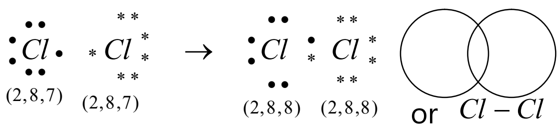
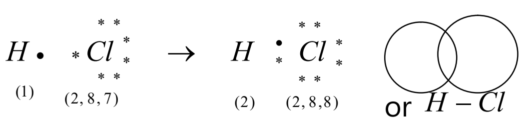
Covalent bond.

Covalent bond was first proposed by Lewis in 1916. The bond formed between the two atoms by mutual sharing of electrons so as to complete their octets or duplets (in case of elements having only one shell) is called covalent bond or covalent linkage. A covalent bond between two similar atoms is non-polar covalent bond while it is polar between two different atom having different electronegativities. Covalent bond may be single, double or a triple bond.

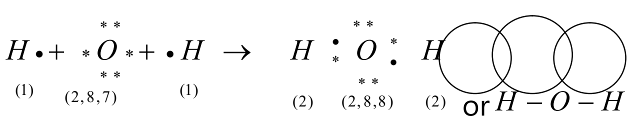
Example: Formation of chlorine molecule : chlorine atom has seven electrons in the valency shell. In the formation of chlorine molecule, each chlorine atom contributes one electron and the pair of electrons is shared between two atoms. both the atoms acquire stable configuration of argon.



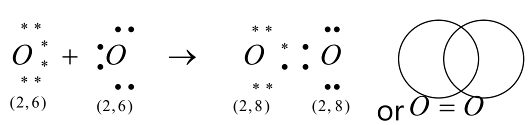
Formation of HCl molecule : Both hydrogen and chlorine contribute one electron each and then the pair of electrons is equally shared. Hydrogen acquires the configuration of helium and chlorine acquires the configuration of argon.



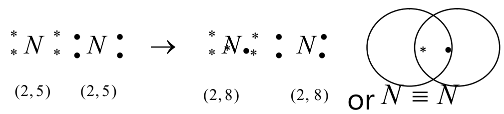
Formation of water molecule : Oxygen atom has 6 valency electrons. It can achieve configuration of neon by sharing two electrons, one with each hydrogen atom.



Formation of O2 molecule : Each oxygen atom contributes two electrons and two pairs of electrons are the shared equally. Both the atoms acquire configuration of neon.



Formation of N2 molecule : Nitrogen atom has five valency electrons. Both nitrogen atoms achieve configuration of neon by sharing 3 pairs of electrons, i.e., each atom contributes 3 electrons.



or $N \equiv N$

Some other examples are: H2S, NH3, HCN, PCl3, PH3, C_2H_2, H2, C2H4, $SnCl_4$, $FeCl_3$, BH_3, graphite, $BeCl_2$ etc.

(1) Conditions for formation of covalent bonds

(i) Number of valency electrons : The combining atoms should be short by 1, 2 or 3 electrons in the valency shell in comparison to stable noble gas configuration.

(ii) Electronegativity difference : Electronegativity difference between the two atoms should be zero or very small.

(iii) Small decrease in energy : The approach of the atoms towards one another should be accompanied by decrease of energy.

(2) Characteristics of covalent compounds

(i) Physical state: These exist as gases or liquids under the normal conditions of temperature and pressure. This is because very weak forces of attraction exist between discrete molecules. Some covalent compounds exist as soft solids.

(ii) Melting and boiling points: Diamond, Carborandum (SiC), Silica (SiO2), AlN etc. have giant three dimensional network structures; therefore have exceptionally high melting points otherwise these compounds have relatively low melting and boiling points. This is due to weak forces of attraction between the molecules.

(iii) Electrical conductivity: In general covalent substances are bad conductor of electricity. Polar covalent compounds like HCl in solution conduct electricity. Graphite can conduct electricity in solid state since electrons can pass from one layer to the other.

(iv) Solubility: These compounds are generally insoluble in polar solvent like water but soluble in non-polar solvents like benzene etc. some covalent compounds like alcohol, dissolve in water due to hydrogen bonding.

