Ancillary Chemistry-II



- Dr. Suman Kushwaha
- Assistant professor
- Department of Chemistry
- Institute of science
- B.H.U Varanasi.

BSC-04A Ancillary Chemistry-II (BASIC ASPECTS OF CHEMISTRY)

Credits: 2

BSC-04A Ancillary Chemistry-II (BASIC ASPECTS OF CHEMISTRY) Credits: 2 Union of elements and its electronic basis, lenic, covalent and hydrogen bonds. Energetics of chemical bond formation. Bond energy, average bond energy, bond lengths and bond Conventional and non-conventional energy sources; a. Petroleum products: their origin and separation into different fractions. Octane and Brief discussion of hydrogen-hydride and lead storage battery. Brief discussion of basic concept of electrode potential and its applications in the metallurgical operations with special reference to iron. The phenomenon of rusting of iron and its prevention through anodic protection. The chemical basis of photosynthesis and respiration (only elementary treatments). I . Natural: Photosynthesis: Light reaction, Dark reaction, Factors affecting photosynthesis, Photorespiration. Respiration: Discussion of the role of Heamoglobin and Myoglobin in carrying Oz. Aerobic and Anzerobic respiration, different steps in aerobic respiration (in brief), respiratory quotient (RQ). II Polymers: Natural and synthetic polymers: a) Polysaccharides: carbohydrates Polypeptides: protein and enzymes, primary, secondary, tertiary and quarternary structures. Molecular disease and primary structure of protein. Enzymes: types of enzymes, co-factor and prosthetic group, denaturation of enzyme. d) Rubber and vulcanization of rubber. III Synthetic: Polyneoprene and Bu-na-S rubber, Nylons, Polyesters, Bakelite and Teflon. Health hazards and environmental problems created by polymers. Chemical Thermodynamics: Systems and surroundings. Extensive and intensive thermodynamic properties, Open, closed and adiabatic systems. Spontaneous and Nonspontaneous processes. Thermodynamic basis for the spontaneity of a process,

Ionic or Electovalent Bond

According to Kossel's theory, in the process of formation of ionic bond the atoms acquire the noble gas electronic configuration by the gain or loss of electrons. Let us consider the formation of NaCl in terms of Kossel's Theory.

The electronic configuration of sodium atom (atomic number 11) is 2,8,1. Since it is highly electropositive, it readily loses an electron to attain the stable configuration of the nearest noble gas (neon) atom. It becomes a positively charged sodium cation (Na⁺) in the process

Na
$$\longrightarrow$$
 Na⁺ + e⁻; Δ H = 493.8 kJ mol⁻¹
2,8,1 2,8 (Δ H is enthalpy change)

On the other hand, a chlorine atom (electronic configuration: 2,8,7) requires one electron to acquire the stable electronic arrangement of an argon atom. It becomes a negatively charged chloride anion (Cl⁻) in the process.

C1 + e⁻
$$\longrightarrow$$
 C1⁻; $\Delta H = -379.5 \text{ kJ mol}^{-1}$
2,8,7 2,8,8

According to **Kossel's** theory, there is a **transfer** of one electron from sodium atom to chlorine atom and both the atoms attain noble gas configuration.

The positively charged sodium ion and the negatively charged chloride ion are held together by electrostatic attractions. The bond so formed is called an **electrovalent** or an **ionic bond**. Thus the ionic bond can be visualised as the electrostatic force of attraction that holds the cation and anion together. The compounds so formed are termed as ionic or electrovalent compounds.

Energetics of Ionic Compound Formation

The formation of NaCl from sodium and chlorine can be broken down into a number of steps as:

a) Sublimation of solid sodium to gaseous sodium atoms.

$$Na(s) \longrightarrow Na(g)$$
; $\Delta H = 108.7 \text{ kJ mol}^{-1}$

b) Ionization of gaseous sodium atom to give sodium ion.

$$Na(g) \longrightarrow Na^{+}(g) + e^{-};$$
 $\Delta H = 493.8 \text{ kJ mol}^{-1}$

c) Dissociation of gaseous chlorine molecule into chlorine atoms

$$\frac{1}{2} \operatorname{Cl}_{2}(g) \longrightarrow \operatorname{Cl}(g) ; \qquad \Delta H = -120.9 \text{ kJ mol}^{-1}$$

d) Conversion of gaseous chlorine atom to chloride ion (addition of electron)

$$Cl(g) + e^{-} \longrightarrow Cl(g); \qquad \Delta H = -379.5 \text{ kJ mol}^{-1}$$

