Chemical Bonding II

Concept of Resonance

The concept of resonance is an essential part of valence bond theory. It is purely a theoretical concept to explain the stability of other properties of a chemical species for which a single unique electron dot structure cannot be assigned. Thus, resonance is a way of describing delocalized electron within certain molecules/polyatomic ions where the bonding cannot be expressed by a single Lewis dot structure. A molecule or ion with such delocalized electron is represented by several contributing structures. Each contributing structure can be represented by Lewis's structure with only an integer number of covalent bonds between each pair of atoms within the structure. However, these individual contributors cannot be observed in actual resonance structure as might be assumed from the word resonance. The resonance between two or more structure is represented by drawing a double-headed arrow between them. The various postulated resonance structures are only a convenient way of picturing a molecule to account for all the properties associated with the molecule. Resonance is distinguished from tautomerism of conformational isomerism, which involves the formation of isomers of the arrangement of nuclear position.

Characteristics of Resonance

Molecule or ions with resonance possess the following characteristics-

1. A molecule/ion can be represented by several formulae known as contributing/canonical/resonance structures. However, the real structure is not a rapid inter-conversion of these contributing structures.

2. The contributing structures are not isomers. They differ only in the position of electrons, not in the position of nucleus.

3. Each Lewis formulae must have some number of valence electrons (and thus the same total charge) and the same number of unpaired electrons if any.

4. Bonds that have different bond orders in different contributing structures do not possess typical bond length.

5. Measurement reveals that bonds are of intermediate length.

6. The real structure has a lower P.E than that of contributing structure, i.e. the real structure is more stable than each of the contributing structure.

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7. None of the contributing structures is considered to represent the actual structure since, bonds that have different bond orders in different contributing forms do not have typical bong lengths. Moreover, the smaller energy of actual structure is lowered with the resonance energy.

Conditions for resonance

1. The canonical forms should possess same atomic position. They differ only in the position/no of electrons.

2. All the contributing structures should exhibit same no of unpaired electrons.

3. The canonical forms should not differ much in their energies.

4. The canonical forms should be represented in such a way that the negative charge reside son the more electronegative element and the positive charge resides on the more electropositive element.

5. In contributing structures, like charge should not resides on the adjacent atoms of the unlike charge should not be widely separated.

Resonance hybrid

The actual structure is an approximate intermediate between different canonical forms but its overall energy is use than each of contributing/canonical forms. This intermediate forms. This intermediate form is known as resonance hybrid. One canonical form may reside the actual molecule more than the other forms (in the sense of energy of stability) structures with lower values of P.E are more stable of resemble the actual structure to a greater extent the most stable canonical/contributing structures are the major contributors whereas energetically favorable (higher energy) & use stable forms are the minor contributors to the actual molecule or the resonance hybrid.

Resonance energy

Every structure is associated with a certain amount of energy, which determines the stability of the species. A resonance hybrid exhibits a structure i.e. intermediate between the contributing structures but the total potential energy is however lower than that of the contributing forms. The molecule is sometimes said to be stabilized by resonance or resonance stabilized. Thus, the resonance energy can be defined as the difference in energies of the resonance hybrid and the most stable canonical form. Resonance energy is equal to energy of resonance hybrid and approximately equal to the energy of the most stable canonical form. Delocalization of pi-electrons lowers the P.E. of the substance and thus makes it more stable than any of the contributing structures. Thus, resonance energy is sometimes also known as delocalization energy. Greater the number of contributing structures, the more stable is the molecule. This is because larger number of forms at lower energy is available to the electrons. In general, higher values of resonance energies are exhibited by aromatic molecule.



The concept of resonance is a theoretical concept to explain most of the properties of a molecule. Resonance energy of a molecule can be determined from the heat of formation of resonance hybrid/actual structures of the canonical forms. Thus, resonance energy is equal to the heat of formation of resonance hybrid/actual structure is equal to the heat of formation of the most stable canonical forms.

Resonance structure of some molecules or ions:

Draw resonating structure of different molecules and ions collecting from various books

Resonance in Benzene:

According to VBT benzene exhibit planar hexagonal structure in which each c-atom is bonded to

- 6-H atoms by single covalent bond.
- 1-C atom by single covalent bond.
- 1-C atom by double covalent bond.



In the 2nd contributing structure single & double bond C-atoms bonds are interchanged & by X-ray diffraction studies, bond length measurement is possible/studied. In localized cyclohexatriene, the C-C bond length are 154 pm (single bond) & 134 pm (double bond) respectively .From X-ray diffraction studies, all C-C bond length of benzene is found to be equal (139pm).A bond length is an intermediate between single & double bond the equivalent of C-C bonds can be explained, with the help of the fell resonating structure.



Kekule structure

Deware structure

Facts on Support of Resonance:

1. It explains the formation of one ortho substitution product because the bonds in benzene are equivalent.

2. The equivalent in bond lengths also supports the existence of resonance in length.

3. The actual structure (resonance hybrid) is much more stable than any of its canonical forms by about 152 kJ/mol. This additional stability of benzene is referred to its resonance energy.

Resonance vs Delocalization in Benzene:

The concept of resonance arises from the planar ring structure of benzene and its reluctance for addition reaction. To explain this property, molecular orbital structure of benzene is proposed. Each C-atom in benzene is sp² hybridized & 3 sp³ hybridized orbital are used in the formation of 3 sigma bonds resulting in a planar hexagonal structure. Each C-atom left with one unhybridized partially filled 2p orbitals which can form $3-\pi$ bonds by sideways overlapping. Resonance each C-atom is sp² hybridized, where 2 hybrid orbitals form sigma bond with the adjacent C-atoms and the other hybrid orbital form sigma bond concept of resonance could not explain the planar ring structure of benzene & its structure for addition reaction to with H.