(v) Isomerism : The covalent bond is rigid and directional. These compounds, thus show isomerism (structural and space).

(vi) Molecular reactions : Covalent substances show molecular reactions. The reaction rates are usually low because it involves two steps (i) breaking of covalent bonds of the reactants and (ii) establishing of new bonds while the ionic reactions involved only regrouping of ions.

(vii) Covalency and Variable covalency : The number of electrons contributed by an atom of the element for sharing with other atoms is called covalency of the element. The variable covalency of an element is equal to the total number of unpaired electrons in s, p and d-orbitals of its valency shell.

Covalency = 8 – [Number of the group to which element belongs]

Examples: Nitrogen $_7N$ = Covalency of N = 3

$$\underset{2s}{\boxed{\uparrow\downarrow}}\quad \underset{2p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$$

The element such as P, S, Cl, Br, I have vacant d-orbitals in their valency shell. These elements show variable covalency by increasing the number of unpaired electrons under excited conditions. The electrons from paired orbitals get excited to vacant d-orbitals of the same shell.

Promotion energy : The energy required for excitation of electrons.

Promotion rule : Excitation of electrons in the same shell

Phosphorus : Ground state

$$\underset{3s}{\boxed{\uparrow\downarrow}}\quad \underset{3p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}\qquad \text{Covalency 3}$$

Phosphorus : Excited state

$$\underset{3s}{\boxed{\uparrow}}\quad \underset{3p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}\quad \underset{3d}{\boxed{\uparrow}\boxed{}\boxed{}\boxed{}\boxed{}}\qquad \text{Covalency-5}$$

PCl3 is more stable due to inert pair effect.

Sulphur : Ground state

$$\underset{3s}{\boxed{\uparrow\downarrow}}\quad \underset{3p}{\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}}\quad \underset{3d}{\boxed{}\boxed{}\boxed{}\boxed{}\boxed{}}\qquad \text{Covalency-2 (as in } SF_2\text{)}$$

Sulphur : Excited state

1st excited state

$$\underset{3s}{\boxed{\uparrow\downarrow}}\quad \underset{3p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}\quad \underset{3d}{\boxed{\uparrow}\boxed{}\boxed{}\boxed{}\boxed{}}\qquad \text{Covalency-4 (as in } SF_4\text{)}$$

2nd excited state

$$\underset{3s}{\boxed{\uparrow}}\quad \underset{3p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}\quad \underset{3d}{\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}\boxed{}}\qquad \text{Covalency-6 (as in } SF_6\text{)}$$

So variable valency of S is 2, 4 and 6.

Iodine can have maximum 7 unpaired electrons in its orbitals. It's variable valencies are 1, 3, 5 and 7.

Four elements, H, N, O and F do not possess d-orbitals in their valency shell. Thus, such an excitation is not possible and variable valency is not shown by these elements. This is reason that NCl3 exists while NCl5 does not.

(3) The Lewis theory : The Lewis theory gave the first explanation of a covalent bond in terms of electrons that was generally accepted. The tendency of atoms to achieve eight electrons in their outermost shell is known as lewis octet rule. Octet rule is the basis of electronic theory of valency. It is suggested that valency electrons themselves are responsible for chemical combination. The valency electrons in atoms are shown in terms of Lewis dot formulae. To write Lewis formulae for an element, we write down its symbol surrounded by a number of dots or crosses equal to the number of valency electrons. Lewis dot formulae are also used to represent atoms covalently bonded in a molecule. Paired and unpaired valency electrons are also indicated.

