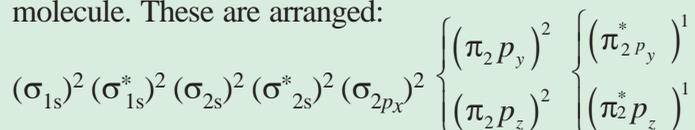
outer shell, making a total of six electrons arranged:



- c He_2^+ Molecule ion. If this is considered as a He atom and a He^+ ion there are three electrons, which are arranged. The filled bonding orbital gives stabilization whilst the half-filled gives destabilization. Overall, there is some stabilization, so the helium molecule ion should exist, and it has been observed spectroscopically.



- d O_2 molecule. Each oxygen has eight electrons, making a total of sixteen for the molecule. These are arranged:



The anti bonding $(\pi_{2p_y}^*)$ and $(\pi_{2p_z}^*)$ orbitals are singly occupied in accordance with Hund's rule. As in previous examples, the inner shell does not participate in bonding and the bonding and antibonding 2s orbitals cancel each other. A σ bond results from the filling of $(\sigma_{2p_x})^2$. Two half π bonds arise from π_{2p_z} and π_{2p_y} bonding and

antibonding. Therefore, $1\sigma + \frac{1}{2}\pi + \frac{1}{2}\pi = 2$ bonds are formed.

Exercise 3.16

Use the molecular orbital theory and derive the electron configuration of the following molecules. Identify those which exist and do not exist.

- a He_2 b Be_2 c B_2 d C_2 e N_2

Bond Order

The term bond order is used to indicate whether a covalent bond is single (bond order = 1), double (bond order = 2) or triple (bond order = 3). For example, in a molecular orbital treatment of oxygen, a sigma bond results from the filling of $(\sigma_{2p_x})^2$. Since $(\pi_{2p_y}^*)^1$ is half-filled therefore cancels half the effect of $(\pi_{2p_y})^2$, half a pi bond results. Similarly another half pi bond arise from π_{2p_z} and $\pi_{2p_z}^*$, giving a total of $1\sigma + \frac{1}{2}\pi + \frac{1}{2}\pi = 2$. The bond order is said to be 2, and it can be calculated in the

above manner, or by calculating the number of electrons occupying bonding orbitals minus the number of electrons in antibonding orbitals, all divided by two.

$$\text{Bond order} = \frac{1}{2} \left[\left(\text{Number of } e^- \text{ in bonding MOs} \right) - \left(\text{Number of } e^- \text{ in antibonding MOs} \right) \right]$$

Activity 3.21



Form a group and use the MO theory to predict the bond order and the number of unpaired electrons in O_2^{2-} , O_2^- , O_2^+ , NO and CO.

Share your findings with the rest of the class.

Magnetic Properties

A species with unpaired electrons exhibits **paramagnetic** property. The species is attracted by an external magnetic field. A species in which all the electrons are paired, exhibits **diamagnetism**. Such species are not attracted (and, in fact, are slightly repelled) by a magnetic field.

The antibonding π^*_{2py} and π^*_{2pz} orbitals for O_2 are singly occupied in accordance with Hund's rule. Unpaired electrons give rise to **paramagnetism**. Since there are two unpaired electrons with parallel spins, this explains why oxygen is paramagnetic. This was the first success of the MO theory in successfully predicting the paramagnetism of O_2 , a fact not even thought of with VB representation of the oxygen molecule ($O = O$).

Exercise 3.17

1. What is the bond order for CN^- , CN and CN^+ ?
2. Which homonuclear diatomic molecules of the second period elements, besides O_2 , should be paramagnetic?

3.6 TYPES OF CRYSTALS

At the end of this section, you should be able to:

- define a crystal;
- name the four types of crystalline solids and give examples;
- mention the types of attractive forces that exist within each type of crystalline solids;
- describe the properties of each type of crystalline solids; and
- build a model of sodium chloride crystal structure.

A crystal is a piece of a solid substance that has plane surface, sharp edges, and a regular geometric shape. The fundamental units-atoms, ions or molecules are assembled in a regular, repeating manner extending in three dimensions throughout the crystal. An essential feature of a crystal is that its entire structure can be figured from a tiny portion of it. Some solids, like glass, lack this long-range order and are said to be amorphous. The structural units of an amorphous solid, whether they are atoms, molecules or ions occur at random positions. As in liquids, there is no ordered pattern to the arrangement of an amorphous solid.