Fig: Sideways overlap of 2p orbital of each c-atom in both directions.

However, each p-orbital can simultaneously overlap with other p-orbital on both sides forming a delocalized π electrons cloud ring giving above and below the plane of the whole ring. This delocalization (the ability of π electrons to participate in several bonds) of π -electrons provides extra stability to the benzene molecule which is responsible by a circle with the hexagon by 6 C-atoms.

Despite delocalization, the π -electrons are most loosely held than the sigma electrons. Due to this benzene is attacked by reagents which are electron deficient electrophile. The delocalized ring system is preserved only if the benzene shows substitution reaction. If benzene undergoes addition reaction easily, destruction of delocalization of π -electrons cloud will result as a consequence of which, the stability of the system will be lowered.



Fig: Simultaneous overlapping of 2p orbital of the carbon in benzene to form delocalized π -electron cloud.

Resonance Energy of Benzene:

Resonance/delocalization energy is the amount of energy needed to convert the true delocalized structure into that of the most stable canonical form. The empirical resonance energy can be estimated by comparing he enthalpy change of hydrogenation of the real substance with that estimated for the most stable canonical form. Resonance energy of benzene can be defined as the difference in energy between one of the existing (if possible) Kekule structure with the energy of benzene in its actual structure resonance form,

 $\Delta E_{benzene} = E_{Kekule benzene} - E_{actual benzene}$

Most stable canonical form Resonance hybrid

Since, Kekule form doesn't exist as a standalone structure; the resonance energy cannot be measured directly. Alternatively, one can compare the enthalpy of combustion between benzene (actual) & a non aromatic hypothetical structures of 1,3,5-cyclohexatriene.



The complete hydrogenation of benzene to cyclohexane via 1,3,5-cyclohexatriene and cyclohexadiene is exothermic. For 1 mole of energy released. Hydrogenation of one double bond delivers about 120 kj/mol (28.6Kcal/mol) of energy is can be obtained from the last step of hydrogenation of cyclohexane. In benzene,

however about 23.4kj/mol (5.6 Kcal/mol) amount of energy needed to hydrogenate one double bond. The actual empirical resonance energy of benzene is found to be 143.1 kJ/mol (34.2Kcal/mol. The net resonance energy relative to the localized cyclohexane-triene is a bit higher; 152kj/mol (36Kcal/mol). This is probably due to the same delocalization energy of about 7.6kj/mol (1.8Kcal/mol) of 1,3-cyclohexadiene. The measured resonance energy is also a difference between the hydrogenation energy of 3-non resonance double bond of the measured hydrogenation energy, thus the resonance energy $\Delta E=(3\times120-208)=152$ kj/mol.

Resonance in HF molecule:

HF is a heteronuclear diatomic molecule; hence we necessarily have the bonds with both ionic & polar character. Even for the pure covalent canonical structure of HF (I), there is polarity because the two different atoms necessarily have different affinities for the electron pair. It is true, not equally shared.

$$\begin{array}{cccc} H - F &\leftrightarrow & H^+ - F^- &\leftrightarrow & H^- - F^+ \\ (I) & (II) & (III) \end{array}$$

It is also accepted to be that ionic structures (II) & (III) makes some contribution. Since fluorine has a higher electronegative than H; the structure (III) is much less energetically favorable and hence contribute much less to the resonance hybrid as compared to the structure (II). Since it is qualitative and hence, the actual structure of HF molecule is a resonance hybrid structure (I) & (II).



Resonance in HCl molecule:

When we turn to a heteronuclear diatomic molecule, we necessarily have bonds which have ionic & polar character. Even for the pure canonical structure of H-Cl (I). There is no bond polarity because two different affinities for the e- pair. It is thus shared but not equally shared.

$$H - Cl \leftrightarrow H^+ - Cl^- \leftrightarrow H^- - Cl^+$$
(I)
(II)
(III)

It is also to be expected that the ionic structure (I) &(II) make some contribution owing to the factors that hydrogen & chlorine have about equal 1st ionization potential but, chlorine has a far higher electron affinity than H, structure (III) is much less energetically favored & hence contributing much less to the resonance hybrid than the structure (II). Since, the whole scheme we are using here is essentially qualitative, we normally ignore structure (III) & consider the ionic covalent resonance in H-Cl to be adequately described by (I) <-> (II).

$$H - Cl \leftrightarrow H^+ - Cl^-$$

Covalent ionic

Resonance Energy in CO₂:

Let us consider, the resonance energy in CO_2 molecule which is supposed to be resonance hybrid of the following three structure



Of these three resonating structures, structure (I) have the maximum bond energy & hence the most stable form. Thus resonance energy, ΔE of CO₂ molecule relative to the resonating structure (I) is given by

- $\Delta E = E_{actual} E(I)$
 - = Experimental value of heat of formation of CO_2 calculated value of heat of formation of structure (I)
 - = 1602.8kj/mol 2 × energy of C=O (in kj/mol)
 - = (1602.8 2×732.3) kj/mol
 - = 138.2 kj/mol

Since, $\Delta E = 138.2$ KJ/mol is the amount of energy lost when one molecule of CO₂ takes the resonance form (I). This also represents the additional energy which has to be supplied to disrupt the bonds due to their increase strength because of resonance. Resonance energy represents the extent to which the actual structure of CO₂ is more stable than the most stable resonating structure (I). ΔE (138.2kj/mol) stabilizes the CO₂ molecule relative to the resonance form (I). The calculated O-O bond distance in structure (I) is 2.44Å while the experimental value 2.30 Å. Thus, we find that in the actual molecule (i.e. resonance hybrid), there is an increase in the value of heat of formation of shortening of bond lengths.

