Chemical bonding

SAP-4

<u>chemical bond</u> ⟶ The attractive force which holds various constituent particles like atoms, ions etc. together in different chemical species is k/a chemical bond.

<u>Types of chemical bond</u> ⟶

(1) Ionic bond   (2) Covalent bond

(3) Coordinate bond   (4) metallic bond
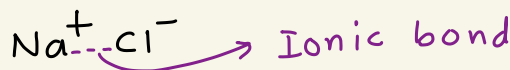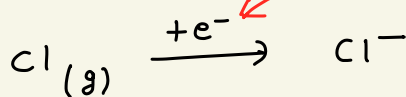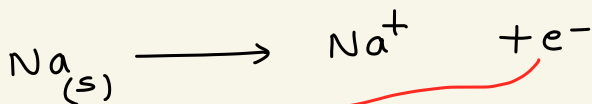
(1) <u>Ionic bond (Electrovalent bond)</u> ⟶ The bond formed as a result of the electrostatic attraction b/w +ve and −ve ions is k/a ionic bond.

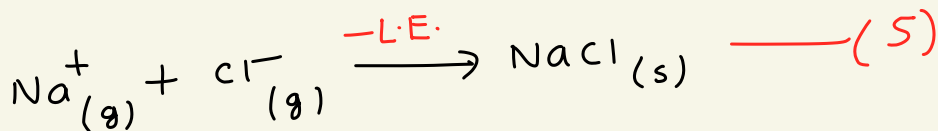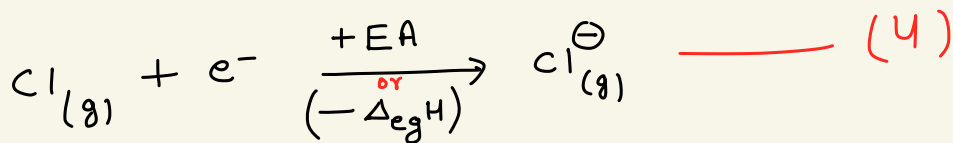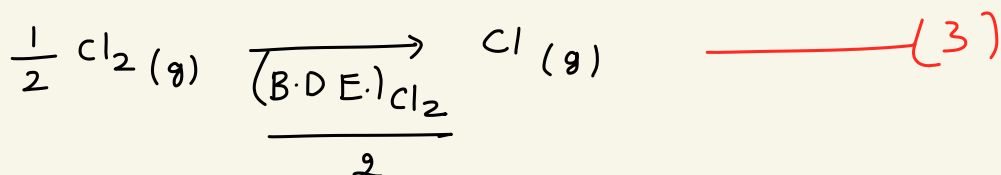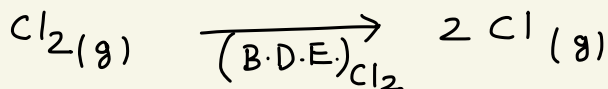*   It is formed b/w metal and non metal.
*   It is formed by transfer of e^-.

<u>Ex.</u>   NaCl

$$Na_{(s)} \longrightarrow Na^+ \; + e^-$$

$$Cl_{(g)} \xrightarrow{+e^-} Cl^-$$

$$Na^+ \text{---} Cl^- \longrightarrow \text{Ionic bond}$$

Formation of ionic bond —

Ex. $NaCl_{(s)}$

$$Na_{(s)} \xrightarrow{\Delta_{sub.}H} Na_{(g)} \qquad ---(1)$$

$$Na_{(g)} \xrightarrow{+I.E.} Na^+_{(g)} + e^- \qquad ---(2)$$

$$Cl_{2(g)} \xrightarrow{(B.D.E.)_{Cl_2}} 2\,Cl_{(g)}$$

$$\tfrac{1}{2}\,Cl_{2\,(g)} \xrightarrow{\dfrac{(B.D.E.)_{Cl_2}}{2}} Cl_{(g)} \qquad ---(3)$$

$$Cl_{(g)} + e^- \xrightarrow[\underset{(-\Delta_{eg}H)}{or}]{+EA} Cl^{\ominus}_{(g)} \qquad ---(4)$$