Lewis symbols for the representative elements are given in the following table :

	1	2	13	14	15	16	17
Group	IA	IIA	IIIA	IVA	VA	VIA	VIIA
Lewis symbol	$X\cdot$	$\cdot X\cdot$	$\cdot\dot{X}\cdot$	$\cdot\dot{\underset{\cdot}{X}}\cdot$	$\cdot\dot{\underset{\cdot\cdot}{X}}\cdot$	$\cdot\ddot{\underset{\cdot\cdot}{X}}\cdot$	$:\ddot{\underset{\cdot\cdot}{X}}\cdot$

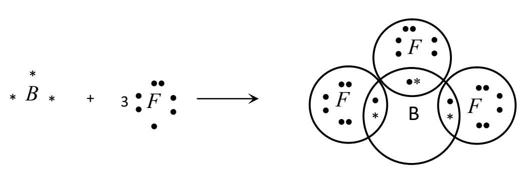
CO is not an exception to octet rule $:\overset{-}{C} \equiv \overset{+}{O}:$ or $:C \equiv \underset{\cdot\cdot}{O}:$

(4) Failure of octet rule :

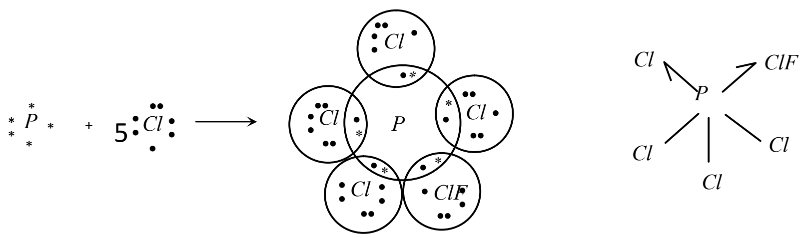
There are several stable molecules known in which the octet rule is violated i.e., atoms in these molecules have number of electrons in the valency shell either short of octet or more than octet.

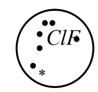
In BF3 molecules, boron atom forms three single covalent bonds with three fluorine atoms, i.e., it attains six electrons in the outer shell.

$$\begin{array}{l} F \\ | \\ B-F \\ | \\ F \end{array}$$

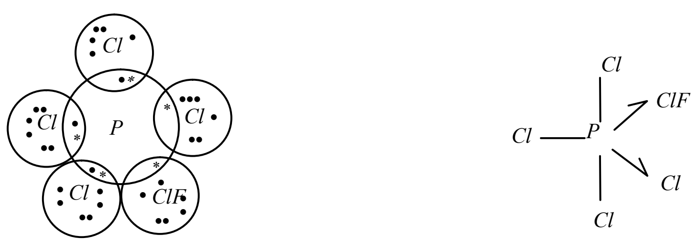


PCl5 molecule : Phosphorus atom have five electrons in valency shell. It forms five single covalent bonds with five chlorine atoms utilising all the valency electrons and thereby attains 10 electrons in the outer shell.





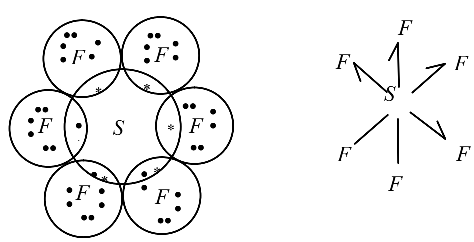
Sugden’s concept of singlet linkage explains the stability of such molecules. In PCl_5, three chlorine atoms are linked by normal covalent bonds and two chlorine atoms are linked by singlet linkages, thus, phosphorus achieves 8 electrons in the outermost shell.



This structure indicates that the nature of two chlorine atoms is different than the other three as singlet linkage is weaker than normal covalent bond. The above observation is confirmed by the fact that on heating, PCl_5 dissociates into PCl_3 and Cl_2.

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Similarly, in SF_6 four singlet linkages are present while in IF_7, six singlet linkages are present.



(ii) Sidgwick's concept of maximum covalency

•This rule states that the covalency of an element may exceed four and octet can be exceeded.

•The maximum covalency of an element actually depends on the period of periodic table to which it belongs.

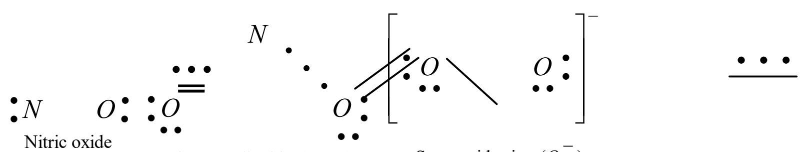
•This rule explains the formation of PCl5 and SF6.

