

1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester - 1)
Module Name/Title	Chemical bonding and molecular structure: Part2
Module Id	kech_10402
Pre-requisites	Knowledge about atomic structure, electronic configuration, kössel-Lewis approach to chemical bonding, octet rule
Objectives	After going through this lesson, the learners will be able to understand the following: <ul style="list-style-type: none">• Explain the formation of different types of bonds• Lattice enthalpy• Bond parameters• Resonance Structures• Polarity of bonds and Dipole moment
Keywords	Electrovalent bond, lattice enthalpy, bond parameters- bond length, bond angle , bond enthalpy, bond order resonance structures, polarity of bonds and dipole moment

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1. Introduction: Ionic or electrovalent bond

An atom can acquire octet by gaining the additional electrons if it has less than eight valence electrons or by losing its all valence electrons. when complete transference of one or more electrons from one atom to another atom takes place an ionic or electrovalent bond is formed. This type of bond is generally formed when a metallic atom combines with a non- metallic atom. Metal completes its octet by losing electron and a non –metal completes its octet by gaining electron.

“An electrovalent bond is formed between the atoms by the transference of one or more valence electrons of one atom to the other atom so as to complete their octet and acquire nearest stable noble gas configuration.”

The atom which loses the electron acquires positive charge and the other atom which gains the electrons acquires negative charge. These two oppositely charged ions come closer due to electrostatic forces of attraction and form an ionic bond.

“The electrostatic forces of attraction which holds the oppositely charged ions together is known as ionic bond or electrovalent bond.” The compounds containing ionic or electrovalent bonds are called ionic or electrovalent compounds.

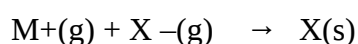
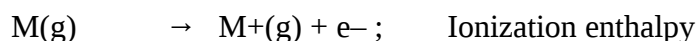
Characteristics of Ionic Solids

- Some common characteristics of ionic solids are as follows:

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- They are hard, brittle and have low volatility.
 - They have high melting points.
 - They are poor conductors of electricity in solid state, however they become good conductors of electricity in molten state or in dissolved state.
 - They are generally soluble in polar solvents like water.

From the **Kössel and Lewis** treatment of the formation of an ionic bond, it follows that the formation of ionic compounds would primarily depend upon:

- The ease of formation of the positive and negative ions from the respective neutral atoms;
- The arrangement of the positive and negative ions in the solid, that is, the lattice of the crystalline compound. The formation of a positive ion involves ionization, i.e., removal of electron(s) from the neutral atom and that of the negative ion involves the addition of electron(s) to the neutral atom.



The **electron gain enthalpy**, $^{\circ}egH$, is the enthalpy change when a gas phase atom in its ground state gains an electron. The electron gain process may be exothermic or endothermic. The ionization, on the other hand, is always endothermic.

Electron affinity, is the negative of the energy change accompanying electron gain.

Obviously ionic bonds will be formed more easily between elements with comparatively low ionization enthalpies and elements with comparatively high negative value of electron gain enthalpy.

Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements. The ammonium ion, NH_4^+ (made up of two non-metallic elements) is an exception. It forms the cation of a number of ionic compounds.

Ionic compounds in the crystalline state consist of orderly three-dimensional arrangements of cations and anions held together by coulombic interaction energies. These compounds crystallise in different crystal structures determined by the size of the ions, their packing

arrangements and other factors. The crystal structure of sodium chloride, NaCl (rock salt), for example is shown below (Fig 1).

Sodium chloride (NaCl)

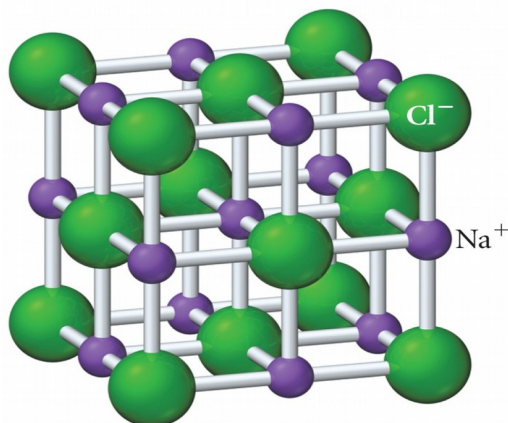


Fig 1: Rock salt structure

In ionic solids, the sum of the electron gain enthalpy and the ionization enthalpy may be positive but still the crystal structure gets stabilized due to the energy released in the formation of the crystal lattice.

For example: the ionization enthalpy for $\text{Na}^+(\text{g})$ formation from $\text{Na}(\text{g})$ is $495.8 \text{ kJ mol}^{-1}$; while the electron gain enthalpy for the change $\text{Cl}(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$ is, $-348.7 \text{ kJ mol}^{-1}$ only.

The sum of the two, $147.1 \text{ kJ mol}^{-1}$ is more than compensated for by the enthalpy of lattice formation of $\text{NaCl}(\text{s})$ (-788 kJ mol^{-1}). Therefore, the energy released in the processes is more than the energy absorbed.

Thus a qualitative measure of the stability of an ionic compound is provided by its enthalpy of lattice formation and not simply by achieving octet of electrons around the ionic species in gaseous state.

Since lattice enthalpy plays a key role in the formation of ionic compounds, it is important that we learn more about it.

3. Lattice Enthalpy

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 kJ mol^{-1} . This means that 788 kJ of energy is required to

separate one mole of solid NaCl into one mole of Na⁺ (g) and one mole of Cl⁻ (g) to an infinite distance.

This process involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charge. The solid crystal being three dimensional; it is not possible to calculate lattice enthalpy directly from the interaction of forces of attraction and repulsion only. Factors associated with the crystal geometry have to be included

4. Bond Parameters

Bond Length

Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.

Bond lengths are measured by spectroscopic, X-ray diffraction and electron-diffraction techniques about which you will learn in higher classes. Each atom of the bonded pair contributes to the bond length (Fig. 2). In the case of a covalent bond, each atom of the bonded pair contributes to bond length. The contribution from each atom is called the **covalent radius** of that atom.

The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation.

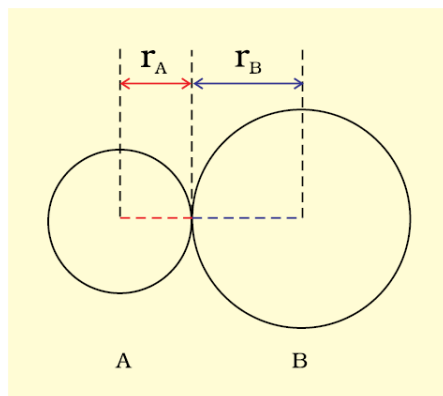


Fig 2: The bond length in a covalent molecule AB

The bond length in a covalent molecule AB can be expressed as $R = r_A + r_B$ where R is the bond length and r_A and r_B are the covalent radii of two atoms.

The covalent radius is half of the distance between two similar atoms joined by a covalent bond in the same molecule. **The van der Waals radius represents the overall size of the atom which includes its valence shell in a non bonded situation.** Further, the van der Waals radius is half of the distance between two similar atoms in separate molecules in a

solid. The van der Waals radii are always larger than covalent radii. Covalent and van der Waals radii of chlorine are depicted in (Fig 3).

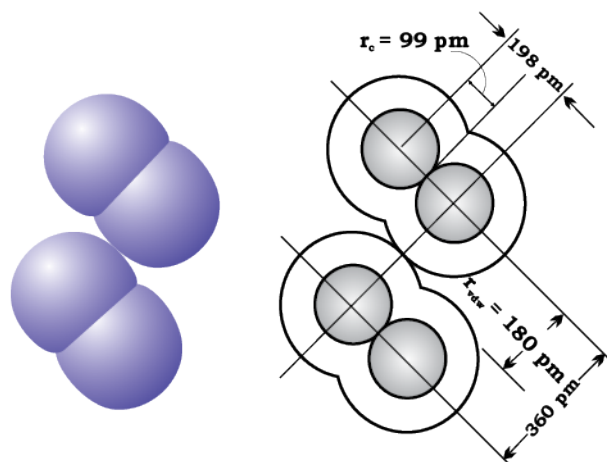


Fig 3: Covalent and van der Waals radii in a chlorine molecule.

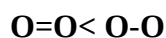
The inner circles correspond to the size of the chlorine atom (r_{vdw} and r_c are van der Waals and covalent radii respectively).

Some typical average bond lengths for single, double and triple bonds are shown in Table 1. The covalent radii of atoms taking part in a multiple bond is smaller than for an atom of the same elements involved in single bond.

Table 1: Average Bond Lengths for some single, double and triple bonds.

Bond Type	Covalent Bond Length (pm)
O-H	96
C-H	107
N-O	136
C-O	143
C-N	143
C-C	154
C=O	121
N=O	122
C=C	133
C=N	138
C≡N	116
C≡C	120

- **Bond length decreases with increase in bond multiplicity**



- **Bond length increases with increase in the size of the atom** because the distance of the valence shell electrons from the nucleus increases successively with the addition of electrons.



Bond lengths for some common molecules are given in **Table 2**.

Table 2: Bond lengths in some common molecules

Molecule	Bond Length (pm)
H ₂ (H – H)	74
F ₂ (F – F)	144
Cl ₂ (Cl – Cl)	199
Br ₂ (Br – Br)	228
I ₂ (I – I)	267
N ₂ (N ≡ N)	109
O ₂ (O = O)	121
HF (H – F)	92
HCl (H – Cl)	127
HBr (H – Br)	141
HI (H – I)	160

The covalent radii of some common elements are listed in Table 3. It is clear from the table that single covalent radii decrease from left to right across a period and increase down a group .

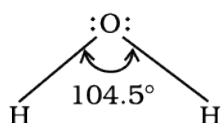
Table 3: Covalent Radii, r_{cov}/(pm)

H	37				
C	77(1)	N	74 (1)	O	66(1)
	67 (2)		65(2)		F
	60(3)		55(3)		64
					99
		P	110	S	104(1)
					Br
					114
					95(2)
		As	121	Se	104
					I
					133
		Sb	141	Te	137

Bond Angle

It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion.

Bond angle is expressed in degree/minute/second which can be experimentally determined by spectroscopic methods. It gives some idea regarding the distribution of orbitals around the central atom in a molecule/complex ion and hence it **helps us in determining its shape**. For example H–O–H bond angle in water can be represented as under :



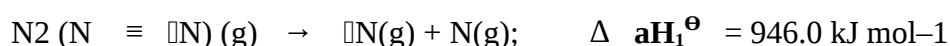
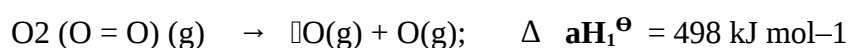
Bond Enthalpy

It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state.

The unit of bond enthalpy is kJ mol^{-1} . For example, the H – H bond enthalpy in hydrogen molecule is $435.8 \text{ kJ mol}^{-1}$.



Similarly the bond enthalpy for molecules containing multiple bonds, for example O_2 and N_2 will be as under :



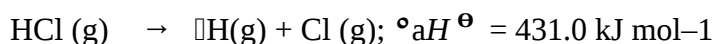
Bond dissociation enthalpy depends upon two factors

(i) **Size of the bonded atom** : The smaller the size of the bonded atoms , the stronger is the bond. Hence larger is the value of bond dissociation enthalpy. Ex bond dissociation enthalpy,of H-H bond is 435.8 kJ/mol is larger than the bond dissociation enthalpy of Cl-Cl bond which is 243.5 kJ/mol .

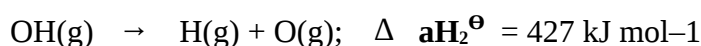
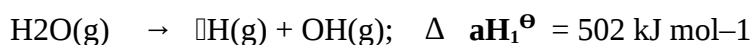
(ii) **Bond length**: Shorter the bond length larger is the value of bond enthalpy. Ex C-C bond length is 154 pm is larger than C=C bond length which is 134 pm . Consequently the bond dissociation enthalpy of C-C bond is 333 kJ/mol and that of C=C bond is 619 kJ/mol .

It is important that larger the bond dissociation enthalpy, stronger will be the bond in the molecule.

For a heteronuclear diatomic molecules like HCl, we have



In case of polyatomic molecules, the measurement of bond strength is more complicated. For example in case of H₂O molecule, the enthalpy needed to break the two O – H bonds is not the same.



The difference in the $\Delta_a H^\ominus$ value shows that the second O – H bond undergoes some change because of changed chemical environment.

This is the reason for some difference in energy of the same O – H bond in different molecules like C₂H₅OH (ethanol) and water. Therefore in polyatomic molecules the term **mean or average bond enthalpy** is used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken as explained below in case of water molecule,

$$\text{Average bond enthalpy} = \frac{502 + 427}{2} = 464.5 \text{ kJ mol}^{-1}$$

Bond Order

In the Lewis description of covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule.

The bond order, for example in H₂ (with a single shared electron pair), in O₂ (with two shared electron pairs) and in N₂ (with three shared electron pairs) is 1,2,3 respectively. Similarly in CO (three shared electron pairs between C and O) the bond order is 3. For N₂, bond order is 3 and its $\Delta_a H^\ominus$ is 946 kJ mol⁻¹; being one of the highest for a diatomic molecule.

Isoelectronic molecules and ions have identical bond orders; for example, F₂ and O₂²⁻ have bond order 1. N₂, CO and NO⁺ have bond order 3.

A general correlation useful for understanding the stabilities of molecules is that: with increase in bond order, bond enthalpy increases and bond length decreases.

5. Resonance Structures

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone, O₃ molecule can be equally represented by the structures I and II.

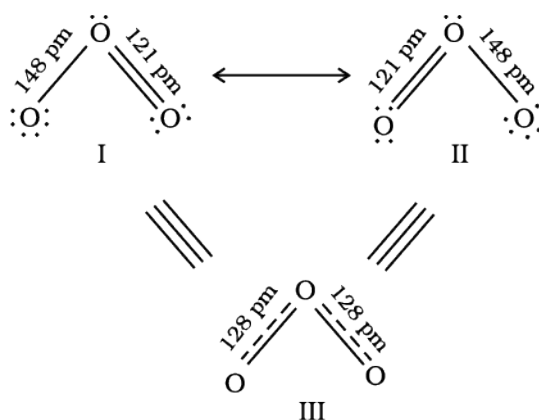


Fig 4: Resonance in o₃ molecule

(structures I and II represent the two canonical forms while the structure III is the resonance hybrid)

In both structures we have a O-O bond and a O=O double bond. The normal O-O and O=O bond lengths are 148 pm and 121 pm respectively. Experimentally determined oxygen-oxygen bond lengths in the O₃ molecule are same (128 pm). Thus the oxygen-oxygen bonds in the O₃ molecule are intermediate between a double and a single bond. Obviously, this cannot be represented by either of the two Lewis structures shown above.

The concept of resonance was introduced to deal with the type of difficulty experienced in the depiction of accurate structures of molecules like O₃. According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately.

Thus for O_3 , the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of O_3 more accurately. This is also called resonance hybrid. Resonance is represented by a double headed arrow. Some of the other examples of resonance structures are provided by the carbonate ion and the carbon dioxide molecule.

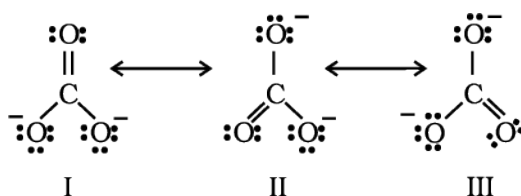
Problem

Explain the structure of CO_3^{2-} ion in terms of resonance.

Solution

The single Lewis structure based on the presence of two single bonds and one double bond between carbon and oxygen atoms is inadequate to represent the molecule accurately as it represents unequal bonds. According to the experimental findings, all carbon to oxygen bonds in CO_3^{2-} are equivalent.

Therefore the carbonate ion is best described as a resonance hybrid of the canonical forms I, II, and III shown below.



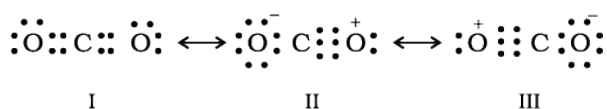
Resonance in CO_3^{2-} , I, II and III represent the three canonical forms.

Problem

Explain the structure of CO_2 molecule.

Solution

The experimentally determined carbon to oxygen bond length in CO_2 is 115 pm. The lengths of a normal carbon to oxygen double bond ($C=O$) and carbon to oxygen triple bond ($C \equiv O$) are 121 pm and 110 pm respectively. The carbon-oxygen bond lengths in CO_2 (115 pm) lie between the values for $C^{\delta+}O$ and $C \equiv O$. Obviously, a single Lewis structure cannot depict this position and it becomes necessary to write more than one Lewis structures and to consider that the structure of CO_2 is best described as a hybrid of the canonical or resonance forms I, II and III.



Resonance in CO₂ molecule, I, II and III represent the three canonical forms.

In general, it may be stated that

- Resonance stabilizes the molecule as the energy of the resonance hybrid is less than the energy of any single canonical structure; and,
- Resonance averages the bond characteristics as a whole.

Thus the energy of the O₃ resonance hybrid is lower than either of the two canonical forms I and II .

Many **misconceptions** are associated with resonance and the same need to be dispelled. You should remember that :

- The canonical forms have no real existence.
- The molecule does not exist for a certain fraction of time in one canonical form and for other fractions of time in other canonical forms.
- There is no such equilibrium between the canonical forms as we have between tautomeric forms (*keto* and *enol*) in tautomerism.
- The molecule as such has a single structure which is the resonance hybrid of the canonical forms and which cannot as such be depicted by a single Lewis structure.

6. Polarity of Bonds and Dipole moment

The existence of a hundred percent ionic or covalent bond represents an ideal situation. **In reality no bond or a compound is either completely covalent or ionic.** Even in case of covalent bond between two hydrogen atoms, there is some ionic character. When covalent bond is formed between two similar atoms, for example in H₂, O₂, Cl₂, N₂ or F₂, the shared pair of electrons is equally attracted by the two atoms. As a result electron pair is situated exactly between the two identical nuclei. The bond so formed is called non polar covalent bond. Contrary to this in case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine since the electronegativity of

fluorine (Unit 3) is far greater than that of hydrogen. The resultant covalent bond is a **polar covalent bond**.

Let us consider example of HCl molecule. The electronegativities of Cl and H are 3.0 and 2.1 respectively. Due to larger electronegativity of Cl the bonded pair of electron is shifted towards Cl atom. Therefore chlorine atom will experience more negative charge around it and the H atom will have slightly positive charge. These are **represented as δ^- and δ^+ + (delta meaning small) charges**. Such molecules having two oppositely charged poles are called **polar molecules and the bond is said to be polar covalent bond**.

As a result of polarisation, the molecule possesses the **dipole moment** (depicted below) which can be **defined as the product of the magnitude of the charge and the distance between the centres of positive and negative charge**.

- It is usually designated by a Greek letter μ .
- Mathematically, it is expressed as follows :

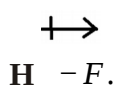
Dipole moment (μ) = charge (Q) \times distance of separation (r)

- Dipole moment is usually expressed in **Debye units (D)**.
- The conversion factor is $1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}$

where C is coulomb and m is meter.

- Further dipole moment is a **vector quantity** and **by convention it is depicted by a small arrow with tail on the positive centre and head pointing towards the negative centre**.

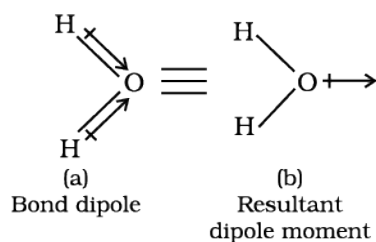
For example the dipole moment of HF may be represented as :



This crossed arrow symbolises the direction of the shift of electron density in the molecule.

In case of polyatomic molecules the dipole moment not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, **the dipole moment of a molecule is the vector sum of the dipole moments of various bonds**.

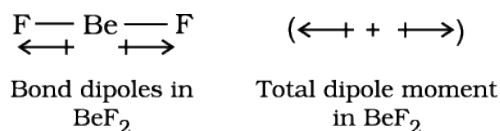
For example in H₂O molecule, which has a bent structure, the two O–H bonds are oriented at an angle of 104.5°. Net dipole moment of $6.17 \times 10^{-30} \text{ C m}$ ($1\text{D} = 3.33564 \times 10^{-30} \text{ C m}$) is the resultant of the dipole moments of two O–H bonds.



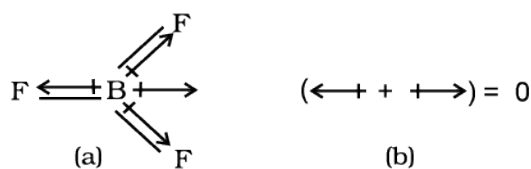
Net Dipole moment, $\mu = 1.85 \text{ D}$

$$= 1.85 \times 3.33564 \times 10^{-30} \text{ C m} = 6.17 \times 10^{-30} \text{ C m}$$

The dipole moment in case of BeF_2 is zero. This is because the two equal bond dipoles point in opposite directions and cancel the effect of each other.

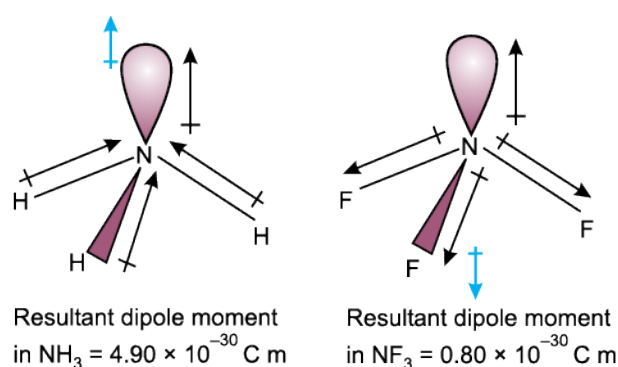


In tetra-atomic molecule, for example in BF_3 , the dipole moment is zero although the B – F bonds are oriented at an angle of 120° to one another, the three bond moments give a net sum of zero as the resultant of any two is equal and opposite to the third.



*BF_3 molecule; representation of
(a) bond dipoles and (b) total dipole moment*

Let us study an interesting **case of NH_3 and NF_3 molecule.** Both the molecules have pyramidal shape with a lone pair of electrons on nitrogen atom. Although fluorine is more electronegative than nitrogen, **the resultant dipole moment of NH_3 ($4.90 \times 10^{-30} \text{ C m}$) is greater than that of NF_3 ($0.8 \times 10^{-30} \text{ C m}$).** This is because, in case of NH_3 the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N – H bonds, whereas in NF_3 the orbital dipole is in the direction opposite to the resultant dipole moment of the three N–F bonds. The orbital dipole because of lone pair decreases the effect of the resultant N – F bond moments, which results in the low dipole moment of NF_3 as represented below :



Just as all the covalent bonds have some partial ionic character, the ionic bonds also have partial covalent character. The partial covalent character of ionic bonds was discussed by Fajans in terms of the following rules:

- The smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond.
- The greater the charge on the cation, the greater the covalent character of the ionic bond.
- For cations of the same size and charge, the one, with electronic configuration $(n-1)d^n ns^0$, typical of transition metals, is more polarising than the one with a noble gas configuration, $ns^2 np^6$, typical of alkali and alkaline earth metal cations.

The cation polarises the anion, pulling the electronic charge toward itself and thereby increasing the electronic charge between the two. This is precisely what happens in a covalent bond, i.e., buildup of electron charge density between the nuclei. The polarising power of the cation, the polarisability of the anion and the extent of distortion (polarisation) of anion are the factors, which determine the percent covalent character of the ionic bond.

Table 4: Dipole moments M(D) of selected molecules

HF	1.78	NH_3	1.47
HCl	1.07	NF_3	0.23
HBr	0.79	BF_3	0
HI	0.38	CH_4	0
H_2	0	CHCl_3	1.04

H ₂ O	1.85	CCl ₄	0
H ₂ S	0.95		
CO ₂	0		

7. Summary

The first description of **covalent bonding** was provided by Lewis in terms of the sharing of electron pairs between atoms and he related the process to the attainment of noble gas configurations by reacting atoms as a result of sharing of electrons. The Lewis dot symbols show the number of valence electrons of the atoms of a given element and Lewis dot structures show pictorial representations of bonding in molecules.

An ionic compound is pictured as a three-dimensional aggregation of positive and negative ions in an ordered arrangement called the crystal lattice. In a crystalline solid there is a charge balance between the positive and negative ions. The crystal lattice is stabilized by the **enthalpy of lattice formation**.

While a single covalent bond is formed by sharing of an electron pair between two atoms, multiple bonds result from the sharing of two or three electron pairs. Some bonded atoms have additional pairs of electrons not involved in bonding. These are called lone pairs of electrons. A Lewis dot structure shows the arrangement of bonded pairs and lone pairs around each atom in a molecule. Important parameters, associated with chemical bonds, like: bond length, bond angle, bond enthalpy, bond order and bond polarity have significant effect on the properties of compounds.

A number of molecules and polyatomic ions cannot be described accurately by a single Lewis structure and a number of descriptions (representations) based on the same skeletal structure are written and these taken together represent the molecule or ion. This is a very important and extremely useful concept called **resonance**. The contributing structures or *canonical forms* taken together constitute the resonance hybrid which represents the molecule or ion.