$$Na^+_{(g)} + Cl^-_{(g)} \xrightarrow{-L.E.} NaCl_{(s)} \qquad ---(5)$$

adding

$$Na_{(s)} + \tfrac{1}{2}\,Cl_{2(g)} \longrightarrow NaCl_{(s)}$$
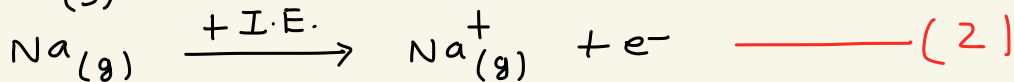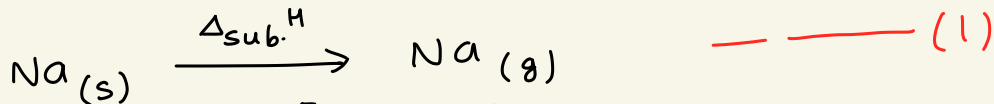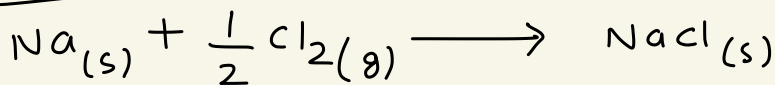
$$\Delta_r H = \Delta_{sub}H + I.E. + \frac{B.D.E.}{2} - \Delta_{eg}H - L.E.$$

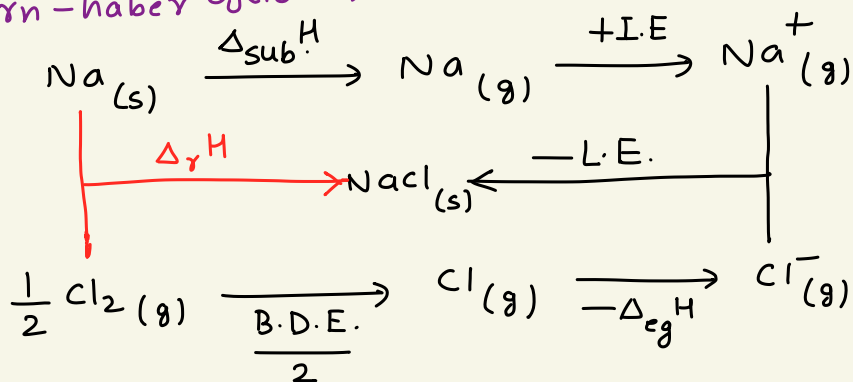$$= \left(\Delta_{sub}H + I.E. + \frac{B.D.E.}{2}\right) - \left(\Delta_{eg}H + L.E.\right)$$

* Ionic bond formation is an exothermic process. i.e. $\Delta_r H = -ve$

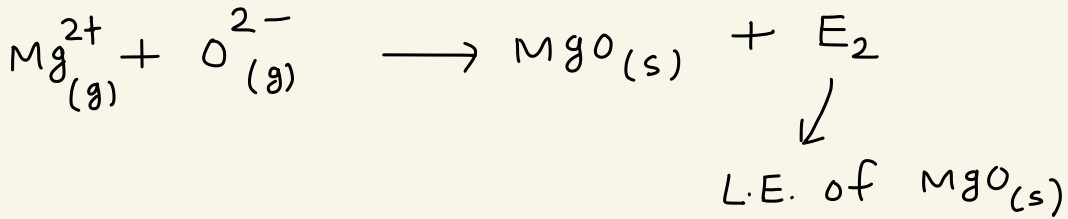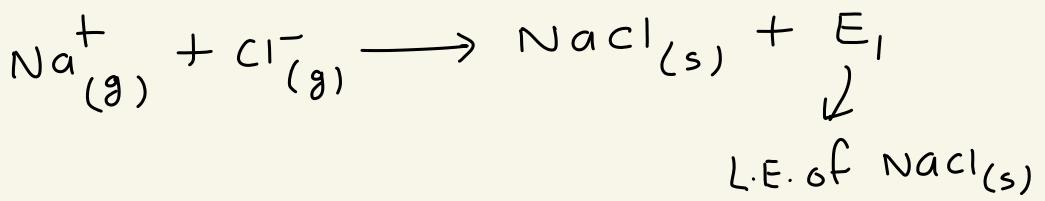$$\Rightarrow \quad \Delta_{eg}H + L.E. > \Delta_{sub}H + I.E. + \frac{B.D.E.}{2}$$

Favourable conditions for ionic bond formation→

(1) Electron gain enthalpy (Electron affinity) of non metal should be high.

(2) Lattice energy of metallic crystal should be high.

(3) $\Delta_{sub}H$ of metallic solid should be low.

(4) I.E. of $M_{(g)}$ should be low.

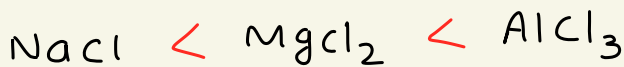(5) B.D.E. of non metallic gas should be low.