Resonance Energy in CO:

The resonating structures of CO are

:C= \ddot{O} : (lowest energy) \leftrightarrow C⁻ \equiv ⁺ O: \leftrightarrow :C⁺- : \ddot{O} :⁻

Energy of the actual species is generally obtained from the heat of formation & energy of the stable canonical form is obtained from the bond energy data relevant to the structure drawn. For CO, the heat of formation from gaseous atom is -1072kj/mol & lowest energy of the CO structure (i.e. highest bond energy for C=O) is - 799kj/mol. Thus-

$$E_{resonance}(CO) = (1072 - 799) \text{ kJ/mol}$$

= 273 kJ/mol

Electronegativity

The term electronegativity has been defined in different ways by different investigators. In generally, electronegativity is defined as a chemical property that describes the tendency of an atom/species/group to attract the shared electron pair (electron density) towards itself from the atom with which it is bonded. Electronegativity is denoted by (χ) . Electronegativity calculated is not strictly a property of an atom in a molecule, environment and under the influence of surrounding atoms.

It is important to note that electron affinity and electronegativity both measures the electron attracting power. But the former refers to an isolated gaseous atom while the later to an atom in a compound. Thus, electron affinity is attraction for a single electron whereas electronegativity is the same for a pair of bonded electrons. Properties of free atom includes ionization energy, electron affinity etc. It is to be expected that the electronegativity of an element will vary with its chemical environment, but it is usually considered to be a transferable property, i.e. similar values will be valid in a variety of situation. The opposite of electronegativity can be referred to as electro positivity, which is defined as the measure of the ability of an element to donate bonded electrons.

Application of electronegativity

Electronegativity is a very important parameter in predicting different molecular properties some of which are given below

1. Nature of the bond and percentage of ionic character: If two atoms have similar electronegativities then the bond type will be covalent i. e; homonuclear diatomic molecules, eg : H_2 , Cl_2 Ionic bonds are formed when there's a considerable difference in electronegativities between the bonded species. If the electronegativity difference is very small, covalent bond formation is feasible.

The nature of bond formed between two species can be predicted from their respective electronegativities. This concept was developed by Pauling according to which;

- (a) X_A - X_B =0; the bond is purely covalent.
- (b) X_A - X_B <1.7; the bond is polar covalent
- (c) $X_A-X_B > 1.7$; the bond is predominantly ionic.
- (d) $X_A-X_B = 1.7$; the bond is 50% ionic and 50% covalent.

Polar character in Molecules:

A molecule is said to be polar if the bonded atoms are different. However, if the molecules are formed from two similar atoms, it will be non-polar in nature. Thus all hom32onuclear polyatomic molecules are non-polar and heteronuclear parts are polar molecules. In more accurate manner, the property polarity of a molecule not only depends upon the nature of bonded atoms, but also on the orientation of different bonds in the molecules. For instance, H₂, N₂, etc. are homonuclear diatomic molecule which is non-polar. HCl, HBr etc are heteronuclear diatomic molecules which are polar. H₂O, NH₃, etc are polyatomic molecules which are polar. CCl₄ is a polyatomic molecule which is non-polar.

H——F	HCI	н——н	o==0	N
hydrofluoric acid	hydrochloric acid	hydrogen	oxygen	nitrogen

Dipole Moment:

In a molecule such as HCl, even though covalent, the bonded electron pair is not shared equally between their two constituting atoms. The Cl⁻ atom with its greater electro-negativity pulls the e⁻ pair towards itself. As a result of which a slight negative charge is developed on Cl-atom and a slight positive charge is developed on H-atom.

Such a molecule with partial positive charge on one end and partial negative charge on the other end can be referred to as an electric dipole or simply a dipole. The degree of polarity of a molecule can be measured by a quantity or dipole moment. The dipole moment of a polar molecule is defined as the product of charge in one end and distance/separation between the two charges. It is denoted by the letter ' μ ' and represented by an arrow with a crossed tail, where the head of the arrow is directed towards the more electronegative species.



If +q and -q are the charges of two species separated by a distance 'd', the dipole moment(μ) is given by-

$\mu = q \cdot d$

The dipole moment is a vector quantity. The arrow, points to the negative charge and its length indicates the magnitude of the dipole moment. Thus a molecule of HCl is represented as-

The unit of dipole moment is Debye and its symbol is 'D' (c.g.s unit). Debye is defined as the magnitude of dipole moment (μ), where charge of (q) is 1×10^{-19} esu (electrostatic unit) and the distance between the two charges (d) is 1Å.

$$\label{eq:multiplicative} \begin{split} \mu &= q \; . \; d \\ &= 1 \times 10^{-19} esu \times 10^{-1} cm \\ 1D &= 10^{-18} esu \; cm = 3.336 \times 10^{-30} Cm \end{split}$$

S.I unit of dipole moment $(\mu) = Cm$.

Relationship between (D) and (Cm) $1D = 3.336 \times 10^{-36}$ cm Relationship between (C) and (esu) $1D = 10^{-18}$ esu cm $= 10^{-20}$ esu m. $1D = 3.336 \times 10^{-30}$ cm $= 3.336 \times 10^{-28}$ C $= 10^{-18}$ esu

> Also, 10^{-20} esu m= 3.336×10^{-30} Cm => 4.8×10^{-10} esu= 1.602×10^{-19} C => 1 esu = 3.336×10^{-10} C.

