Polarization of Molecules

(Non-polar and Polar Covalent Bonds)

1. Covalent bond between two similar atoms-Non-polar covalent bond.

The bonding electron pair constituting the covalent bond between two similar atoms which have the same electronegativity or zero electronegativity difference is equally shared by both the linked atoms, i.e. the shared electron pair is placed at the "centre" of the distance between the nuclei of the linked atoms. The equal sharing of the electron pair is because of the fact that both the linked atoms, due to their same electronegativity or zero electronegativity difference, have the same tendency to attract the shared electron pair towards them. It is because of equal sharing of the electron pair that the resulted covalent bond has no polarity or ionic character, i.e., the bond is non-polar and non-ionised. This bond is, therefore, called non-polar or homo-polar covalent bond or simply covalent bond. Thus:

A covalent bond between two similar atoms which have the same

electronegativity or zero electro negativity difference is called a non-polar or homopolar covalent bond.

OR

A covalent bond in which electrons are shared equally between the linked atoms is called a non-polar or homo-polar covalent bond.

Since the two atoms which have the same electronegativity are the atoms of the same element, all covalent bonds between two similar atoms are non-polar or homo-polar covalent bonds.

A non-polar covalent bond is a true or purely covalent bond, since it has no or negligible polarity or ionic character. H-H, F-F etc are the examples of nonpolar covalent bonds. The molecules like H_2, F_2 etc which have non-polar covalent bonds are called non-polar molecules. Such molecules are the true covalent compounds.

2. Covalent bond between two dissimilar atoms-Polar covalent bond. The bonding electron pair constituting the covalent bond between two dissimilar atoms like Hand Cl which have different electronegativity values (H = 2.1, Cl = 3.3) is not equally shared by the linked atoms, i.e. the electron pair is not placed at the center of the distance between the nuclei of the two atoms viz. Hand Cl.

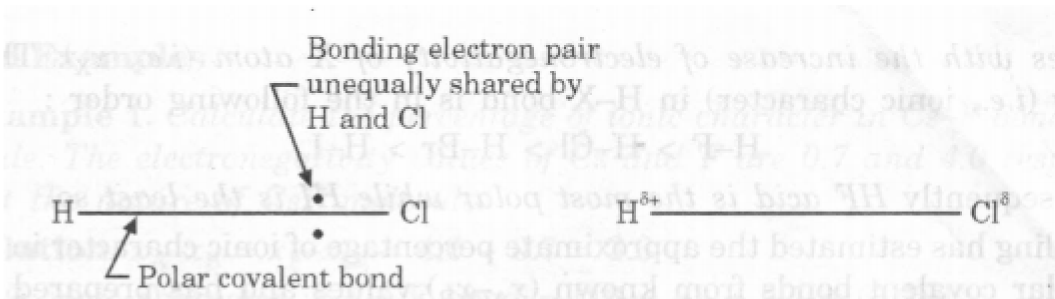
Rather, it is partially displaced (i.e. attracted) towards the more electronegative Cl atom owing to its greater affinity for electron pair. This type of partial displacement of the shared electron pair towards the more electronegative Cl atom develops a small (fractional) negative charge (represented as δ-) on more electronegative Cl atom and an equal amount of small positive charge (represented as δ+) on less electronegative H atom, and HCl molecule appears to be containing two oppositely charged poles (called charge-centres or electrical poles) namely $H^{\delta+}$ and $Cl^{\delta-}$ at the end of the bond and the molecule is depicted as $H^{\delta+}$ - $Cl^{\delta-}$. The covalent bond between Hand Cl atoms develops some polarity or partial ionic character and hence is called *polar covalent bond*.

Thus polar covalent bond can be defined as follows;

A covalent bond between two dissimilar atoms which have different electronegativity values is called a polar covalent bond.

OR

A covalent bond in which electrons are shared unequally between the linked atoms and the linked atoms acquire fractional positive and negative charge is called a polar covalent bond.



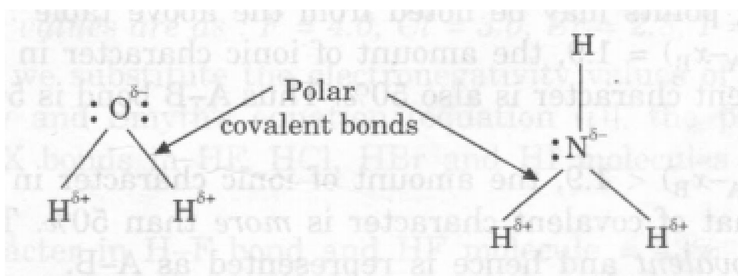
Polar covalent bond is not a true or purely covalent bond, since it has some polarity or ionic character. Thus it is neither wholly covalent nor wholly ionic but has an intermediate character. The molecules like HCl which have polar covalent bonds are called polar molecules.