A structural unit of a crystalline solid has a characteristic repetitive pattern. The crystal types and their basic units are (i) ionic (electrostatic attraction of ions), (ii) Molecular (electrostatic attraction of dipoles in molecules) (a) Polar (dipole-dipole and H-bonding) and (b) Non-polar (London forces) (iii) Network (covalently bonded atoms); and (iv) metallic (positive nuclei in electron sea).

There are four important classes of crystalline solids.

Ionic Crystals

The fundamental units of an ionic solids are positive and negative ions. As a result, the inter-particle forces (ionic bonds) are much stronger than the **van der Waals** forces in molecular solids. To maximize attractions, cations are surrounded by as many anions as possible, and vice versa.

The properties of ionic solids are direct consequences of the strong inter-ionic forces, which create a high lattice energy. Crystalline ionic solids are usually, brittle, and non-

conductors of electricity, although molten crystals may be good conductors. They usually have high melting points. Some of the more familiar ionic solids are table salt (NaCl), saltpeter (KNO_3), washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), and black board chalk (CaCO_3).

Group Assignment



With the help of balls and sticks of any material or any other modelling material build the model of crystal sodium chloride. [Hint-Take help of Figure 3.25]

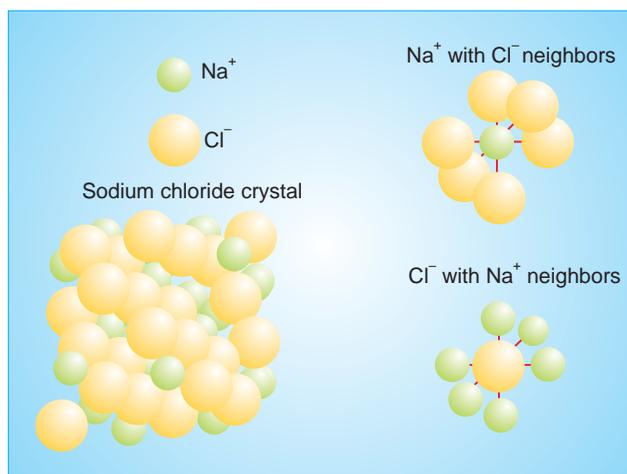


Figure: 3.25 Crystal model of sodium chloride.

Molecular Crystals

Various combinations of dipole-dipole, dispersion and hydrogen-bonding forces are operative in molecular solids, which accounts for their wide range of physical properties. Dispersion forces are the principal forces acting in non-polar substances, so melting points generally increase with molar mass. Among polar molecules, dipole-dipole forces and where ever possible, hydrogen-bonding dominate. Nevertheless, intermolecular forces are still relatively weak, so the melting points are much lower than ionic, metallic and network covalent solids.

The fundamental unit of a molecular solid is the molecule. Such solids are common among organic compounds and simple inorganic compounds. Molecular crystals are usually transparent, brittle, and break easily when stressed. They are usually non conductors of heat and electricity and usually have low melting points. Familiar

molecular crystalline solids include sugar, dry ice (solid carbon dioxide), glucose and aspirin.

Covalent Network Crystals

In this type of crystalline solids, separate particles are not present. Instead, strong covalent bonds link the atoms together throughout the network of covalent solid. As a consequence of the strong bonding, all these substances have extremely high melting and boiling points, but their conductivity and hardness depend on the nature of their bonding. The two common crystalline forms of elemental carbon are examples of network covalent solids. Although graphite and diamond have the same composition, their properties are strikingly different, graphite occurs as stacked flat sheets of hexagonal carbon rings with a strong sigma-bond framework and delocalized pi-electrons over the entire sheet. These mobile electrons allow graphite to conduct electricity. Common impurities, such as O_2 makes graphite soft. In diamond, each carbon atom is bonded to four other carbon atoms tetrahedrally in a giant structure. The carbons are joined by single bonds. Strong single bonds throughout the crystal make diamond among the hardest substance known. Because of its localized bonding electrons, diamond (like most network covalent solids) is unable to conduct electricity. The most important network covalent solids are the silicates. In a covalent network solid, the whole crystal is one giant molecule. The fundamental units are atoms covalently bonded to their neighbours. These crystals are usually hard, non conductors of heat and electricity, and have high melting points. Examples of covalent network solids include quartz (SiO_2) and diamond.

Metallic Crystals

The strong metallic bonding forces hold individual atoms together in metallic solids. The properties of metals, such as high electrical and thermal conductivity, luster and malleability result from the presence of delocalized electrons, the essential feature of metallic bonding (introduced in Section 3.4). Metals have a wide range of melting points and hardness, which are related to the packing efficiency of the crystal structure and the number of valence electrons available for bonding. For example, Group IIA metals are harder and higher melting than Group IA metals, because the IIA metals have closer packed structures and twice as many delocalized valence electrons. The

fundamental units of pure metallic solids are identical metal atoms. Metallic crystals are opaque with reflective surfaces. They are ductile and malleable, good conductor of heat and electricity, and they usually have high melting points. Copper, silver, gold, iron and aluminium are familiar examples of metals.