Bond Moment (individual polarity assigned to atoms):

Any bond which has a degree of polarity has a dipole moment. This is called bond moment. The dipole moment of H - H bonds is zero (0) because it is non-polar and the same for H - Cl bond is 1.08D because it is polar. In a diatomic molecule, bond moment corresponds to the dipole moment whereas in case of polyatomic molecule, the bond moment of the hydrogen halide corresponds to their respective values of D. It is given-

Hydrogen halides	Dipole moments
H - F	1.91 D
H - Cl	1.08 D
H – Br	0.80 D
H – I	0.42 D

The bond moment decreases with electro-negativity difference between two bonded atoms. When a molecule contains 3 or more constituting atom (polyatomic molecule), its bond possess a specific dipole moment. For examples

$$\begin{array}{ccc} C - H & 0.4D & O - H & 1.5D \\ \leftarrow & & & \\ O - CI & 1.5D & N - H & 1.3D \\ \leftarrow & \leftarrow & \\ \leftarrow & & \\ \leftarrow & & \\ \leftarrow & & \\ \end{array}$$

The net dipole moment of the molecules is the vector resultant of all the individual bond moments. If a molecule is symmetrical having identical bonds, even though its bond have a specific moment, the resultant dipole moment is zero(0). This is due to the orientation of the bonds for which the bond moment get cancel each other. The overall value of the dipole moment of a polar molecule depends upon its geometry of shape, i.e., vectorial addition of dipole moment of the constituent bonds. A symmetrical molecule is non-polar even though it contains polar bonds. Examples are- CO₂, BF₃, CH₄, CCl₄, etc, being symmetrical molecules have zero resultant dipole moment and hence are non-polar., since dipole moment summation of all the bonds present in the molecule cancel each other.



Unsymmetrical non-linear polyatomic molecules always have a net value of dipole moment, thus, such molecules are polar in nature. Examples are - H₂O, CH₃Cl, SO₂, etc. are polar molecules as they have positive value of dipole moments.



Note: A molecule having two or more polar bonds may have zero net dipole moment when the molecule have regular structure as expected from hybridization and centre of action of positive and negative poles coincide. Examples-

<u>Molecules</u>	Hybridisation	Bond angle
CCl ₄	sp ³	109°28'
PCl ₅	sp ³ d	120°90'
SF_6	sp ³ d ²	90°
IF ₇	sp ³ d ³	72°90'

Calculation of resultant Bond Moment:

Let AB and AC be two polar bonds inclined at an angle θ . Their dipole moments are μ_1 and μ_2 . Resultant dipole moment can be calculated using vectorial method,

 $\mu_{\rm R} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$

when, $\theta = 0^{\circ}$, the resultant is maximum; $\mu_R = \mu_1 + \mu_2$

and, $\theta=180^\circ,$ the resultant is minimum, $\mu_R=\mu_1$ - μ_2

As bond angle increases, dipole moment decreases.

Application of Dipole Moment:

1. To decide the polarity of the molecule: Molecules having zero dipole moment are said to be non-polar molecule and those having μ are polar in nature.

2. To determine geometry of molecules: Dipole moment can provide important in above geometry of molecular structure. If there are 2 or more possible structures for a molecule, the correct one can be identified from a study of its dipole moment.

H₂O has a bent structure: H₂O molecule can have a linear or bent structure.



net dipole moment.

The dipole moment of 2 O–H bonds in the 1st structure being equal in magnitude and opposite in direction will cancel out. The net dipole moment (μ) would be 0. In the 2nd structure, the bond moment will add vectorially to give a definite net dipole moment. Since water actually has dipole moment (1.85D), its linear structure is ruled out. Thus, H₂O has a bent structure as in 2nd structure.

CO₂ has a linear structure whereas SO₂ has a bent structure: CO₂ has no dipole moment (μ =0). This is possible only if the molecule has a linear structure of the bond moments of the two C = O units cancel each other.

$$\overrightarrow{o=c=0}$$
 $\overrightarrow{s=0}$

On the other hand, SO₂ has a dipole moment of $\mu = 1.63D$. Evidently here the individual dipole moments of the 2 S=O units gives the net dipole moment, $\mu = 1.63D$.

BF₃ has a planer and NH₃ is a pyramidal structure: The dipole moment of BF₃ molecule is 0. This is possible if the 3 B – F bonds are arranged symmetrical around the B-atom in the same plane. The bond moment of the 3 B – F bonds cancel each other effect and the net $\mu = 0$.



NH₃ molecule has a dipole moment (μ = 1.47D). This is explained by its pyramidal structure. The 3 H-atom lies in one plane symmetrically with N-atom at the apex of the regular pyramid. The dipole moments of the 3 N – H bonds on vector addition contribute to the net dipole moment. In addition, there is a lone pair of electrons on the N-atom. Since, it has no atom attached to it, to neutralize its negative charge; the lone pair makes a large contribution to the net dipole moment. Thus the overall dipole moment of the NH₃ molecule is the resultant of the bond moments of 3 N – H and that due to lone pair. It may be recalled that the high dipole moment of H₂O can also be explained by the presence of 2 lone pairs of electrons on O-atom.

CH₄ has a tetrahedral structure: CH₄ has zero dipole moment, despite the fact that each C – H bond possess a dipole moment of 0.4D. This can be explained if the molecule has a symmetrical tetrahedral structure. Each C – H bond in the pyramidal CH₃ group contains $1/3\mu$ ($\mu = 70.5D$) to the resultant dipole moment. Thus, the net dipole moment of CH₃ group is equal to μ . This acts in a direction opposite to that of the 4th C – H bond moment, thereby cancelling each other.

3. To distinguish cis and trans isomers: The cis has a definite dipole moment, while the trans isomer has no dipole moment ($\mu = 0$).vIt should be noted that if 2 groups have opposite inductive character, then trans isomer will have greater dipole moment. Example – in cis isomer, the bond moment add vectorially to give a net dipole moment. The trans isomer is symmetrical and the effect of opposite bond moments cancel so that $\mu = 0$.





4. Bond moments: The contribution of individual bond in the dipole moment of a polyatomic is termed a bond moment. The measured dipole moment of H_2O molecule is 1.85D. The dipole moment is the vectorial sum of the individual bond moment of 2 O – H bonds having bond angle 104.5°. Thus,

$$\begin{split} \mu_{obs} &= 2\mu_{O-H} \times cos \ 52.25 \\ &=> 1.85 = 2\mu_{O-H} \times 0.6129 \\ &=> \mu_{O-H} = 1.510 D \end{split}$$

5. To determine orientation in benzene ring: Benzene has a 0-dipole moment. Thus, it is a planar regular hexagon. Let us examine the dipole moments of the 3 isomeric dichlorobenzene $[C_6H_4Cl_2]$. Therefore, the benzene ring is flat, the angle between the bond moments of the 2 C – Cl bond is 60° for ortho, 120° for meta and 180° for para. On vector addition of bond moments in each case, the calculated dipole moments are ortho 2.6D, meta-1.5D and para 0D. Thus, the above structure of ortho, meta, para – isomers stand confirmed. In general, a p-disubstituted benzene has a 0-dipole moment while that of the o-isomer is higher than that of the misomer. This provides a method for distinguishing between the isomeric o-, m-, p- disubstituted benzene derivatives.



Molecular Geometry and Dipole Moments:

Formula	Molecular Geometry	Dipole	Examples
		Moment	
AX	linear	May be non-zero	HF, HCl
AX_2	Linear,	0	CO ₂ ,
	bent or V-shaped	non-zero	H ₂ O, NO ₂ ,

AX ₃	Triangular planner,	0	BF ₃
	pyramidal,	0	NH ₃ , PCl ₃
	T-shaped	Non-zero	ClF ₃
AX_4	Tetrahedral	0	CH ₄ , CCl ₄
	Square planar	0	XeF ₄
	See-saw	Non-zero	SF4, TeCl4
AX ₅	Trigonal bipyramidal	0	PCl ₅
	Square pyramidal	Non-zero	BeCl ₅
AX ₆	Octahedral	0	SF ₆
	Distorted octahedral	Non-zero	XeF ₆
AX ₇	Pentagonal bipyramidal	0	IF ₇

Q. 1: Arrange the following in order of increasing dipole moments. a) CH₃I, CH₃Cl, CH₃Br, CH₃F b) BF₃, H₂S, H₂O

Answer: a) As the electronegativity of halogens increase, the dipole moment also increases. F>Cl>Br>I

Increasing dipole moment order: CH₃I< CH₃Br< CH₃Cl< CH₃F

b) $BF_3 < H_2S < H_2O$. In BF_3 , the 3 B – F bonds are polar in nature and the bond moment of the 3 B – F bonds cancel each other's effect and the net $\mu = 0$. As O is more electronegative than sulphur, H_2O has a greater dipole moment than H_2S .

Q 2: Explain why – a) CO_2 has no dipole moment but SO_2 does b) CH_4 is a non-polar but CH_2Cl_2 is polar.

c) The dipole moment of BF₃ is less than NH_3 d) NH_3 is more polar than NF_3 .

Q. 3: The dipole moment of chlorobenzene is 1.57D. Estimate the ratio of the dipole moments of 1,2-(ortho) and 1,3-(meta) dichlorobenzene.

Q. 4: Using symmetry arguments discuss whether the molecules CH₃Cl, CH₂Cl₂ and CHCl₃ will have dipole moments.

Q. 5: Which of the following molecules will have dipole moment? FCl, BF₃, CS₂ and OF₂.

Q. 6: Arrange the bonds in order of increasing ionic character in the molecules – LiF, K₂O, N₂, SO₂ and ClF₃

Q. 7: Explain why BeH₂ molecule has a zero-dipole moment although the Be – H bonds are polar.

Q. 8: Which out of NH₃ and NF₃ has higher dipole moment and why?

Percent of Ionic Character

All covalent molecules, other than homonuclear ones, even though are predominantly covalent, some sort of ionic character is developed in them. In general, the ionic character of a polar covalent bond found to be predominantly dependent on electronegativity of the bonded atoms and dipole moment of molecules.

The percent of ionic character of a polar covalent bond depends upon two factors:

- 1. The electronegativity difference of the bonded atoms and
- 2. Dipole moment of the compound formed

Electronegativity difference and % of ionic character:

If two bonded atoms are of different electronegativity, the resulting bond will be a polar bond. Consequently, some sort of excess positive and negative charge is developed on the less and more electronegative element respectively and partial ionic character in the molecule is developed. Thus, from the values of electronegativity of bonded atoms, we can predict the extent of ionic character in a molecule. Several empirical equations have been developed to calculate the % of ionic character of a polar covalent bond from the electronegativity of the bonded atoms. Some of these are discussed below

1. Pauling equation: If X_A and X_B are the electronegativity of A & B respectively, the % of ionic character of the bond formed between A & B is given by–

% of ionic character = $100[1 - e^{-1/4}(X_A - X_B)^2]$, where e = 2.732

Pauling calculated the % of ionic character of molecules by using the above equation and proposed an empirical relationship between $X_A - X_B$ and % of ionic character.

X _A - X _B	% of ionic character	
0.6	9	
1.0	22	
1.4	39	
1.7	50	
2.0	63	
2.4	76	

Thus, if the bonded atoms exhibit an electronegativity difference value less than 1.7, the bond will be significantly covalent in nature whereas if the difference is more than 1.7, the bond will be predominantly ionic.

Thus, the higher the electronegativity difference between the two bonded atoms, higher is the % of ionic character.

2. Hannay-Smith equation: If X_A and X_B represent the electronegativity of A & B respectively forming a polar covalent bond between them, the % of ionic character of the bond is given by –

% of ionic character = $16(X_A - X_B) + 3.5(X_A - X_B)^2$

Since both the above equations purely use the concept of electronegativity in determining the % of ionic character, only the approximate values are expected.

Q1. The electronegativity difference of the elements in H-F is 1.9. Calculate the % of ionic character of the bond.

Solⁿ: According to Hannay-Smith eqⁿ-

% of ionic character = $16(X_A - X_B) + 3.5(X_A - X_B)^2$

$$=16 \text{ x } 1.9 + 3.5 \text{ x } (1.9)^2$$

$$=30.4 + 12.635 = 43.0$$

Q2. Calculate the % of ionic character of C-Cl bond in CCl₄ if electronegativity of C & Cl are 3.5 and 3.0 respectively.

solⁿ: Given, $X_A = 3.5$, $X_B = 3.0$ % of ionic character = $16(X_A - X_B) + 3.5(X_A - X_B)^2$ = $16(3.5 - 3.0) + 3.5(3.5 - 3.0)^2$ = 8.9

Q3. Arrange HCl, HBr and HI in increasing order of their % of ionic character. The electronegativity of H, Cl, Br & I are 2.1, 3.0, 2.8 & 2.4 resp.

Solⁿ: For HCl, % of ionic character = $1.6 (3.0 - 2.1) + 3.5(3.0 - 2.1)^2$

=17.2

For HBr, % of ionic character = $1.6 (2.8 - 2.1) + 3.5(2.8 - 2.1)^2$

For HI, % of ionic character = $1.6 (2.4 - 2.1) + 3.5(2.4 - 2.1)^2$

= 5.1

Q4. The electronegativity difference between the two atoms A & B is 1.0. Calculate the % of ionic character in the A-B bond using Pauling eq^n .

 Sol^n : Given, $X_A - X_B = 1.0$

Using Pauling eqn, % of ionic character = $(1 - e^{-1/4}) \times 100\%$

$$= (1 - \frac{1}{(2.732)1/4}) \times 100\%$$
$$= 22.3\%$$

Dipole moment and % of ionic character:

The magnitude of dipole moment can also be used to determine the % of ionic character of a composition. The quantity of dipole moment is related to the % of ionic character of a molecule as given below –

% of ionic character =
$$\frac{experimental value of dipole moment}{theorytical value of dipole moment} \times 100$$

= $\frac{\mu exp}{\mu theo} \times 100$
= $\frac{\mu obs}{\mu ionic} \times 100$

The theoretical value of dipole moment means the dipole moment of 100% ionic bond which can be calculated as follows

$$\mu_{\text{theo}} = \mu_{\text{ionic}} = q \mathbf{x} \mathbf{d},$$

 $d \rightarrow$ distance separating the two species or intermolecular distance and q is the charge.

For Example, Let us consider HBr molecule whose measure D.M = 0.75D and bond length= 1.41Å. If the molecule is completely ionic, then the theoretical value of D.M. is given by

$$\mu_{\text{theo}} = \mu_{\text{ionic}} = q \ge d$$

$$q = 1.602 \ge 10^{-19} \text{ C}$$

$$= 4.8 \ge 10^{-10} \text{ esu}$$

$$d = 1.41 \text{ Å} = 1.41 \ge 10^{-8} \text{ cm}$$

$$\mu_{\text{theo}} = 4.8 \ge 10^{-10} \text{ esu} \ge 1.41 \ge 10^{8} \text{ cm}$$

$$= 6.76 \text{ D}$$

% of ionic character = $\frac{0.75D}{0.76D} \times 100 = 11.67\%$

Q.1 Dipole moment of KCl is 3.336×10^{-2} cm. The interionic distance between K and Cl is 2.6×10^{-10} m.

Calculate the D.M. of KCl molecule and % of ionic character of the molecule.

Soln :- Given, $d= 2.6 \times 10^{-10} \text{ m} = 2.6 \times 10^{-8} \text{ cm}$

$$q = 1.602 \text{ x } 10^{-19} \text{ C} = 4.8 \text{ x } 10^{-10} \text{ esu}$$

 $\mu_{theo} = q \ x \ d = 4.8 \ x \ 10^{-10} \ esu \ x \ 2.6 \ x \ 10^{-8} \ cm$

$$= 12.48D$$

% of ionic character = $\frac{\mu exp}{\mu theo} \ge 100 = 0.26 \ge 10^{-11} esu$

Q.2. Calculate the % of ionic character having length 0.83Å and 182D as its observed D.M.

Solⁿ :- Given, d= 0.83Å = 0.83 x 10⁻⁸ cm

 $q=1.602 \text{ x } 10^{-19} \text{ C} = 4.8 \text{ x } 10^{-10} \text{ esu}$ $\mu_{exp} = 1.82 \text{D}, \mu_{theo} = q \text{ x } d = 3.984 \text{D}$

% of ionic character = $\frac{1.82D}{3.984D}$ x 100% = 45.68%

Q.3. The D.M. of HCl is 1.083D and bond length is 1.27Å. Calculate the % of ionic character and covalent character in the molecule.

Solⁿ :- Given, $\mu_{obs} = 1.083D$

$$d=1.27$$
Å $=1.27 \times 10^{-8}$ cm

 $\mu_{theo} = q \ x \ d = 6.096D$

% of ionic character = $\frac{1.083D}{6.096D} \times 100\% = 17.7\%$

Covalent = 100 - 17.7%

Q.4. Calculate the % of ionic character in HI from the following data: the equivalent bond distance = 1.62Å,

 $\mu_{obs} = 0.83D$

Given, $\mu_{\text{theo}} = q \times d = 7.76D$

% ionic character = $\frac{0.38D}{7.76D} \times 100\% = 4.8\%$

Q. 1. The electronegativity difference of the elements in HF is 1.9. Calculate the percent ionic character of the H-F bond.

Q. 2. Calculate the percentage ionic character of C-Cl bond in CCl₄ if the electronegativities of C and Cl are 3.5 and 3.0 respectively.

Q. 3. Arrange HCl, HBr and HI in the increasing order of their percentage ionic character. The electronegativities of H, Cl, Br and I are 2.1, 3.0, 2.8 and 2.4 respectively.

Q. 4. The electronegativity difference between two atoms A and B is 1.0. Calculate the percent ionic character in the A-B bond using Pauling equation.

Q. 5. The dipole moment of HCl is 1.03 D and bond length is 1.27A°. Calculate the percent ionic and covalent character in HCl molecule.

Q. 6. Calculate the percent ionic character in the HI molecule from the following data. The equilibrium bond distance is 1.62 A^o and the observed dipole moment is 0.38 D.

Q.7. The dipole moment of LiH is 1.964x10-29Cm, and the interatomic distance between Li and H in this molecule is 1.596A°. What is the percent ionic character in LiH?

Modern Concept of Bonding

The Lewis or the octet concept has many limitations. It cannot satisfactorily explain the following points

(i) The cause of covalent bond formation

(ii) Nature of the forces operating between the covalently bonded atoms

(iii) Shapes and geometry of the molecules

(iv) Some molecules are found to be stable even thought octet rule is not satisfied.

To overcome these limitations, two theories viz. Valence Bond Theory and Molecular orbital Theory based on quantum mechanics have been proposed.

Valence Bond Theory, VBT

The valence bond theory was first put forwarded by Heitler and London in 1927. It was later modified and improved by Pauling and Slater in 1931. The theory is based on the concept of atomic orbital, overlap criteria of atomic orbital and stability of molecules.

Consider two hydrogen atoms A and B approaching each other having nuclei N_A and N_B and electrons present in them are represented by e_A and e_B . When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate. Attractive forces arise between (i) nucleus of one atom and its own electron that is N_A – e_A and N_B – e_B . (ii) Nucleus of one atom and electron of another atom i.e., N_A – e_B , N_B – e_A . Similarly repulsive forces arise between (i) electrons of two atoms like e_A – e_B , (ii) nuclei of two atoms N_A – N_A . Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart







Fig. 4.8 The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2

Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy.

Orbital Overlap Concept

In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbital undergo partial interpenetration. This partial merging of atomic orbital is called overlapping of atomic orbital which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins.

Directional Properties of Bonds

As we have already seen the formation of covalent bond depends on the overlapping of atomic orbital. The molecule of hydrogen is formed due to the overlap of 1s-orbitals of two H atoms, when they combine with each other.

In case of polyatomic molecules like CH₄, NH₃ and H₂O, the geometry of the molecules is also important in addition to the bond formation. The valence bond theory explains the formation and directional properties of bonds in polyatomic molecules like CH₄, NH₃ and H₂O, etc. in terms of overlap and hybridization of atomic orbital.

Overlapping of Atomic Orbital

When two atoms come close to each other, there is overlapping of atomic orbital. This overlap may be positive, negative or zero depending upon the properties of overlapping of atomic orbital. The various arrangements of s and p orbital resulting in positive, negative and zero overlap are depicted.



The criterion of overlap is the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules and polyatomic molecules.

The basic assumptions of this theory (VBT) are

(i) A covalent bond is formed by the overlapping of the valence shell atomic orbital.

(ii) The bond is formed due to the interaction of only the valence electrons and they lose their identity. The inner electrons do not participate in the bond formation and remains unaffected.

(iii) Only half-filled atomic orbital with proper orientation can enter the overlapping process. The resulting bond acquires a pair of electrons of opposite spins.

(iv) As a result of overlapping, there is maximum electron density somewhere between the two atoms. Greater the overlapping more is the energy released and higher is the strength of the bond formed.

(v) The overlapping between two orbital of almost equivalent energy and more directionally concentrated will be more effective and form stronger bond.

Overlap of atomic orbital – sigma (σ) and pi (π) bonds:

Depending upon the type of atomic orbital involved in bond formation we may consider different types of overlap. Overlapping of atomic orbital may be head on or sideways. As a result, a covalent bond may be either a sigma (σ) bond or a pi (π) bond. A sigma (σ) bond is formed by the head on overlapping of atomic orbitals. The overlapping occurs through their axes. All bonds have axial symmetry. Since the overlap of two atomic orbitals along their axes is maximum a σ - bond is a strong bond. If z-axis is assumed to be the molecular axis, σ bond is given by s-s, s-p_z and p_z-p_z overlaps.

s-s overlapping: In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below:



s-p overlapping: This type of overlap occurs between half filled s-orbitals of one atom and half filled p-orbitals of another atom.



 $\mathbf{p} - \mathbf{p}$ overlapping: This type of overlap takes place between half filled p-orbitals of the two approaching atoms.



A pi (π) bond is formed by the lateral or sideways overlapping of atomic orbitals. The overlapping occurs along a line perpendicular to the molecular axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms. If z axis is assumed to be the molecular axis, a π -bond is given by p_x - p_x , p_y - p_y overlaps.



Strength of Sigma and pi Bonds

Basically, the strength of a bond depends upon the extent of overlapping. In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that pi bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules containing multiple bonds (double or triple bonds)

sigma (σ) bond vs pi (π) bond:

sigma (σ) bond	pi (π) bond
-------------------------	-------------

1. It is formed by the head on overlap.	1. It is formed by the lateral overlap	
2. Extent of overlapping is more and hence σ	2. Extent of overlapping is less and hence π	
bonds are strong	bonds are weak.	
3. Electron cloud of a σ -bond is symmetrical	3. Electron cloud of a π -bond is unsymmetrical	
4. Free rotations of the atoms in a σ -bond is	4. Free rotations of the atoms in a π -bond is not	
possible	possible	
5. A σ -bond determines the direction of the	5. A π -bond has no primary effect on the	
bond	direction of the bond	

Valence bond theory (Hitler-London Approach) of H2 molecule

Discussed in Class

Limitations:

1. Since the two electrons of the shared pair constituting the covalent bond must come from two different atoms, it is evident that VBT has no explanation for the formation of coordinate covalent bond.

2. Magnetic character of a molecule cannot be explained by VBT.

3. VBT does not consider the formation of odd electron molecules or ions such as H_2^+ where no pairing of electrons occurs.

Equivalent and non-equivalent hybrid orbitals

Hybrid orbitals where the ratios of participating atomic orbitals are same for all the orbitals called Equivalent hybrid orbitals. For example, any symmetrical molecules with no lone pairs of electrons or without dissimilar surrounding elements have equivalent hybrid orbitals.

Hybrid orbitals where the ratios of participating atomic orbitals are different or not same for all the orbitals called non-equivalent hybrid orbitals. Non-equivalent hybrid orbitals can arise from presence of lone pair of electrons on the central atom and/or presence of dissimilar atoms rather than central atoms. For example, CH₃Cl, NH₃ etc.

sp³ hybridization

Hybrid orbitals in presence of lone pairs or dissimilar atoms (substituents) with high electronegativity difference become non-equivalent containing bond pairs of electrons. As a result of this, variations in bond lengths and bond angles are observed.

In C₂H₂F₂, the H-C-H angle is 111.9° while F-C-F angle is 108.3°

C-F bond length in CH₃F is 1.39 Å while that in CF₄ is 1.32 Å

C-Cl bond length in CH₃Cl is 1.78 Å, in CH₂Cl₂ is 1.77 Å, in CHCl₃ is 1.76 Å and in CCl₄ is 1.77 C-C bond length in C₂H₆ is 1.53 Å and in C₂F₆ is 1.51 Å

C=O bond length in H₂CO is 1.22 Å, in HFCO is 1.19 Å and in F₂CO is 1.17 Å

These data indicate that replacement of H by F of Cl results in a decrease in adjacent bond lengths. With increase in participation of s -orbitals in a bond, bond length or bond strength increases. s-character increases in the orbitals forming bond to less electronegative substituents and p-character concentrates in the orbitals directed towards the electronegative substituents. This is because an electron in a p orbital is on the average farther from the nucleus than an electron in an s-orbital and is more readily shared by an orbital centered on the more electronegative atom. Hence replacement of a substituent by a more electronegative one causes a fine change in the hybridization-p character shifts to the bonds connecting the electronegative atoms and correspondingly there is a shift in s-character in the adjacent bonds, which become stronger and shorter.

sp³d hybridization

The sp³d hybridization is a combination of 2 sets viz. a set of three sp_xp_y hybrid orbitals distributed in the equatorial xy-plane forming a trigonal plane and a set of two $p_zd_z^2$ hybrid orbitals oriented in axial position forming a linear shape passing through the center of the trigonal plane. For this sp³d hybridization we can divide it into two parts sp² (trigonal plane, more s character) + pd (axial, less s character-lower electronegativity).

Apicophilicity: It is the propensity of more electronegative substituents to search for the low electronegative $[p_z d_z^2]$ apical orbitals in the TBP structures.

Substituents at the equatorial plane are bonded through the s-rich (sp²) hybrid orbitals; the bond lengths in this plane are expected to be shorter. If there are any lone pairs of electrons, they will also preferably occupy the axial s-rich orbitals.



Bents' Rule

It is the preference of atoms having different electronegativity to occupy the hybrid orbitals which are nonequivalent: different s-character and different p-character.

- 1. More electronegative substituents prefer hybrid orbitals of the central atom with greater p-character and less s-character.
- 2. Less electronegative substituents prefer hybrid orbitals of the central atom with greater s-character and less p-character.
- 3. The central atom involved hybrid orbitals with higher s-character to develop higher covalence and less s-character in the bond with greater ionic character.

In compounds like PCl_3F_2 , $PF_4(CH_3)$ or $PF_3(CH_3)_2$, the fluorine atoms occur at the axial positions. The aptitude of s-rich orbitals for greater covalence thus gives rise to a structural modification in a molecule with highly electronegative atoms.

Bent's rule agrees well with VSEPR theory. An electronegative substituent will displace the bond pairs of electrons away from the central atom to itself, thereby reducing bond pair bond pair repulsion. This is most favored by orbitals with more p-character, since the p-orbitals generally have a larger spatial distribution compared to the compact s-orbitals. On the other hand, the s-rich covalent bonds require a larger angular volume and lead to widening of bond angle.

The criterion of overlap and covalence seems to be ruling in certain cases. π -bond results in a shorter bond with higher covalence. In such cases, the central atom projects more s-character in the direction of the π -bond to ensure better covalence.

In (RO)2BrP=O, the tetrahedrally hybridized phosphorous atom does not extend higher s-character in its bond with bromine, the least electronegative element in the molecule. Rather it exerts more s-character in the P=O link for the sake of better covalence and efficient overlap with the shortened double bond.