Since the linked atoms having different electronegativity may not be the atoms of the same elements, all covalent bonds between two dissimilar atoms are polar covalent bonds. **For example** :

(a) H_2O molecule contains two O-H covalent bonds. Since Hand O atoms

have different electronegativity (H = 2.1, 0 = 3.5), both O-H covalent bonds are polar covalent bonds and H_2O is a polar molecule.

(b) NH_3 molecule has three N - H covalent bonds. Since Hand N have different electronegativity (H = 2.1, N = 3.0), all the three N-H covalent bonds are polar covalent bonds and NH_3 is a polar molecule



Percentage of Ionic Character in a Polar Covalent Bond

If two atoms A and B are linked together by a polar covalent bond (A & BO+), the amount of ionic character in this bond depends on the difference of electronegativity values of A and B. Greater is the difference, (xA - xB), greater is the percentage of ionic character in A-B bond. Here the electronegativity of atom A (XA) has been assumed to be higher than that of B (xB). This point can be illustrated by considering the nature of X-H bond in halogen acids of HX type (e.g. HF, HCl, HBr and HI). The polarity of H-X bond in HX acids increases with the increase of electronegativity difference, (xx-xJJ. Since electronegativity of H atom (i.e. xJJ remains the same throughout the series, the polarity of H-X bond increases with the increase of electronegativity of X atom (i.e., xxJ. Thus the polarity (i.e., ionic character) in H-X bond is in the following order:

H-F > H-Cl > H-Br > H-I

Consequently HF acid is the most polar while HI is the least so.

Pauling has estimated the approximate percentage of ionic character in various A-B polar covalent bonds from known (XA-XB) values and has prepared a table (given below) which gives a relation between (XA-XB) values, percentage ionic character in A-B bond and the nature of this bond.

Table 1. Relation between ($X_A - X_B$) values, percentage ionic character in A-B bond

$(x_A - x_B)$	% ionic character in A–B bond	Nature of A–B bond and its representation	Examples of bonds
0	0	Purely covalent (A–B)	N≡N, O=O, Cl–Cl, H–H.
0.1–0.8	0.5–15	Covalent (A–B)	C–S, C–I, N–Cl, P–H
0.9–1.6	19–47	Polar covalent ($A^{\delta-} - B^{\delta+}$)	Both O–H bonds in H_2O molecule are polar covalent bonds and are represented as $O^{\delta-}–H^{\delta+}$
1.9	50	50% ionic and 50% covalent	—
1.9–2.0	55–63	Ionic ($A^-–B^+$)	—
2.0–2.3	67–74	Ionic ($A^-–B^+$)	Na–Cl (Na^+Cl^-)
2.3–3.3	76–93	Ionic ($A^-–B^+$)	Cs–F (Cs^+F^-)

The following points may be noted from the above table 1:

(i) When (x_A - x_B) = 1.9, the amount of ionic character in A-B bond is 50%and that of covalent character is also 50%. Thus A-B bond is 50% ionic and, 50% covalent.

(ii) When (x_A - x_B) < 1.9, the amount of ionic character in A-B bond is less than 50% and that of covalent character is more than 50%. Thus A-B bond is predominantly covalent and hence is represented as A-B.

(iii) When (x_A - x_B) > 1.9, the amount of ionic character in A-B bond is more than 50% and that of covalent ,character is less than 50%. Hence A-B bond is predominantly ionic and hence is represented as A - B+.

Hanny and Smyth Equation

Hanny and Smyth took some heterodiatomic molecules of AB type like HF, HCI, HBr, HI, NaI, KI, KCl, etc and plotted a graph between the percentage of ionic character in A-B bond and electronegativity difference,

(x_A - x_B) with the help of this graph they obtained the following equation which gives the percentage of ionic character in a given A-B bond in AB molecule.

% ionic character in A-B bond = $[0.16\ (x_A - x_B) + 0.035\ (x_A - x_B)^2]$ x 1000%

= $[16\ (x_A - x_B) + 3.5\ (x_A - x_B)^2]$%

Example 1.

Calculate the percentage of ionic character in Cs-F bond in CsF molecule. The electro negativity values of Cs and Fare 0.7 and 4.0 respectively.

Predict the nature of CsF molecule.

Solution. $x_A - x_B = x_F - x_{Cs} = 4.0 - 0.7 = 3.3$

% ionic character in Cs - F bond = $[16 \times 33 + 3.5 \times (3.3)^2]$% = 90.9%

Since the ionic character is more than 50%, CsF is a purely ionic molecule.