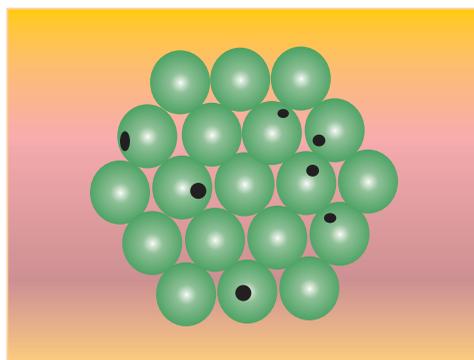


Figure 3.26 Model of metallic crystal.

Table 3.2 Comparison of the four types of crystals

| Type of Solid | Interaction | Properties | Examples |
|---------------|--|--|---|
| Ionic | Ionic | High melting point, brittle, hard | NaCl, MgO |
| Molecular | Hydrogen bonding, Dipole-Dipole, London dispersion | Low melting point, non-conducting | H ₂ , CO ₂ |
| Network | Covalent bonding | High melting point, hard, non-conducting | C (diamond), SiO ₂ (quartz) |
| Metallic | Metallic bonding | Variable hardness and melting point (depending upon strength of metallic bonding), conducting | Fe, Mg |

Exercise 3.18

Match the substances from list A with the best suited characteristics given in list B and justify your answer.

| List A Substances | | List B Characteristics |
|----------------------|---|---|
| a Fe | a | Forces of attractions are between positive ions and 'sea of electrons' |
| b I ₂ | b | High boiling point due to strong covalent bonds |
| c H ₂ O | c | High boiling point due to hydrogen bond |
| d SiO ₂ | d | Weak van der Waal's forces |
| e Na | e | Giant metallic lattice, ions packed together very closely leading to high density |
| | f | Non-polar solvent |

Unit Summary

- *Lewis symbols of representative elements are related to their location in the periodic table. The lattice energy and enthalpy of formation of an ionic compound, together with other atomic and molecular properties, can be related in a thermochemical cycle called Born-Haber cycle.*
- *A covalent bond is created by the sharing of an electron-pair between atoms.*
- *In a Lewis structure representing covalent bonds, electron-pairs are either bonding-pairs or lone-pairs.*
- *In a covalent bond between atoms of different electronegativity, electrons are displaced toward the atom with the higher electronegativity. In terms of electronegativity differences chemical bonds vary over the range: non polar to polar covalent to ionic.*

- *In some cases of covalent bonding, one atom appears to provide both electrons in the bonding pair; the bond is known as coordinate-covalent bond.*
- *Bonded atoms may share more than one pair of electrons between them, giving rise to multiple covalent bonding.*
- *In the phenomenon of resonance, two or more Lewis structures have the same skeletal structure but different bonding arrangements. The best description of the resonance structure (resonance hybrid) is obtained by combining plausible structures (contributing structures).*
- *Exceptions to the octet rule are found in odd-electron molecules and molecular fragments called free radicals. A few structures appear to have too few electrons to complete all the octets. Some structures appear to have too many. In the latter case, a central atom may employ an "expanded" octet with five or six electron-pairs.*
- *Valence shell electron pair repulsion theory (VSEPR) predicts the geometrical structures of molecules and polyatomic ions based on mutual repulsions among valence shell electron groups.*
- *Multiple bonds, whether they consist of four electrons (double bond) or six electrons (triple bond), are treated as one electron set.*
- *The separation of the centres of positive and negative charge in a polar covalent bond creates a bond moment. Whether a molecule as a whole is polar, that is, whether there is a resultant dipole moment, is established by bond moments and molecular geometry.*
- *A symmetrical distribution of identical bond moments about a central atom results in a cancellation of all bond moments, with the result that the molecule is nonpolar, as in the case of CCl_4 .*
- *In the valence bond method (VB) a covalent bond is viewed as the overlap of atomic orbitals of the bonded atoms in a region between the atomic nuclei.*
- *Molecular geometry is determined by the spatial orientations of the atomic orbitals involved in bonding.*
- *The VB method often requires that bonding atomic orbitals be hybridized in order to rationalize known structures of molecules. A hybridized orbital is some combination of s, p and d orbitals, such as sp, sp^2 , sp^3 ,*

sp^3d and sp^3d^2 . The geometric distribution of hybridized orbitals in the valence bond method is the same as the electron set geometry proposed by VSEPR theory.