•This also explains why nitrogen does not form NF_5 or NCl_5 because nitrogen belongs to second period and the maximum covalency of nitrogen is three.

(iii) Odd electron bond : In 1916 Luder postulated that there are number of stable molecules in which double bonds are formed by sharing of an odd number of electrons, i.e., one, three, five, etc., between the two bonded atoms. the bonds of this type are called odd electron bonds.

The normal valence bond structure of oxygen molecule, $:\ddot{O}=\ddot{O}:$, fails to account for the paramagnetic nature of oxygen. Thus, structure involving three electrons bond has been suggested by Pauling. The following structure $:O \xrightarrow[\cdot\;\cdot\;\cdot]{\cdot\;\cdot\;\cdot} O:$. Explains the paramagnetic nature and high dissociation energy of oxygen molecule.

Some other examples are :



Nitric oxide (NO) Nitrogen dioxide (NO_2) Superoxide ion (O_2^-)

The number of singlet bonds = Total number of bonds – Number of electrons required to complete the octet.

Properties of Odd Electron bond

(i) The odd electron bonds are generally established either between two like atoms or between different atoms which have not more than 0.5 difference in their electronegativities.

(ii) Odd electron bonds are approximately half as strong as a normal covalent bond.

(iii) Molecules containing odd electrons are extremely reactive and have the tendency to dimerise.

(iv) Bond length of one electron bond is greater than that of a normal covalent bond. Whereas the bond length of a three electron bond is intermediate between those of a double and a triple bond.

(v) One electron bond is a resonance hybrid of the two structures i.e., $A \bullet B \longleftrightarrow A \bullet B$

Similarly, a three electron bond is a resonance hybrid of the two structures i.e.,
$A \bullet \vdots\, B \longleftrightarrow A \vdots \bullet B$

(5) Construction of structures for molecules and poly atomic ions : The following method is applicable to species in which the octet rule is not violated.

(i) Determine the total number of valence electrons in all the atoms present, including the net charge on the species (n1).

(ii) Determine n2 = [2 × (number of H atoms) + 8 × (number of other atoms)].

(iii) Determine the number of bonding electrons, n3, which equals n2 – n1. No. of bonds equals n3/2.

(iv) Determine the number of non-bonding electrons, n4, which equals n1 – n3. No. of lone pairs equals n4/2.

(v) Knowing the central atom (you'll need to know some chemistry here, math will not help!), arrange and distribute other atoms and n3/2 bonds. Then complete octets using n4/2 lone pairs.

(vi) Determine the 'formal charge' on each atom.

(vii) Formal Charge = [valence electrons in atom) – (no. of bonds) – (no. of unshared electrons)]

(viii) Other aspects like resonance etc. can now be incorporated.

Illustrative examples :

(i) $CO_3^{2-}; n_1 = 4 + (6 \times 3) + 2 = 24$ [2 added for net charge]

n_2 = (2 × 0) + (8 × 4) = 32 (no. H atom, 4 other atoms (1'C' and 3 'O')

n_3 = 32 – 24 = 8, hence 8/2 = 4 bonds

n_4 = 24 – 8 = 16, hence 8 lone pairs.

Since carbon is the central atom, 3 oxygen atoms are to be arranged around it, thus,

$O - \overset{\overset{O}{|}}{C} - O$, but total bonds are equal to 4.

Hence, we get $O - \overset{\overset{O}{|}}{C} = O$. Now, arrange lone pairs to complete octet $:\underset{..}{\dot{O}} - \overset{\overset{.\overset{..}{O}:}{|}}{C} = \overset{..}{O}:$

(ii) CO_2; n1 = 4 + (6 × 2) = 16

n2 = (2 × 0) + (8 × 3) = 24

n3 = 24 – 16 = 8, hence 4 bonds

n4 = 16 – 8 = 8, hence 4 lone-pairs

Since C is the central atom, the two oxygen atoms are around to be arranged it thus the structure would be; O – C – O, but total no. of bonds = 4

Thus, O = C = O. After arrangement of lone pairs to complete octets, we get, $:\ddot{O} = C = \ddot{O}:$ and thus final structure is $:\ddot{O} = C = \ddot{O}:$