Born − haber cycle →

$$Na_{(s)} \xrightarrow{\Delta_{sub}H} Na_{(g)} \xrightarrow{+I.E} Na^+_{(g)}$$

$$Na_{(s)} \xrightarrow{\Delta_r H} NaCl_{(s)} \xleftarrow{-L.E.}$$

$$\frac{1}{2} Cl_{2\,(g)} \xrightarrow[\frac{B.D.E.}{2}]{} Cl_{(g)} \xrightarrow{-\Delta_{eg}H} Cl^-_{(g)}$$
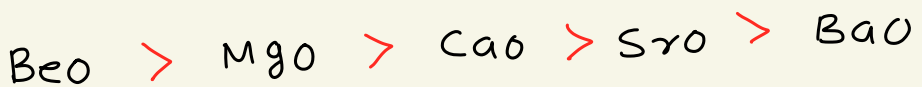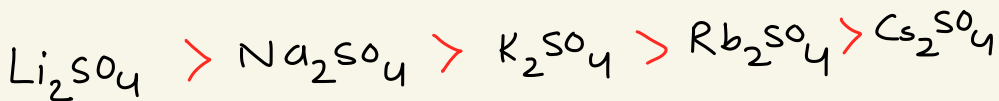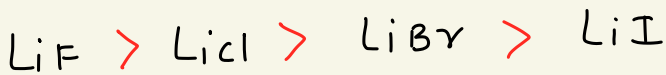
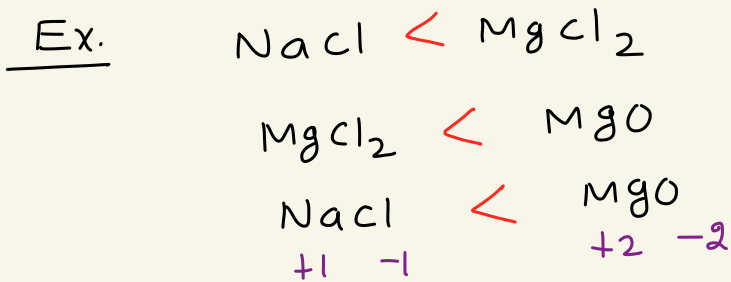Lattice enthalpy → It is the amount of energy released in the formation of 1 mole ionic comp. from its constituent gaseous ions.

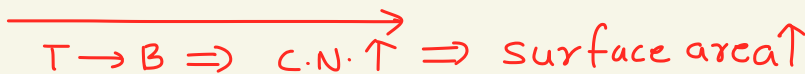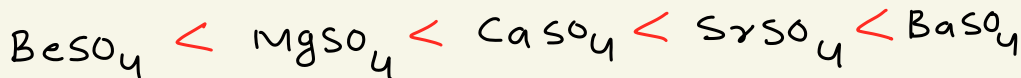$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)} + E_1$$

$$\downarrow$$

L.E. of $NaCl_{(s)}$

$$Mg^{2+}_{(g)} + O^{2-}_{(g)} \longrightarrow MgO_{(s)} + E_2$$

$$\downarrow$$

L.E. of $MgO_{(s)}$

It can be measured exp.

$$L.E. \propto |q_+ \cdot q_-|$$

$$\propto \frac{1}{r_+ + r_-}$$

Ex.

$$NaCl < MgCl_2$$

$$MgCl_2 < MgO$$

$$\underset{+1 \quad -1}{NaCl} < \underset{+2 \quad -2}{MgO}$$

$$LiF > LiCl > LiBr > LiI$$

$$Li_2SO_4 > Na_2SO_4 > K_2SO_4 > Rb_2SO_4 > Cs_2SO_4$$

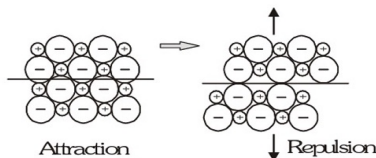$$BeO > MgO > CaO > SrO > BaO$$

$$NaCl < MgCl_2 < AlCl_3$$

PROPERTIES OF IONIC COMPOUND

(a) **Physical state** – Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction.

Brittleness → {Same charged ions comes nearer. So they repel each other}

Attraction   Repulsion

(b) **Isomorphism :** Different ionic compounds, having same configuration/geometry of ions are isomorphs of each other and phenomenon is known as isomorphism

→ crystal structure

Ex.   NaF, MgO, $ZnSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$. All alums $M_2'SO$ $M_2''(SO_4)_3$ $24H_2O$.

(c) **Boiling point and melting point** –

Ionic compounds have high boiling point and melting point due to strong electrostatic force of attraction among oppositely charged ions.