- Hybrid orbitals overlap in the usual way (end-to-end) and form σ bonds. Unhybridized p orbitals overlap in a side-by-side manner and give rise to π bonds. A double bond consists of one σ bond and one π bond; a triple bond, one σ bond and two π bonds.
- Acceptable solutions to wave equations written for the electrons in a molecule are called molecular orbitals (MO). The two main types of MOs are bonding molecular orbitals, which concentrate electron charge density between atoms or just above and below the imaginary line joining the two nuclei and antibonding molecular orbitals, which concentrate electron charge densities away from the intermolecular bonding region.
- Electrons can be assigned to molecular orbitals by the scheme similar to the aufbau process. MO theory provides more satisfactory descriptions for certain structures than does the VB method, for example, some odd-electron species and the O_2 molecule.

Check list

Key terms of the unit

- Anion
- Atomic orbital
- Covalent bond
- Crystal
- Delocalisation of electrons
- Dipole
- Dipole moment
- Double bond
- Electric charge
- Ionic bond
- Ionization
- Kinetic energy
- Lattice
- London dispersion forces
- Molecule
- Molecular orbital
- Noble gases
- Potential energy
- Single bond
- Substance
- Triple bond
- Unit cell
- Valence electron
- Valence bond theory
- Van der Waals force

REVIEW EXERCISE

Part I: Multiple Choice Questions

- "Two atoms each provide two electrons that are shared by the two atoms" This is a description of a
 - triple covalent bond
 - coordinate covalent bond
 - double covalent bond
 - single covalent bond
- A non-metal usually forms two covalent bonds in its compounds. How many electrons will it have in its valence shell?
 - 2
 - 4
 - 6
 - 8
- The noble gases do not usually form chemical compounds because:
 - they have very stable nuclei.
 - the bonds between their atoms are very strong.
 - they already have paired valence shell electrons.
 - they are not polar.
- Which of the following compounds contain both ionic and covalent bonds?
 - CO_2
 - Cl_2O
 - Na_2CO_3
 - BaCl_2
- Which of the following molecules would you expect to be non-planar?
 - CH_4
 - BCl_3
 - XeF_4
 - HCHO
- If a molecule has a trigonal pyramidal shape, how many non-bonding pairs of electrons are present in the valence shell of the central atom?
 - 1
 - 2
 - 3
 - 4
- Of the following, the most polar bond is:
 - $\text{P} - \text{Cl}$
 - $\text{Si} - \text{F}$
 - $\text{S} - \text{O}$
 - $\text{C} - \text{N}$

8. Carbon and chlorine form a series of compounds: CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4 . Which of these will be polar:
- a CCl_4 only
 - b CH_3Cl and CHCl_3 only
 - c CH_3Cl , CH_2Cl_2 and CHCl_3 only
 - d CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4
9. The carbon atoms in ethane (C_2H_6), ethene (C_2H_4) and ethyne (C_2H_2) provide, respectively, examples of the three common types of hybridization corresponding to:
- a sp , sp^2 , sp^3
 - b sp^3 , sp^2 , sp
 - c sp , sp^3 , sp^2
 - d sp^3 , sp , sp^2
10. Which of the following correctly describes a π bond?
- a It is formed by the end-to-end interaction of p -orbitals and has a low electron density on the internuclear axis.
 - b It is formed by the parallel interaction of p -orbitals and has a high electron density just above and below the internuclear axis.
 - c It is formed by the interaction of s -orbitals and has a low electron density on the internuclear axis.
 - d It is formed by the interaction of s -orbitals and has a high electron density on the internuclear axis.
11. Which of the following species cannot be adequately described by a single Lewis structure?
- a OH^-
 - b C_2H_2
 - c NH_4^+
 - d HCO_3^-
12. In which of the following compounds would inter-molecular hydrogen-bonding occur?
- a HCHO
 - b PH_3
 - c CH_3OH
 - d COCl_2