Formation of NaCl from sodium and chloride ions.(Crystal or lattice formation).

$$Na^{+}(g) + Cl^{-}(g) \longrightarrow Na^{+}Cl^{-}(s); \qquad \Delta H = -754.8 \text{ kJ mol}^{-1}$$

The energy released in this step is lattice energy.

The net reaction would be

Na(s) +
$$\frac{1}{2}$$
Cl₂(g) \longrightarrow Na⁺Cl⁻(s); Δ H = -410.9 kJ mol⁻¹

The overall energy change can be computed by taking the sum of all the energy changes:

$$\Delta H = (180.7 + 493.8 + 120.9 - 379.5 - 754.8) = -410.9 \text{ kJ mol}^{-1}$$

Thus we see that the net process of formation of NaCl from sodium and chlorine is accompanied by a large decrease in the energy. The approach we have just followed is based on the law of conservation of energy and is known as **Born-Haber cycle**.

Thus we see that the net process of formation of NaCl from sodium and chlorine is accompanied by a large decrease in the energy. The approach we have just followed is based on the law of conservation of energy and is known as **Born-Haber cycle**.

Of the five different types of energies involved, two (sublimation and dissociation energies) are generally have low values than the rest. Therefore, the three energy terms i.e., ionization energy, electron affinity and lattice energy are important in determining the formation of an ionic compound. On the basis of the above discussion we can say that the formation of an ionic compound is favoured by

- Low ionisation energy of the metal,
- ii. High electron affinity of the other element (non-metal), and
- iii. High lattice energy

Characteristic Properties of Ionic Compounds

- These exist as crystalline solids in which the ions are arranged in a regular three dimensional structure. The ionic compounds are generally hard and brittle in nature.
- These compounds have high melting and boiling points due to strong electrostatic interactions between the ions.
- These are generally soluble in water and less soluble in non-polar solvents like ether, alcohol, etc.
- These conduct electricity when in molten state or in aqueous solutions.

Kossel's theory explains bonding quite well but only for a small class of solids composed of electropositive elements of Group 1 and 2 with highly electronegative elements. Secondly, this theory is incapable of explaining the formation of compounds like, SO_2 or O_2 , etc. For example in case of O_2 , there is no reason to expect that one atom of oxygen would lose two electrons while the other accepts them. The problem was solved by Lewis theory of covalent bonding.

Covalent Bond

Like Kossel, Lewis also assumed that atoms attain noble gas electronic configuration in the process of bond formation. However, the way the noble gas electronic configuration

is achieved, is different. Lewis proposed that this is achieved by "sharing of a pair of electrons" between the two atoms. Both the atoms contribute an electron each to this pair. For example, two hydrogen atoms form a molecule by sharing a pair of electrons. If electrons are indicated as dots, formation of hydrogen molecule can be shown as

$$H. + .H \longrightarrow H : H \longrightarrow H - H$$

This shared pair of electrons contributes towards the stability of both the atoms and is said to be responsible for 'bonding' between the two atoms. Such a bond is called **covalent bond** and the compounds so obtained are called covalent compounds. In the process of suggesting the process of chemical bonding Lewis provided a very convenient way of representing bonding in simple molecules. This is called **Lewis electron-dot structures** or simply **Lewis structures**.

In Lewis structure each element is represented by a **Lewis symbol**. This symbol consists of the normal chemical symbol of the element surrounded by number of dots representing the electrons in the valence shell. Since the electrons are represented by dots, these are called electron-dot structures. The Lewis symbols of some elements are as:

```
·Li ; ·Be · ; ·B · ; ·C · ; : N ' ; : O ' ; : F ' ; : Ne :
```

You may note here that while writing the Lewis symbols, single dots are placed first on each side of the chemical symbol then they are paired up. The Lewis structure of a molecule is written in terms of these symbols

You may note here that while writing the Lewis symbols, single dots are placed first on each side of the chemical symbol then they are paired up. The Lewis structure of a molecule is written in terms of these symbols

In terms of Lewis symbols the ionic bond formation in NaCl can be represented as

and the covalent bond formation in HCl is represented as

Sometimes the electrons contributed by different atoms are represented by different symbols. For example, formation of HF may also be shown as

$$H_x + F : \longrightarrow H_x F$$
:

In this case the hydrogen electron is shown as a cross while the electrons of fluorine are represented by dots. There is no difference between electrons; it is just a presentation for the sake of convenience.

In terms of Lewis structures the formation of a chlorine molecule from two chlorine atoms may be represented as

Here each chlorine atom with seven valence electrons, contributes one electron to the shared pair. In the process of bond formation both the chlorine atoms acquire the electronic configuration of argon. In the same way, the formation of oxygen molecule involves sharing of two pairs of electrons between the two oxygen atoms. In this case both the atoms contribute two electrons each and acquire eight electrons or an octet in their valence shell.

$$\vdots \circ . + \cdot \vdots \longrightarrow 0 \vdots \vdots \circ \longrightarrow 0 = 0$$

You may have noticed that in the process of bond formation, the elements of second period acquire eight electrons in their valence shell. This is called 'Octet rule'. You may also note that in case of H_2 and Cl_2 the atoms are linked by a single line while in case of O_2 the atoms are linked by two lines. These lines represent bonds. When two atoms are bound by sharing a single pair of electron, they are said to be joined by a single bond. And when, two pairs of electrons are shared (as in case of O_2), the two atoms are said to be bound by a double bond. In nitrogen (N_2) the two atoms are joined by a triple bond as they share three pairs of electrons.

In a Lewis representation the electrons shown to be involved in the bond formation are called bonding electrons; the pair of electrons is called 'bond pair' and the pairs of electrons not involved in the bonding process are called 'lone pairs'. The nature of the electron pair plays an important role in determining the shapes of the molecules.

Polar Covalent Bond

In a chemical bond the shared electron pair is attracted by the nuclei of both the atoms. When we write the electron dot formula for a given molecule this shared electron pair is generally shown in the middle of the two atoms indicating that the two atoms attract it equally. However, actually different kinds of atoms exert different degrees of attraction on the shared pair of electrons. A more electronegative atom has greater attraction for the shared pair of electrons in a molecule. As a consequence in most cases the sharing is not equal and the shared electron pair lies more towards the atom with a higher electronegativity. For example, in HCl, the shared pair of electron is attracted more towards more electronegative chlorine atom. As a result of this unequal sharing of the electron pair, the bond acquires polarity or partial ionic character.

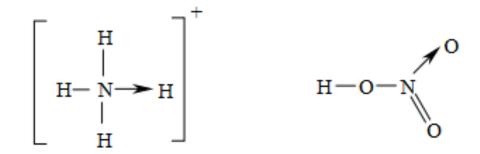
In an extreme case, the difference in the electronegativity may be so high that the electron pair is practically under the influence of a single atom. In other words the polarization of the bond is complete i.e., we have a case of ionic bonding. Thus, though the Lewis theory talks about covalent bonding it can account for the formation of ionic compounds also.

Coordinate Covalent Bond

You have learnt that in the formation of a covalent bond between the atoms, each atom contributes one electron to the shared electron pair, However, in some cases both the electrons of the shared pair are contributed by only one species (atom, molecule or ion) A

common example is the formation of a bond between boron trifluoride (BF₃) and ammonia (NH₃). BF₃ is an electron deficient molecule and can accept a pair of electrons. The molecule of ammonia on the other hand is electron rich. It has a lone pair of electron on the nitrogen atom and that can be donated. Electron rich ammonia donates a pair of electron to electron deficient BF₃. Such electron donor-acceptor bonds are called **coordinate** covalent or dative bonds.

A coordinate bond is normally represented by an arrow pointing from a donor atom to the acceptor atom. A coordinate bond is identical to a covalent bond in terms of its polarity and strength. The two are different only in the way they are formed. We cannot distinguish between covalent and coordinate covalent bond, once these are formed. HNO₃ and NH₄⁺ ion are some more common examples of formation of a coordinate bond.

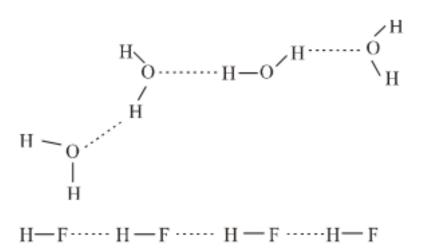


Characteristic properties of Covalent Compounds

- 1. The covalent compounds have low melting and boiling points due to weak forces of interaction between the molecules.
- 2. The covalent compounds are poor conductors of electricity as these lack ionic species.
- 3. The covalent compounds are generally insoluble in water and dissolve in nonpolar solvents like benzene, carbon tetrachloride etc.

Hydrogen Bonding

It is a special type of attraction between a hydrogen atom bonded to a strongly electronegative atom (like nitrogen, oxygen or fluorine) and the unshared pair of electrons on another electronegative atom. Hydrogen bond is a weak bond, the strength being just about 4-25 kJ mol⁻¹. It is quite small as compared to the covalent bond, which needs a few hundreds of kJ mol⁻¹ of energy to break. However, it is strong enough to be responsible for the high boiling points of H₂O and HF etc. In fact it is due to hydrogen bonding only that water exists as a liquid. The low density of ice also can be explained in terms of hydrogen bonding.



Due to the difference in the electronegativity between hydrogen and the other electronegative atom, the bond connecting them becomes polar. The hydrogen atom acquires a positive charge while the electronegative atom bears the negative charge. Hydrogen bonding results from the electrostatic interaction between the positively charged hydrogen atom and the negatively charged electronegative atom. The second electronegative atom may be a part of the same molecule or it may belong to a different molecule. Accordingly, there are two types of hydrogen bonds. If the hydrogen bond is formed between two different molecules it is called **intermolecular hydrogen bond**. When the hydrogen bond exists within the same molecule, it is called **intramolecular hydrogen bonding**. Salicyldehyde ad o-nitrophenol are two common examples of the molecules showing intramolecular hydrogen bonding whereas in water, intermolecular hydrogen bonding exists.

Hydrogen bonding plays an important role in the structure and function of many biomolecules like proteins and nucleic acids.

Valence Shell Electron Pair Repulsion (VSEPR) Theory

In a molecule the constituent atoms have definite positions relative to one another i.e., the molecules have a definite shape. The theories of bonding that we have discussed so far do not say anything about the shape of the molecules. A simple theory called VSEPR theory was put forth by Sidgwick and Powell in 1940 to explain the shapes of molecules. It was later refined and extended by Nyholm and Gillespie in1957. This theory focuses on the electron pairs present in the valence shell of the central atom of the molecule and can be stated in terms of two postulates:

The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize their mutual repulsion. In other words, the chemical bonds in the molecule will be energetically most stable when they are as far apart from each other as possible. Let us take up some examples.

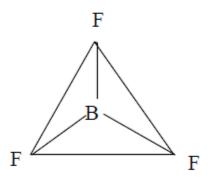
BeCl₂ is one of the simple triatomic molecules. In this molecule, the central atom, beryllium has an electronic configuration of 1s² 2s². That is it has two electrons in its valence shell. In the process of covalent bond formation with two chlorine atoms two more electrons are contributed (one by each chlorine atom) to the valence shell. Thus there are a total of 4 valence electrons or two pairs of valence electrons. According to the postulate given above, these electron pairs would try to keep as far away as possible. It makes the two electron pairs to be at an angle of 180° which gives the molecule a linear shape.



Other molecules of this type would also have a similar shape.



BF₃: In boron trifluoride, the central atom, boron has an electronic configuration of 1s² 2s² 2p¹. That is, it has three electrons in its valence shell. In the process of covalent bond formation with three fluorine atoms three more electrons are contributed (one by each fluorine atom) to the valence shell. Thus there are a total of 6 valence electrons or three pairs of valence electrons. According to the VSEPR postulate, these electron pairs would try to keep as far apart as possible. It makes the three electron pairs to be located at an angle of 120° which gives the molecule a planar trigonal shape.



Planar trigonal shape

Thus different molecules would have different shapes depending on the number of valence shell electrons involved. The geometric shapes associated with various numbers of electron pairs surrounding the central atom are given in Table 5.1.

Table 5.1: Geometric arrangements of electron pairs around central atom.

Molecule Type	Number of electron pairs	Predicted geometry	Representative structure	Examples
AX ₂ AX ₃	2 3	Linear Planer trigonal	180°	HgCl ₂ , BeH ₂ BF ₃ , BCl ₃
\mathbf{AX}_4	4	Tetrahedral		CCl ₄ , CH ₄ , SiCl ₄
$AX_{\mathfrak{s}}$	5	Trigonal bipyramidal	: 90° :	PCl ₅ , PF ₅
\mathbf{AX}_6	6	Octahedral	A 999	SF ₆ , PF ₆

POSTULATE 2

The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is greater than that between two bond pairs The order of repulsive force between different possibilities is as under.

lone pair - lone pair - lone pair - bond pair - bond pair - bond pair

The shapes of molecules containing a combination of lone pairs and bond pairs would be distorted from the above mentioned shapes.

Let us take an example of three molecules namely, methane, ammonia and water. All the three contain a total of 4 electron pairs around their central atom. But the nature of these is different in the three cases. In methane molecule the central carbon atom has 4 valence electrons and it shares 4 electrons with four hydrogen atoms. So there are a total of 4 bond pairs and according to Table 5.1 it should have a tetrahedral shape. In case of ammonia also there are four pairs of electrons but their nature is different. Three of these are bond pairs while one is a lone pair. Similarly, in case of water again there are four pairs of electrons; two are bond pairs while two are lone pairs. Due to the differences in the mutual repulsion between bond pair - bond pair and lone pair - bond pair the molecular shape would be slightly distorted from the expected tetrahedral shape. The number and nature of electron pairs and the geometries of these three molecules are given in Table 5.2.

Table 5.2: Molecular geometries of molecules with 4 electron pairs with different combinations of lone pairs and bond pairs.

Molecule	Number of bond pairs	Number of lone pairs	Molecular geometry	Molecular Shape	Bond angle (in degrees)
CH ₄	4	0	tetrahedral	H C H	109.5
NH ₃	3	1	trigonal pyramidal	H H H H H H H H H H	107
H ₂ O	2	2	angular or bent	H O	104.5

We have so far learnt that a chemical bond formation between two atoms can occur by transfer (ionic bonding) or sharing (covalent bonding) of electrons. The processes of bond formation and the bonding in simple molecules can be conveniently represented in terms of electron – dot structures. Further, the VSEPR theory provides a good idea of the shapes of the molecules. But! have you noticed that we have been representing electrons as well defined dots i.e., localized particles. This is in contradiction with the probabilistic (orbital) representation of the electron that you have learnt in lesson 3. Let us learn how do we explain the process of bond formation in terms of modern theories that incorporate the wave mechanical representation of atom.

Modern Theories of Chemical Bonding

The theories of chemical bonding proposed (in 1916) by Kossel and Lewis are called as classical theories of bonding. These do not take into account the wave mechanical or quantum mechanical principles. After the development of quantum mechanical description of atomic structure two more theories were proposed to explain the bonding between atoms. These are called modern theories of chemical bonding. These are Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT). Let us discuss these theories in brief.

Valence Bond Theory

Valence bond theory was proposed by Heitler and London in 1927, to describe the formation of hydrogen molecule from its atoms. Linus Pauling and others further developed it. In this approach the process of chemical bond formation can be visualised as the overlapping of atomic orbitals of the two atoms as they approach each other. The strength of the bond depends on the effectiveness or extent of the overlapping. Greater the overlapping of the orbitals, stronger is the bond formed. Let us take the example of bonding in hydrogen molecule to understand the VB approach.

Suppose that the two hydrogen atoms are at infinite distance from each other. Their electrons are in their respective 1s orbitals and are under the influence of the corresponding nuclei. As the two atoms approach each other their 1s orbitals begin to overlap which lead to decrease in energy, Fig.5.1. At a distance equal to the bond length the overlapping is maximum and the energy is minimum. The overlapping can be equated to the sharing of electrons between the atoms. The electrons occupying the shared region of orbitals are under the influence of both the nuclei.

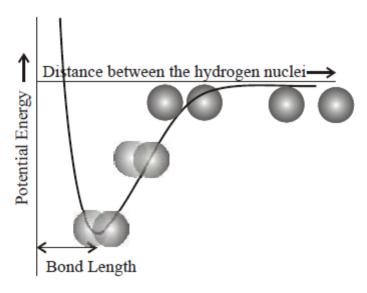


Fig. 5.1: Formation of hydrogen molecule from overlapping of two hydrogen atoms

This simple approach can be used to explain the bonding in simple diatomic molecules like HF,F₂ etc.. However, to explain bonding in molecules containing more than two atoms some additional concepts like excitation and hybridisation need to be used.

BOND STRENGTH

By bond strength we mean how strong is the bond between the atoms in a molecule. Bond length, bond multiplicity and extent of overlapping of atomic orbitals in addition to bond energy are the factors which determine the bond strength.

It has been observed that as the bond multiplicity increases, the bond length decreases thereby increasing the bond strength. Similarly, as the extent of overlapping between the atomic orbitals increases, the bond formed becomes stronger. That is why a σ bond is stronger than a π bond. Another important factor influencing the bond strength is the bond energy(bond strength α bond energy).

Bond energy:

The bond energy can be explained in two ways:

- (i) Bond formation energy (ii) bond dissociation energy
- (i) Bond Formation Energy:

(i) Bond Formation Energy:

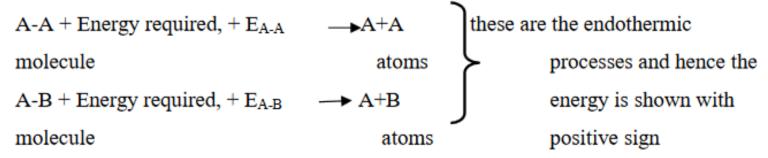
The bond formation energy of a covalent bond A-A or A-B in a diatomic molecule A₂ or AB is the amount of energy released during the formation of these molecules from the atoms A and B.

$$A+A \longrightarrow A-A + Energy \ released, -E_{A-A}$$
 these are the exothermic atoms molecule $A+B \longrightarrow A-B + Energy \ released, -E_{A-B}$ energy is shown with atoms molecule negative sign

This can be defined as "the amount of energy released when one mole (Avogadro's number) of bonds are formed between the constituent atoms in gaseous state of a molecule of A_2 or AB type". This energy is expressed in kJ mol⁻¹.

(ii) Bond dissociation energy

It is the energy required to break the A-A bond in A₂ or A-B bond in A-B molecule into the constituent atoms, i.e.



This can be defined as "the amount of energy required to break one mole of bonds in gaseous state of a molecule of A_2 or AB type into the constituent atoms."

Evidently both the bond formation energy and bond dissociation energy for A-A or A-B bonds in A₂ or AB diatomic molecule are equal in magnitude but are associated with opposite processes.

. .

In polyatomic molecules of AB_n type, n numbers of A-B covalent bonds are present e.g. H₂O

Each bond requires 1/n bond dissociation energy in these molecules to break up that bond. In such cases the bond energy is actually an average bond energy. For example, there are two bonds in H₂O molecule:

H₂O OH+H, D_{HO-H}
$$\longrightarrow$$
 = 496 KJ Total bond dissociation energy of two covalent bond in H₂O molecule = 496+426.5 =922.5 J mol⁻¹

The average bond energy for O-H bond in water is 461.2 kJ mol⁻¹. Thus, it can be generalized as:

Average bond dissociation energy of A-B bond in AB_n gaseous molecule

= <u>sum of successive A-B bond dissociation energires</u>

Total number of A-B bonds in AB_n molecule (n)

Measurement of bond energy

In diatomic molecules

The determination of bond energy in a diatomic molecule containing a covalent bond involves the measurement of heat of formation of the molecule from its free atoms. But normally this cannot be measured directly because a compound is formed from molecules and not from free atom as well as a compound on dissociation splits up into molecules and not into free atoms of its component elements. Further, a molecule cannot be completely dissociated into its free atoms merely by heating. This can, however, be obtained from heat of reaction which, in turn, is measured from the change in the degree of dissociation with temperature and from heat of sublimation.