(d) **Conductivity** – It depends on ionic mobility.

(i) In solid state - No free ions - Bad conductor of electricity.

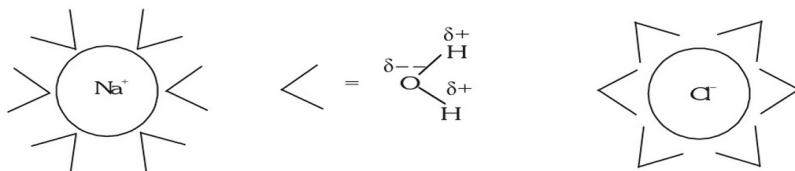(ii) In fused state or aqueous solution Due to free ions - Good conductor of electricity.

Conductivity order   Solid state < fused state < Aqueous solution

(e) **Solubility** – Highly soluble in water (Polar solvents) **Ex.** NaCl in water

(i) The Na^+ ions get associates with - vely charged 'O' of water.

(ii) And Cl^- ions associates with +vely charged 'H' of water.

(iii) Thus charge on Na^+ and Cl^- decreases and electrostatic force of attraction also decreases which leads to produce free ion.

(iv) The energy released due to interaction between solvent and solute is called solvation energy. If water is used as solvent it is called hydration energy.
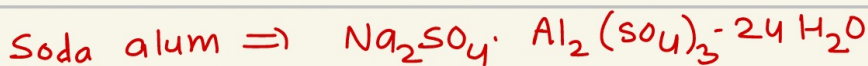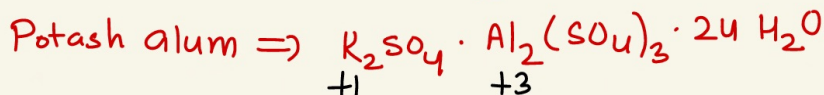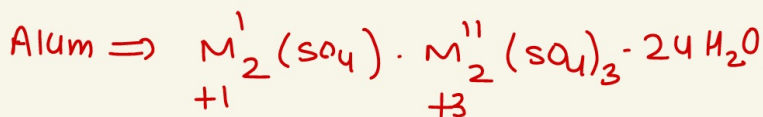
(v) For an ionic compound to be soluble in water – Hydration energy > Lattice energy

$$\text{Lattice energy } \alpha \ \frac{1}{\text{Solubility}}$$

Hydration energy α Solubility.

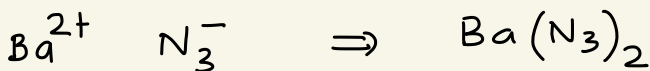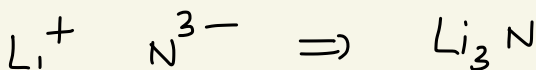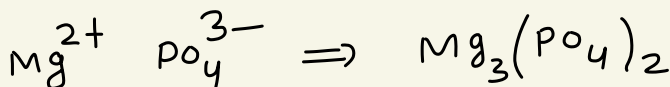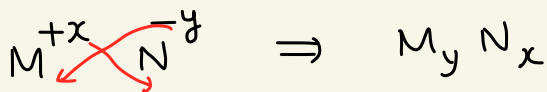Hydration energy (H) $\alpha \ \dfrac{1}{r^+} + \dfrac{1}{r^-}$ { r^+ & r^- are radius of cation and anion}

(vi) Hydration energy mainly depends on the cation radius because the value of $\frac{1}{r^-}$ is negligible in comparision to $\frac{1}{r^+}$

(vii) Down the group both the lattice energy & hydration energy decreases, if decrease in lattice energy is greater than hydration energy, solubility increases down the group and vice versa.

$$Alum \Rightarrow \underset{+1}{M^1_2(SO_4)} \cdot \underset{+3}{M^{11}_2(SO_4)_3} \cdot 24H_2O$$

$$Potash\ alum \Rightarrow \underset{+1}{K_2SO_4} \cdot \underset{+3}{Al_2(SO_4)_3} \cdot 24H_2O$$

$$Soda\ alum \Rightarrow Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$

* Ionic bond is nondirectional bond.

* Ionic compounds are soluble in the solvents which have high dielectric constant.

   Dielectric constant is the capacity of a solvent which decreases the electrostatic attraction between oppositely charged ions.

* Ionic compounds are generally diamagnetic and colourless.

$$M^{+x} \diagdown N^{-y} \Rightarrow M_y N_x$$

$$Mg^{2+} \quad PO_4^{3-} \Rightarrow Mg_3(PO_4)_2$$

$$Li^+ \quad N^{3-} \Rightarrow Li_3N$$

$$Ba^{2+} \quad N_3^- \Rightarrow Ba(N_3)_2$$

(2) <u>Covalent bond</u> ⟶ The bond which is formed by mutual sharing of e⁻ b/w two atoms is K/a covalent bond.

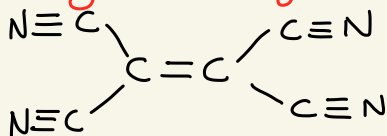* In the formation of covalent bond, valence e⁻ (outermost shell e⁻) take part.

H   He·   Li   Be·   ·B·   ·C·   ·N·

:O: :F: :Ne:
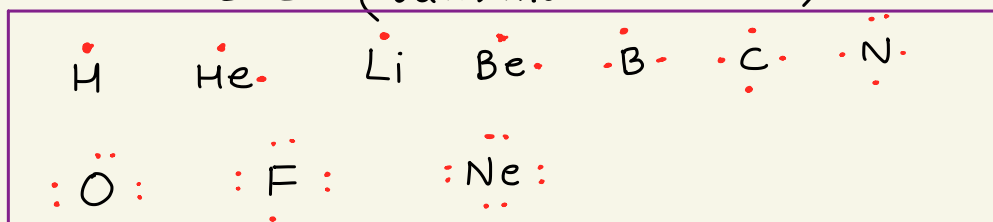
Lewis dot Symbol

Sharing of 1−1 e⁻ ⟹ Single bond (1σ)

— " — 2−2 e⁻ ⟹ Double bond (1σ + 1π)

— " — 3−3 e⁻ ⟹ Triple bond (1σ + 2π)

<u>Ex.</u>   Tetracyanoethylene $\left[C_2(CN)_4 \right]$

$$N≡C \diagdown \quad \diagup C≡N$$
$$\qquad C=C$$
$$N≡C \diagup \quad \diagdown C≡N$$

9σ, 9π

Dicyano ethyne $\left[C_2(CN)_2 \right]$

N≡C—C≡C—C≡N   5σ
                6π

Benzene   12σ
           3π
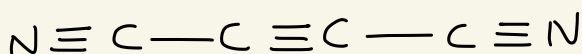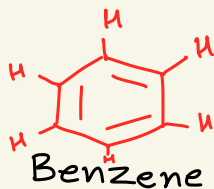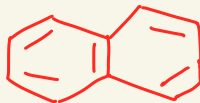
Naphthalene   5π, 19σ
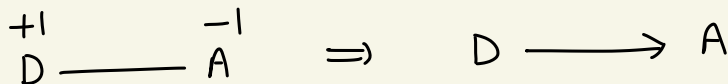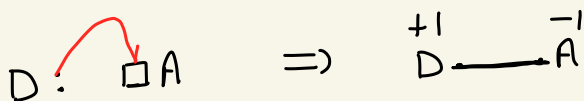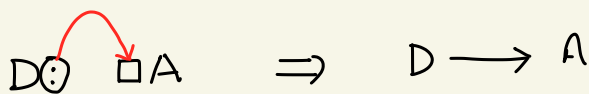
(3) <u>Coordinate bond (Dative bond)</u> ⟶ The
bond formed by unequal sharing of e^- is
b/w two atoms (Donor & Acceptor) is
K/a Coordinate bond.

Donor ⟹ which have complete octet
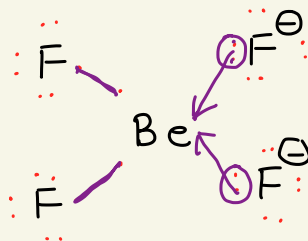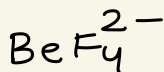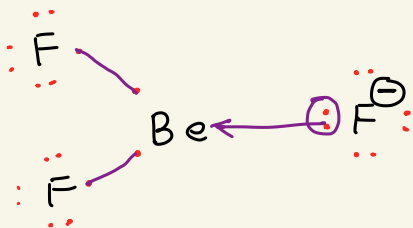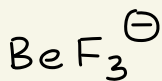($8e^-$ in valence shell)
+
having unshared e^-
(lone pair e^-)

Acceptor ⟹ which have vacant orbitals
to accept lone pair e^-s.

D⦂ □A ⟹ D⟶A

D⦂ □A ⟹ $\overset{+1}{D}$———$\overset{-1}{A}$

$\overset{+1}{D}$———$\overset{-1}{A}$ ⟹ D⟶A

$\overset{-1}{P}$———$\overset{+1}{q}$ ⟹ P⟵q

BeF$_2$

$$:\ddot{F} \!-\!\!\!-\!\!\!- Be \!-\!\!\!-\!\!\!- \ddot{F}:$$

Ex.   BeF$_3^{\ominus}$

BeF$_4^{2-}$

Ex.   BeF$_5^{3-}$ $\longrightarrow$ not possible.

EX.   NH$_4^+$

Ex.   H$_3$O$^+$

<u>Ex.</u>   B F$_3$

<u>Ex.</u>   B F$_4^{\ominus}$

Total ℓp = 12

<u>Ex.</u>   B F$_5^{2-}$,   B F$_6^{3-}$ $\longrightarrow$ not Possible
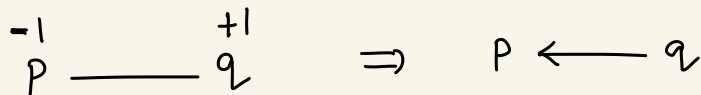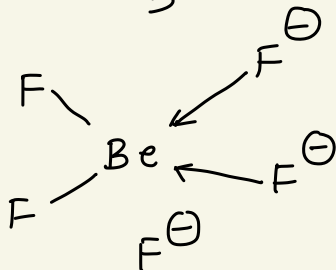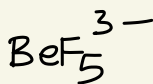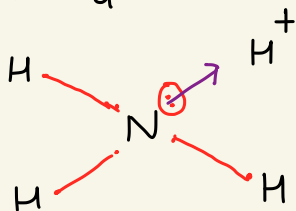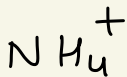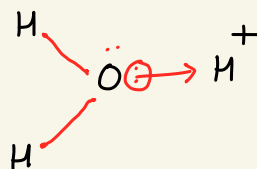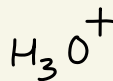
<u>Lewis Kossel theory to chemical bonding</u> $\longrightarrow$

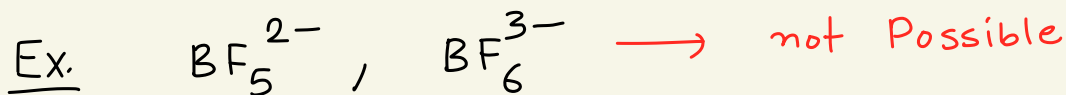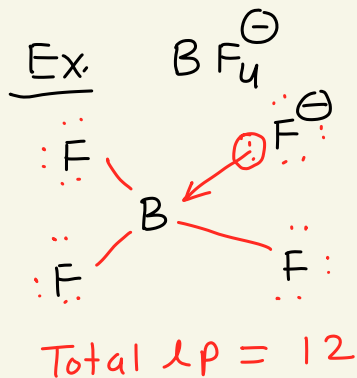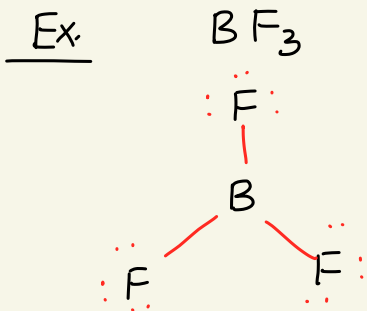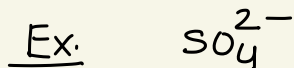<u>(octet rule)</u> $\longrightarrow$ Each atom wants to achieve
Stable octet (8 e$^-$ in valence shell).

<u>Exception</u> $\longrightarrow$ 1st period elements try to achieve
duplet (2 e$^-$ in valence shell)

<u>Lewis dot structures</u> $\longrightarrow$

<u>Ex.</u>   SO$_4^{2-}$

<u>Step-1</u>   Calculate 'N$_1$'.

N_1 = Total no. of valence e$^-$s of each
atom $\pm$ charge

+ sign $\Rightarrow$ $-ve$ charge
$-$ sign $\Rightarrow$ $+ve$ charge

$$N_1 = 6 + 24 + 2 = 32$$

Step-2   calculate $'N_2'$.

$N_2 =$ No. of $\bar{e}$s   after completing
the octet

$= 8 + 32 = 40$

step-3   Calculate $'N_3'$.

$N_3 =$ No. of e^-s taking Part in
bond formation

$= N_2 - N_1$

$= 40 - 32 = 8 \ e^-$

step-4   Calculate Total No. of bonds. $= \dfrac{N_3}{2}$

$= \dfrac{8}{2} = 4 \ bond$
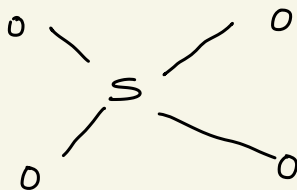
step-5   Calculate formal charge on each
atom.

$F.C. =$ (Valence e^-) $-$ (No. of bonds)
$-$ (No. of non bonding e^-)

No. of bonds   No. of non bonding e^-

$$1 \qquad\qquad 6 \ e^-$$

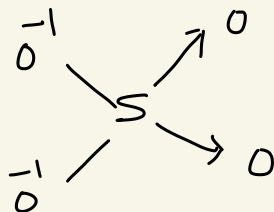$$2 \qquad\qquad 4 \ e^-$$

$$3 \qquad\qquad 2 \ e^-$$

$$4 \qquad\qquad 0 \ e^-$$

$$(F.c.)_O = 6 - 1 - 6 = -1$$

$$(F.c.)_S = 6 - 4 - 0 = +2$$

$$\overset{+1}{A} — \overset{-1}{B} \quad\Rightarrow\quad A \longrightarrow B$$

Ex. PO_4^{3-}
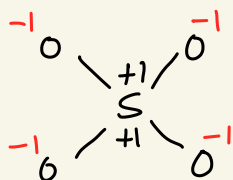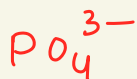
$$N_1 = 5 + 24 + 3 = 32$$

$$N_2 = 8 + 32 = 40$$

$$N_3 = 8 \ e^-$$

$$N_u = 4 \text{ bonds}$$

$$(F.c.)_P = 5 - 4 - 0 = +1$$
$$(F.c.)_O = 6 - 1 - 6 = -1$$

Ex.
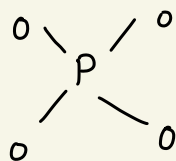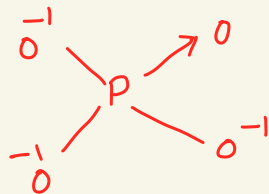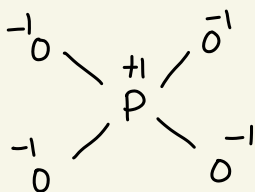
CO

$$N_1 = 10 \quad , \quad N_2 = 16$$
$$N_3 = 6 \, e^- \quad ; \quad N_u = 3 \text{ bond}$$

$$C \equiv O$$

$$(F.c.)_C = 4 - 3 - 2 = -1$$
$$(F.c.)_O = 6 - 3 - 2 = +1$$

$$\overset{-1}{C} \equiv \overset{+1}{O} \quad \Rightarrow \quad C \overset{=}{\equiv} O$$

Ex. O_3

$$N_1 = 18 \quad , \quad N_2 = 24$$
$$N_3 = 6 \, e^- \quad , \quad N_u = 3 \text{ bonds}$$

$F.c. = 6 - 3 - 2 = +1$

$F.c. = 6 - 2 - 4 = 0$

$F.c. = 6 - 1 - 6 = -1$

$\Downarrow$

$+1$ -1

$\Longrightarrow$

Ex. ClO_4^-

Ex. ClO_3^-

Ex. SO_3^{2-}

Ex. $NO_3^{\ominus}$

Ex. CO_3^{2-}

Ex. $NO_2^{\ominus}$
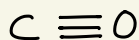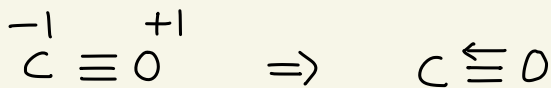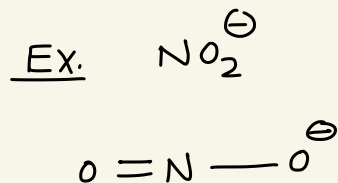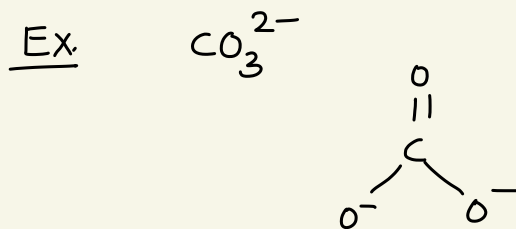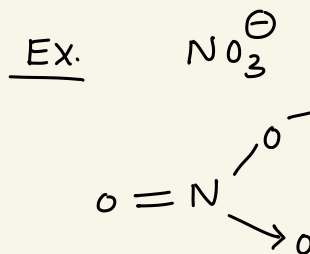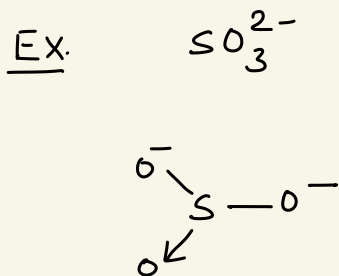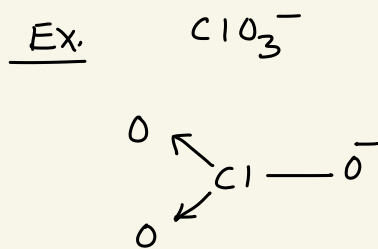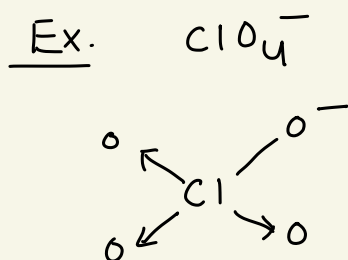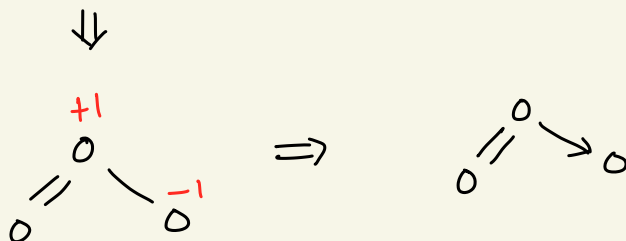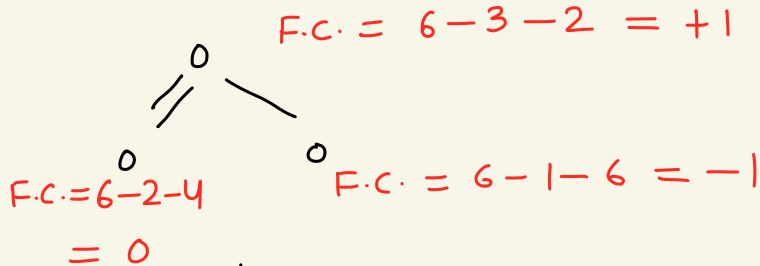
Exception to Octet Rule

The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. Up to now we have studied the molecules which follow Lewis Octet Rule while forming bonds. It is observed that atoms in some molecules could exist with some other number of electrons in their valence shells, rather than eight electrons without affecting the stability.

There are three types of exceptions to the octet rule :

(i) The incomplete octet of the central atom

In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are $LiCl$, BeH_2, BCl_3, $AlCl_3$, BF_3 etc. Li, Be and B have 1,2 and 3 valence electrons only.

BF_3 : Boron atom has only six electrons in its outer-shell even after making three single bonds with three F atoms (i.e., it completes only sixet).
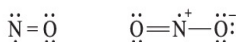
$$F-B\underset{F}{\overset{F}{\big<}}$$

$BeCl_2$: Beryllium has only four electrons in its outershell even after making two single bonds with two Cl atoms.

$$Cl-Be-Cl$$

(ii) Odd-electron molecules

In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO_2, the octet rule is not satisfied for all the atoms (as shown below)

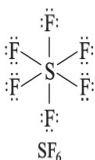$$\ddot{N}=\ddot{O} \qquad \ddot{O}=\overset{+}{N}-\ddot{\underset{..}{O}}\bar{\ }$$
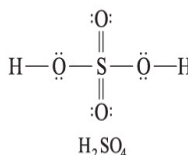
(iii) The expanded octet

Elements in and beyond the third period of the periodic table have, apart from $3s$ and $3p$ orbitals, $3d$ orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases. Eg : PF_5, SF_6, H_2SO_4 and a number of coordination compounds.
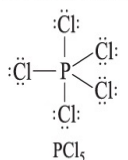
PCl₅	SF₆	H₂SO₄
10 electrons around the P atom	12 electrons around the S atom	12 electrons around the S atom

PCl_5 : Phosphorus after making five single bonds with five Cl atoms has ten electrons in its outershell.

SF_6 : Sulphur makes six single bonds with six F atoms and thus has 12 electrons in its outershell.

H_2SO_4 : Sulphur makes 2 single bonds and 2 double bonds with 4 oxygen atoms and thereby has 12 electrons in its outermost shell

Other drawbacks of the octet theory

➤ It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2, KrF_2, $XeOF_2$ etc.,

➤ This theory does not account for the shape of molecules.

➤ It does not explain the relative stability and energy of the molecules.

Homework

DTS-1 to 11
Q.1,4,6,7,9-13,15,17,19,22,23,61,84,101,130,132