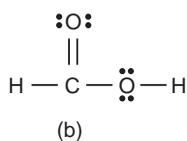
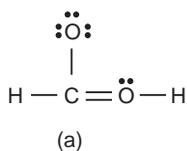
13. Which of the following molecules would you expect to have the highest boiling point?
- a $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$
 - b $\text{CH}_3\text{-CH}(\text{CH}_3)\text{-CH}_2\text{-CH}_2\text{-CH}_3$
 - c $\text{CH}_3\text{-CH}_2\text{-CH}(\text{CH}_3)\text{-CH}_2\text{-CH}_3$
 - d $\text{CH}_3\text{-C}(\text{CH}_3)_2\text{-CH}_2\text{-CH}_3$
14. Which of the following molecules possesses the strongest forces between the molecules?
- a N_2
 - b $\text{CH}_3\text{-CH}_3$
 - c H_2CO
 - d CH_4
15. Which one of the following usually produces the weakest interaction between particles of similar molar mass?
- a Van der Waals forces
 - b Dipole-dipole forces
 - c Covalent bonds
 - d Hydrogen-bonding
16. The hydrogen bonding is not significant in:
- a DNA
 - b protein
 - c ice
 - d polyethylene
17. A gas is likely to:
- a have its atoms held together by metallic bonds.
 - b have a giant covalent structure.
 - c be a compound of a metal.
 - d have a molecular covalent structure.
18. If an element in group IIA of the periodic table formed a compound with an element in group VIIA of the periodic table, the compound formed is likely to:
- a be a crystalline solid
 - b dissolve in non-polar solvents
 - c have a low boiling point
 - d conduct electricity in the solid state
19. Which of the following substances would you expect to have the lowest boiling point?
- a CsCl
 - b SrSO_4
 - c Sc_2O_3
 - d AsCl_3

20. Which of the following would not conduct an electric current?
- | | |
|---------------------------|--------------------------|
| a solid mercury | c liquid sodium chloride |
| b Aqueous sodium chloride | d solid sodium chloride |

Part II: Answer the following questions:

21. Name the following compounds:
- | | |
|---------------------|-------|
| a KBr | d BeO |
| b Al I ₃ | e BaS |
| c Li ₃ N | |
22. Predict the shape for the following molecules:
- | | |
|--------------------|--------------------|
| a SiF ₄ | d NF ₃ |
| b PCl ₃ | e CCl ₄ |
| c H ₂ S | f PCl ₅ |
23. Draw Lewis structures and predict the shapes, giving approximate bond angles for:
- CH₃⁺, CH₃⁻, ·CH₃ (methyl radical), HCN, ICl₂, NH₂⁻, NO₂, ClO₂.
24. Classify the given molecules as polar or non-polar:
- | | |
|--------------------|--------------------|
| a SiF ₄ | d H ₂ S |
| b NF ₃ | e CCl ₄ |
| c PCl ₃ | f CO ₂ |
25. Which atom (if any), in each of the following bonds would you expect to carry a partial negative charge?
- | | |
|---------|---------|
| a H – N | d C – F |
| b S – S | e B – O |
| c O – P | f I – F |
26. Draw the Lewis structure for the given molecules and state whether the molecule is polar or non-polar:
- | | |
|--|---------------------------------|
| a PF ₄ ⁻ | b ICl ₄ ⁻ |
| c N ₂ F ₂ (2 forms possible) | |
27. Boron trifluoride can react with a fluoride ion to give the tetrahedral BF₄⁻ ion. What type of hybridization would you expect the boron to have in BF₄⁻?

28. Carbon and oxygen can bond either by a single bond (as in $\text{CH}_3\text{-OH}$), a double bond (as in $\text{O}=\text{C}=\text{O}$), or a triple bond (as in $\text{HC}\equiv\text{CH}$).
- Describe these three types of bonds in terms of σ -bonds and π -bonds.
 - How would you expect the length of the carbon-oxygen bond to vary in the three given examples?
29. Explain the following in terms of the intermolecular forces that exist in them:
- Water is a liquid at room temperature and atmospheric pressure, but hydrogen sulphide is a gas.
 - At room temperature and atmospheric pressure chlorine is a gas, bromine is a liquid and iodine is a solid.
 - Pentan-1-ol boils at 137°C , where as pentan-3-ol boils at 116°C .
 - The boiling point of sulphur dioxide is 24°C higher than that of chlorine.
30. Of the two possible valence-bond formulas for formic acid (HCO_2H), which one is the more reasonable structure?



31. Draw the correct valence-bond formula for hydrazine (N_2H_4).
32. Draw the resonance hybrid of SO_2 .
33. Based on the VB approach, predict the shape of a ClO_3^- ion.
34. The molecular orbital description of NO is similar to that of O_2 except that the energies of the oxygen atomic orbitals are slightly lower than those of nitrogen atomic orbitals and NO molecule contains different number electrons than O_2 .
- Draw an energy diagram to show how the atomic orbitals of N and O combine to form molecular orbitals of NO .
 - How many unpaired electrons are present in the NO molecule?
 - What is the bond order in NO molecule?
 - Is NO paramagnetic or diamagnetic?
35. List the following in order of increasing O – O bond length : O_2 , O_2^+ , O_2^-
36. Show the direction of the bond moment (dipole moment) in each of the following bonds:

