

INORGANIC POLYMER

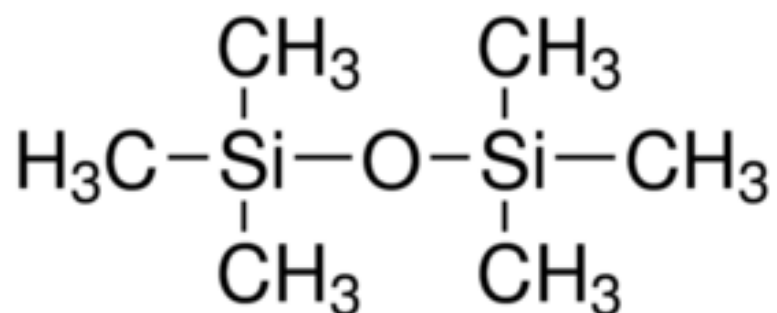
SILICONES

Silicones are organopolysiloxanes. They are also known as organosilicones or organosilicon polymer. General formula is $(R_2SiO)_n$

Types of Silicones:

1) Linear (straight chain silicones):

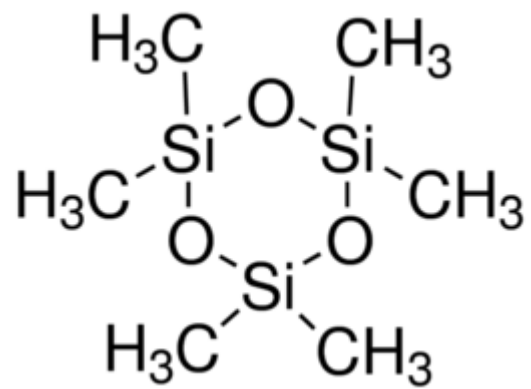
For example. They have straight chain structures



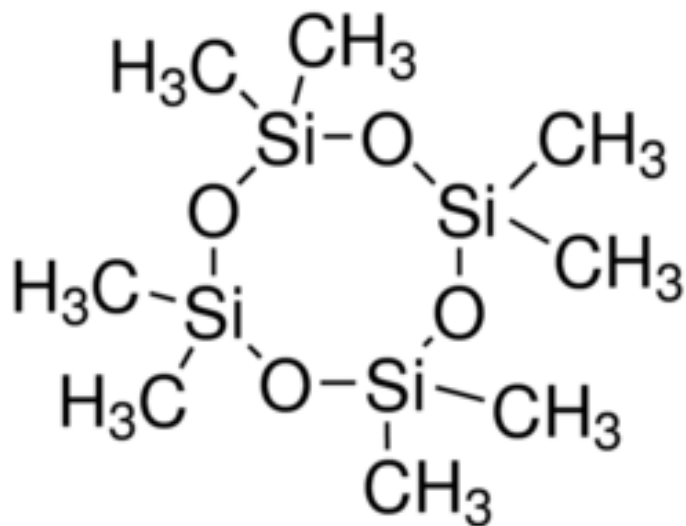
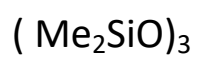
Polydimethyl Siloxane Linear Silicon

They are prepared by hydrolysis and condensation polymerisation of dialkyl or diaryl Substituted Silicon Chloride (R_2SiCl_2).

2) Cyclic Silicones: They are obtained by hydrolysis and controlled polymerisation of dialkyl or diaryl Substituted Silicon Chlorides (R_2SiCl_2) in presence of cyclic catalyst.

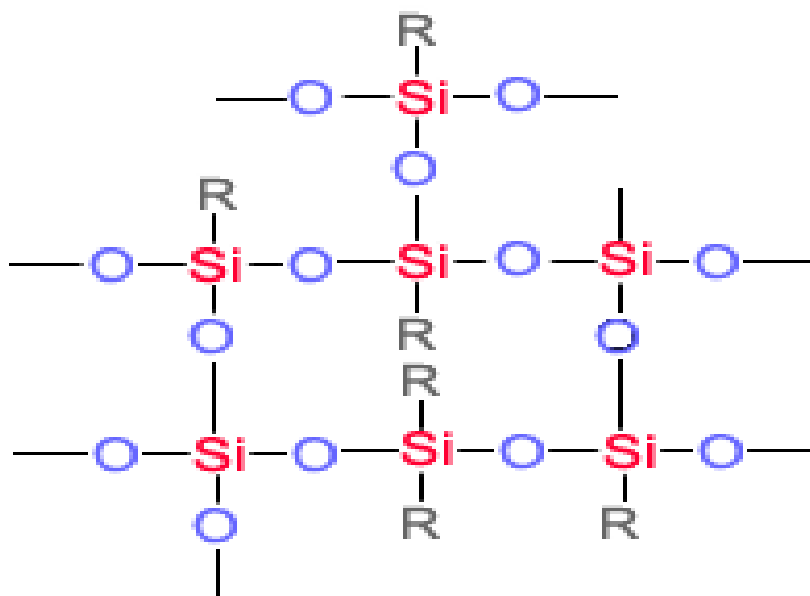


Hexamethyl Cyclic trisiloxane



Octa Methyl Cyclic Tetra Siloxane

Cross Linked: These are obtained by hydrolysis and condensation polymerisation of mono alkyl or mono aryl substituted Silicon Chloride (RSiCl₃)



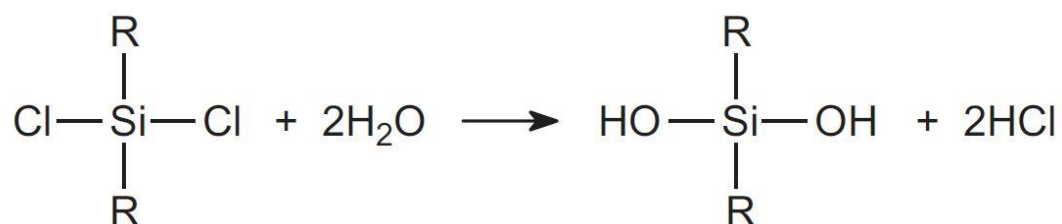
Cross Linked Structures

Preparation of Linear Silicons

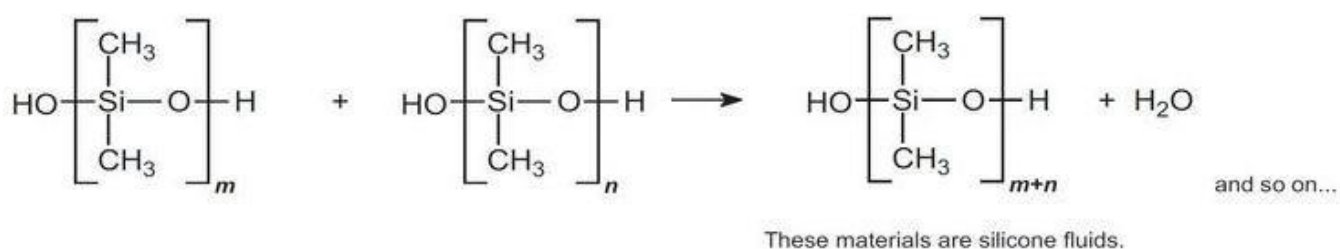
Preparation: These are obtained by the reaction of alkyls or aryl halides with silicon in the presence of copper



By hydrolysis of chloroderivative:



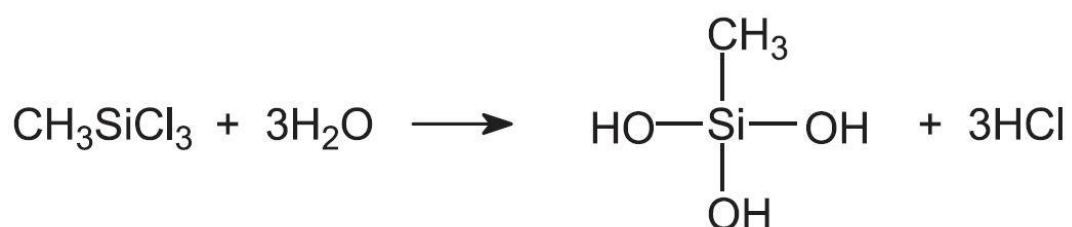
The dialkyl silicane diol undergoes condensation polymerisation to linear silicane:



Cyclic Silicon

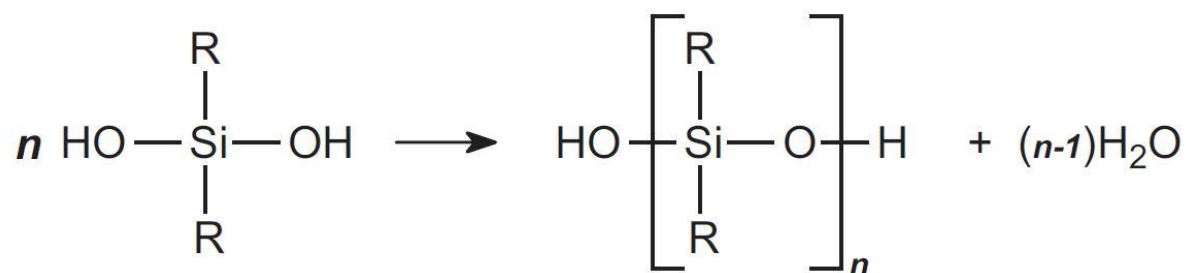
The controlled Condensation Polymerisation of dialkyl or diaryl Silane

Cross Linked Silicones: These are formed by the hydrolysis of trichloro silane



Alkyl Silane Triol

Condensation Polymerisation



Properties:

- 1.) They are highly resistive to heat.
- 2.) Lower silicones are soluble in organic solvents like CCl_4
- 3.) They are chemically inert.
- 4.) They are resistant to oxidation.
- 5.) The lower silicones are oily liquids.
- 6.) The nature of a silicon polymer depends upon the length of the chain, size of the alkyl or aryl group.

Uses :

- 1.) Silicones are water repellent hence they are used in making waterproof clothes.
- 2.) Due to their insulating property, these are used as insulating materials for electric motors and other electrical appliances.
- 3.) These are used as lubricants at both high and low temperature.
- 4.) Silicones are used to coat wires used for winding refrigerators.
- 5.) They are mixed in paints to make them temperature resistance.

PHOSPHAZENES

These are Inorganic Polymer having Phosphorus , Nitrogen (P=N) double bonds(ene) . In phosphozenes, oxidation number of phosphorus is +5 Nitrogen is in 2 coordination state and phosphorus is in 4. They are unsaturated having general formula $(PNX_2)_n$ where X= Cl, F ,Br, SCN,etc. They are cyclic or chain inorganic polymer. The value of N ranges from 3 to 7.

$(PNCl_2)_3$ – Tri Phospho Nitrilic Chloride

$(PNCl_2)_4$ - Tetra Phospho Nitrilic Chloride

$(PNCl_2)_5$ - Penta Phospho Nitrilic Chloride

$(PNCl_2)_6$ - Hexa Phospho Nitrilic Chloride

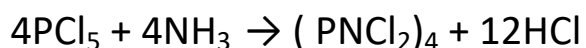
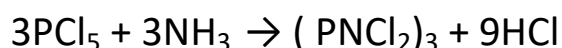
$(PNCl_2)_7$ - Hepta Phospho Nitrilic Chloride

Polyphosphonitrilic halides are $(NPF_2)_n$, $(NPCL_2)_n$ has been studied.

Polymethoxy Phosphazene and Polyethoxy Phosphazene are also linear.

PREPARATION:

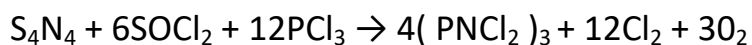
1.) Reaction with PCl_5 and NH_3



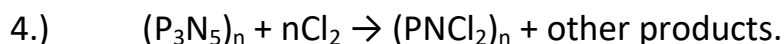
They are separated as $(PNCl_2)_3$ sublime at $50^\circ C$ where as $(PNCl_2)_4$

white crystalline solid is left.

2.) S_4N_4 reacts with $SOCl_2$ in presence of PCl_3



PCl_5 and NH_4Cl are taken in equimolar amount in a sealed tube at 16C in presence of tetrachloro ethane.



Analogous Bromo compound can also be prepared

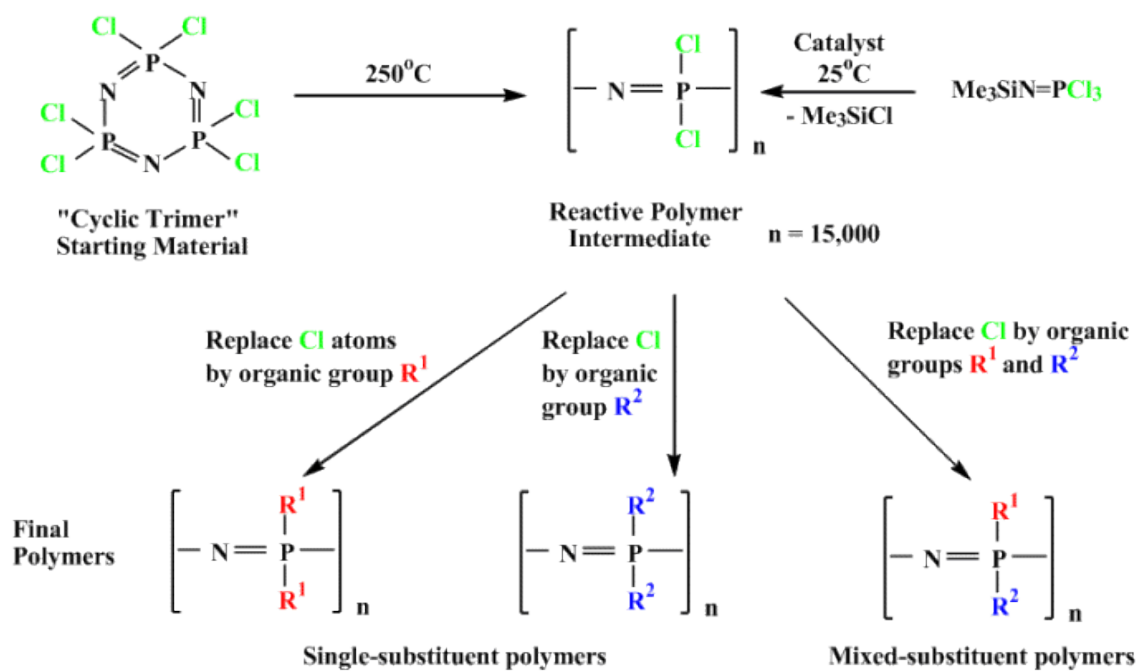


PROPERTIES:

1. $(\text{PNCl}_2)_3$ is a white crystalline solid melting point 114°C and boiling point at 256°C . Soluble in C_6H_6 , CCl_4 and ether. $(\text{PNCl}_2)_4$ is crystalline solid m.p. 123°C and b.p. 328°C They are poisonous and irritating substances.

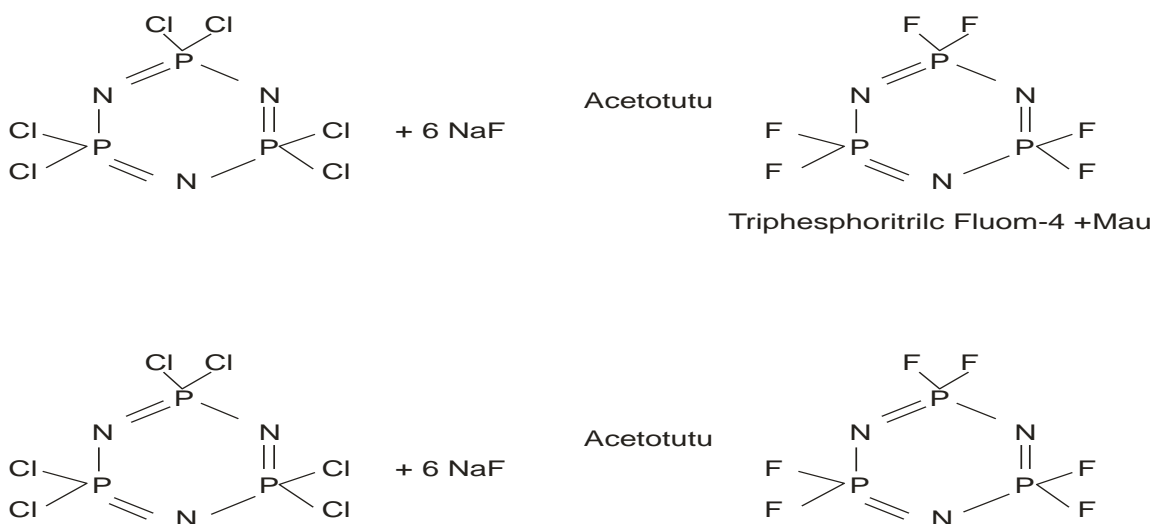
2. Action of Heat: On heating at 250°C $(\text{PNCl}_2)_3$ or $(\text{PNCl}_2)_4$ polymerises to rubber like substances.

3. They undergo nucleophilic substitution reaction.



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4.) Reaction with Sodium Fluoride:



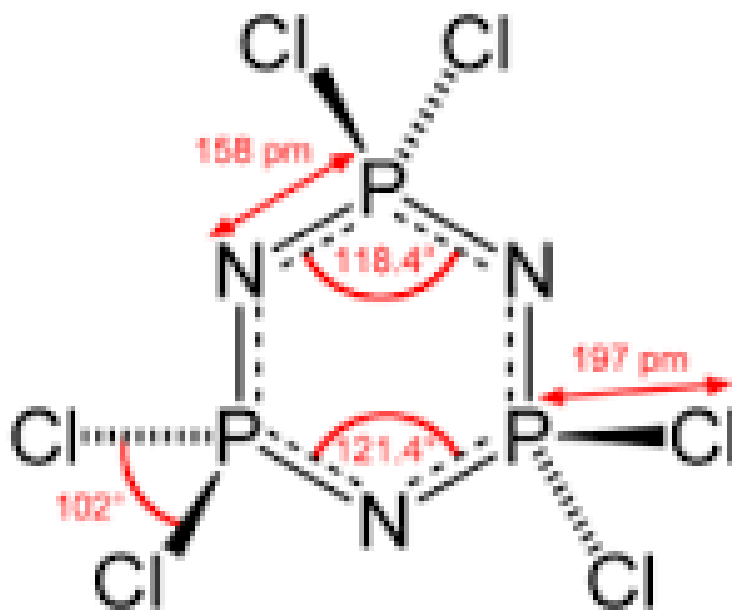
heavy lone pair of electron, hence they act as a base. They react with SO_3 or AlCl_3 to form addition compound.

Uses:

- 1) They form flame proof fabrics, as they are flame resistant.
- 2.) Used as catalyst in Silicon manufacturer.
- 3.) They are used as flexible plastic.
- 4.) Thin films of amino phosphazenes are used to cover severe burns and serious wounds because they prevent the loss of body fluids and keep germs away.

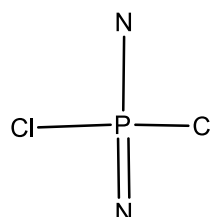
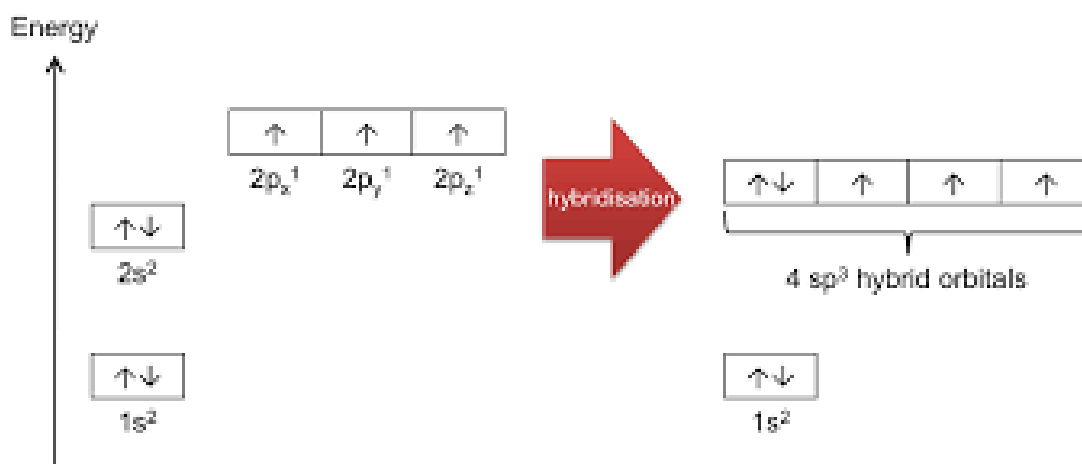
Structure:

X-ray studies shows it has six-membered planar ring structure each N-atom is sp^2 hybridized and each P atom is sp^3 hybridise. The lone pair of electrons on each N atom is present in sp^2 hybrid orbital. Therefore such molecules show basic properties:



N=P bond length $\approx 1.6 \text{ \AA}$. In nitrogen and phosphorus double bond is a quite stable because it is $(d\pi-p\pi)$ bond, P-N single bond is σ bond and P-Cl bond are also σ bond

N-atom sp^2 hybridised



Two P-N σ bonds

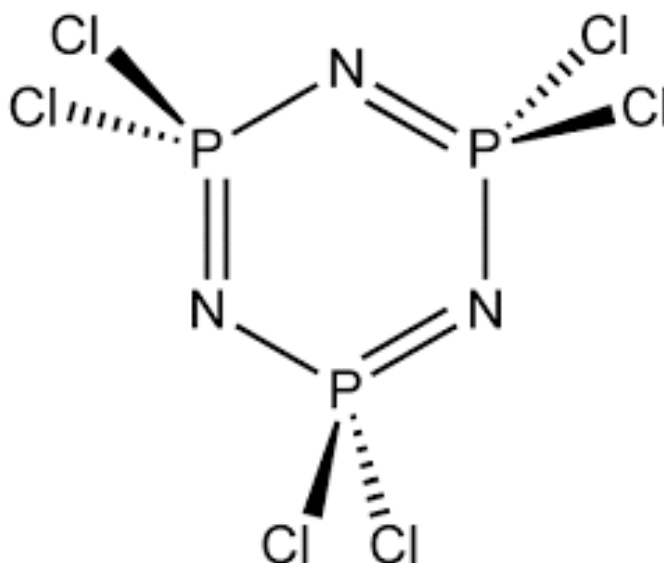
Two P-Cl σ bonds

One P-N π bonds

Formation of Island type π bond in $(N=PCl_2)_3$

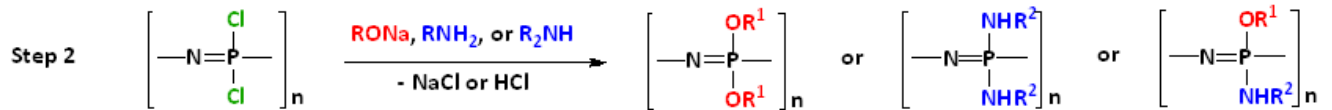
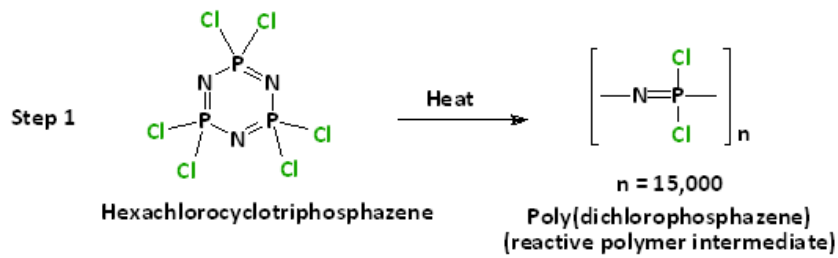
Dewar and his co-workers have given Island-type π bond. In this structure D_{x^2} and D_{y^2} orbitals of P-atom hybridised to form two orbitals which are directed towards adjacent N-atoms. This type of three-centred bonds is at about each N-atom. This type of bond is

called Island type π -bond. In this type of bond formation dilocalisation of π -electron cloud and all the three PNP atoms of the rings which has nodes at each P atom.



Action of air:

(NCl_2) polymer are stored in air they become brittle because H_2O forms O-bridge between P-atom.



Questions:

Q.1 What are silicones? How they are synthesised? Describe the important properties and uses.

Q.2 How crossed-linked silicones are prepared? Write about the technical uses of crossed linked polymer.

Q.3 What are phosphagenes? How it is prepared?

Q.4 Explain the structure of triphosphagenes.

Q.5 Discuss the nature of bonding in phosphagene and explain the mechanism of formation of hexachlorocyclophosphagene.

Q.6 What is Island // -bond?

Q.7 what is meant by phosphonitrilic halides? Discuss their structure uses and nature of bonding.

Hard and Soft Acids and Bases

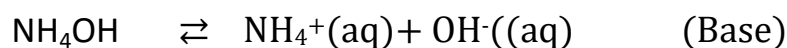
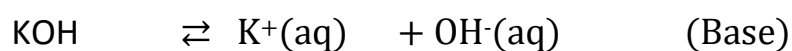
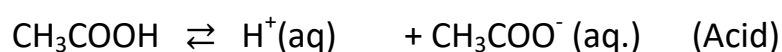
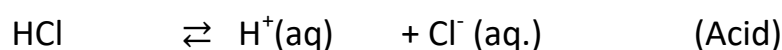
One of the objects of chemistry is to arrange substance into groups which have certain properties in common. Three important groups are acids, bases and salts.

Common acids met in the laboratory are sulphuric, hydrochloric, Nitric acids and caustic soda, caustic potash, ammonia and lime are common examples of bases. The best known salt is common salt, but others such as nitre (or salt peter), Glauber's salt (sodium sulphate) and Epsom salt (magnesium sulphate) are well known. Soda potash and ammonia are examples of alkalis, all alkalis are bases, but there are bases such as lime which are not alkalis.

Chemists have been classifying substances as acids and bases since long. Three hundred years ago Robert Boyle (who gave us the famous gas law that goes by his name) suggested that salts are formed by the reaction of an acid with an alkali (a base). According to Boyle an acid was a compound that possessed many characteristic properties such as (i) sour taste (hence the name from the latin word acidus, (meaning sourness) (ii) changes the colour of certain plant dyes (litmus) to red (iii) liberates gaseous hydrogen from metal and (iv) gets neutralised by an alkali. Similarly, an alkali was defined as a

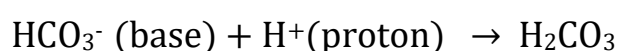
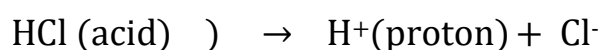
compound which (i) changes litmus to blue (ii) reacts with acids to give salts (iii) has a bitter taste (although one should never taste the chemicals in the laboratory).

As ideas on acids and bases developed ,The French chemist Lavoisier postulated that all acids contain oxygen, this was shown to be not always true (e.g. HCl, HCN). In 1884 Arrhenius suggested that an acid is a substance that produces hydrogen ion in water and that a base is one that produces hydroxyl ions (OH⁻) in water. This is a theory that assumes simple dissociation of these substances



Although this concept of acids and bases is useful in many case, it suffers from many inadequices.

In 1923, a useful modification of the Arrhenius idea came from Bronsted and Lowry, they defined an acid as a substance that yields a hydrogen ion and base is that which accepts proton. Thus neutralization reaction involves donation of the proton by the acid to the base or neutralization is regarded as a proton transfer reaction.

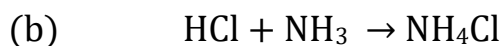
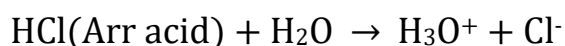


A still more general and fundamental concept of acid- base behaviour was proposed by G.N.LEWIS .in 1923, but his theory got the recognition in 1938. According to Lewis an acid is a substance which can donate a pair of electrons. In other words an acid is an electron pair acceptor while a base is an electron pair donor.

Comparison between Arrhenius ,Lowry Bronsted and Lewis Acid and Bases:

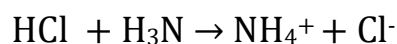
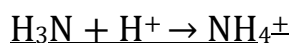
We can compare Arrhenius acid and bases by the following example:





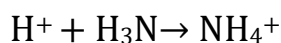
(a) Because HCl gives H_3O^+ ion in water therefore it acts as Arrhenius acid.

(b) The formation of NH_4^+Cl^- takes place through the following steps:



In this reaction HCl after ionisation gives H^+ and Cl^- ion. H^+ ion has an empty orbital and hence accept an electron pair from NH_3 molecule and thus form NH_4^+ ION. The H^+ ion obtain from HCl accept an electron pair and hence act as Lewis acid. This shows that HCl, which acts as a Arrhenius acid also act behaves as Lewis acid.

Bronsted and Lewis bases are the same substance. According to Bronsted concept formation of NH_4^+ ion can be shown as



In the above reaction, NH_3 molecule loses a pair of electron and therefore acts as Lewis base. Thus NH_3 molecule which act as a bronsted base also acts as a Lewis base.

Hard and Soft Acids and Bases:

Arlland, Chatt and Daviers(1958) classified the metal ions and the ligands. Certain ligands tend to form more stable complexes with heavier ions such as Ag^+ , Hg^+ , Pd^{+2} , Pt^{+3} with nearly full d-electrons. Other prefer to form complexes with lighter ions such as Be^{+2} , Al^{+3} , Ti^{+4} with no or lesser no. Of d-electrons. Based on these preferential bonding metal ions as well as ligands have been classified in two categories:

(a) **Hard Acid and Hard Base:** Alkali metal ions, alkaline earth metal ions, light metal ions in higher oxidation states are classified as hard acids. In general. All metal ions and H^+ ions are Lewis acids. These Hard acids have the following properties:

1.) They have small size.

- 2.) They have high polarising power.
- 3.) Their valency electrons are not easily distorted.
- 4.) They are generally associated with high oxidation state.
- 5.) Their electronic configuration is like noble gases.
- 6.) They have high positively charged acceptor ions.

Ligands which prefer to form most stable complexes with light metal ions are classified as hard bases. Hard bases have following characteristics:

- 1.) They coordinate with hard acids.
- 2.) The lower atoms have low polarisability.
- 3.) They have high electronegative donor atoms.
- 4.) These are anions or neutral molecules which are not easily polarisable.

Soft Acids and Soft Bases: Heavier metal ions with nearly full d-orbitals are known as soft bases. These ions have the following characteristics:

- 1.) These are the heavier transition metals of second and third transition series viz Cd^{2+} , Hg^{2+} , Pd^{2+} , Pt^{2+} etc.
- 2.) They have large size.
- 3.) They have low polarising power i.e. their electron charge cloud can be easily distorted.
- 4.) Lower oxidation state viz Ag^+ , Hg^{2+} , Cu^+ etc
- 5.) They do not have noble gas electronic configuration.

Soft bases are those ligands which prefer to form most stable complexes with heavy metal ions, following features are observed in case of soft bases:

- 1.) They contain donor atoms of low electronegativity.
- 2.) These are anions or neutral molecules which are easily polarisable.
- 3.) Soft metal gets easily oxidised.
- 4.) Soft bases are associated with empty low lying in energy orbitals.

From the above classification it is clear that soft acid prefer bonding with soft bases and hard acids prefer bonding with hard acids.

A general classification of some hard and soft acids are presented in Table1 :

Table -1

Examples of Lewis acids are shown in the following table:

Hard	Borderline	Soft
H ⁺ Li ⁺ Na ⁺ K ⁺ Be ²⁺	Fe ²⁺ Co ²⁺ Ni ²⁺	Cu ⁺ Ag ⁺ Au ⁺ Tl ⁺ Hg ⁺
Mg ²⁺ Ca ²⁺ Sr ²⁺ Mn ²⁺	Cu ²⁺ Zn ²⁺ Pb ²⁺	Pd ²⁺ Cd ²⁺ Pt ²⁺ Hg ²⁺
Al ³⁺ Sc ³⁺ Ga ³⁺ In ³⁺ La ³⁺	Sn ²⁺ Sb ³⁺ SO ₂	CH ₃ Hg ⁺ Pt ⁴⁺ Te ⁴⁺ Tl ³⁺
N ³⁺ Cl ³⁺ Gd ³⁺ Lu ³⁺ Cr ³⁺	Ir ³⁺ Bi ³⁺ Rh ³⁺	Tl(CH ₃) ₃ BH ₃ Ga(CH ₃) ₃
Co ³⁺ Fe ³⁺ As ³⁺ CH ₃ Sn ³⁺	NO ⁺ Ru ²⁺ Os ²⁺	GaCl ₃ GaI ₃ InCl ₃
Si ⁴⁺ Ti ⁴⁺ Zr ⁴⁺ Th ⁴⁺ U ⁴⁺	B(CH ₃) ₃ GaH ₃	RS ⁺ RSe ⁺ RTe ⁺
Pu ⁴⁺ Ce ³⁺ Hf ⁴⁺ Sn ⁴⁺	R ₃ C ⁺ C ₆ H ₅ ⁺	I ⁺ Br ⁺ HO ⁺ RO ⁺
UO ²⁺ VO ²⁺ WO ⁴⁺ MnO ³⁺		I ₂ Br ₂ ICN etc.
(CH ₃) ₂ Sn ²⁺ Be(CH ₃) ₂ BF ₃		Trinitrobenzene etc.
B(OR) ₃ Al(CH ₃) ₃ AlCl ₃		Chloranil, Quinones etc.
AlH ₃ RPO ₂ ⁺ SO ₃ RCO ⁺		Tetracyanoethylene etc.
I ⁷⁺ I ⁵⁺ Cl ⁷⁺ Cr ⁶⁺ CO ₂ NC ⁺		O Cl Br I N RO RO ₂
HX (hydrogen bonding molecules)		M ⁰ (metal atoms) Bulk metals
		CH ₂ carbenes

From the above table it is clear that hard acids are cation generally of small size and associated with high oxidation states. Their electronic configuration are such that their electronic charge clouds cannot be distorted.

Soft Acids on the other hand are generally in large size cations with low oxidation state. Their electronic charge clouds can be easily distorted.

A general classification of some common anions into hard and soft are shown in the table2:

Table-2
Classification of Bases

Hard	Soft
$\text{H}_2\text{O}, \text{OH}^-, \text{F}^-$ $\text{CH}_3\text{CO}_2^-, \text{PO}_4^{3-}, \text{SO}_4^{2-}$ $\text{Cl}^-, \text{CO}_3^{2-}, \text{ClO}_4^-, \text{NO}_3^-$ $\text{ROH}, \text{RO}^-, \text{R}_2\text{O}$ $\text{NH}_3, \text{RNH}_2, \text{N}_2\text{H}_4$	$\text{R}_2\text{S}, \text{RSH}, \text{RS}^-$ $\text{I}^-, \text{SCN}^-, \text{S}_2\text{O}_3^{2-}$ $\text{R}_3\text{P}, \text{R}_3\text{As}, (\text{RO})_3\text{P}$ $\text{CN}^-, \text{RNC}, \text{CO}$ $\text{C}_2\text{H}_4, \text{C}_6\text{H}_6$ H^-, R^-
Borderline	
$\text{C}_6\text{H}_5\text{NH}_2, \text{C}_5\text{H}_5\text{N}, \text{N}_3^-, \text{Br}^-, \text{NO}_2^-, \text{SO}_3^{2-}, \text{N}_2$	

To sum up Hard acids and Lewis acids which are small in size and whose electron clouds have low polarizability. These are generally high metal ions associated with high positive oxidation state.

Soft acids are Lewis acids which are comparatively larger in size and whose electron clouds are easily polarisable. These are mostly heavy metal ions associated with low positive oxidation state.

Hard Bases: are lewis bases which prefer to coordinate with hard acids. The donor atom in these bases is of high electro negativity and low polarizability.

Soft Bases: are lewis bases which prefer to coordinate with soft acids. These contains less electronegative non-metals. These are anions or neutral molecules which are easily polarisable.

Just as there are border lines acids, there are borderlines bases also . The properties of border lines bases are in between those of the soft and hard bases. It is important to note that the categories are not rigidly divided for example the halide ions form a series from the very hard ions through the hard borderline chloride ion to the borderline bromide ion and the soft iodide ion.

PEARSONS HSAB PRINCIPLE AND ITS APPLICATIONS

1965- Ralph Pearson introduced the hard-soft-acid-base (HSAB) principle. "Hard acids prefer to coordinate the hard bases and soft acids to soft bases" This very simple concept was used by Pearson to rationalize a variety of chemical information. 1983 – the qualitative definition of HSAB was converted to a quantitative one by using the idea of polarizability. A less polarizable atom or ion is "hard" and a more easily polarized atom or ion is "soft". This principle does not state, that hard soft or soft hard combination cannot exist. It only states that if there is a choice, a hard-hard and soft-soft combination to be preferred to a soft-hard or hard-soft combination.

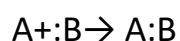
It is important to note that hardness and softness of acids and bases refer only to hard-hard and soft-soft interactions. It is by no mean related to the strength of acids and bases. For example Both F^- and OH^- ions are hard but the basic strength of OH^- ions is 10^3 times that of F^- ions.

APPLICATIONS OF HSAB PRINCIPLE:

This principle has a several application, some of which are discussed below:

1.)Stability of the complexes:

On the basis of HSAB Principle Pearson (1963) explained the relativity stability of complex . Lets consider the complex AB it is formed as follows :



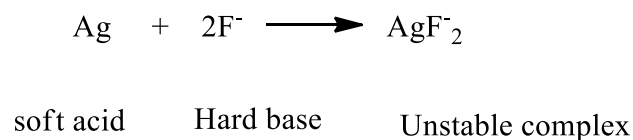
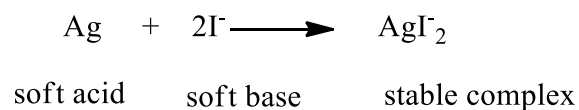
THE complex AB would be more stable if A and B are either both hard or both soft .

The complex would be stable if A is hard B is soft or vice versa . For example, while AgI_2^- exist as a stable compound , AgF_2^- does not. This can be explained as Ag^+ ion is soft acid and I^- are soft base. Their interaction yield soft complex AgI_2^- where as the interaction of F^- ion hard base with Ag^+ soft acid yields an unstable complex AgF_2^-

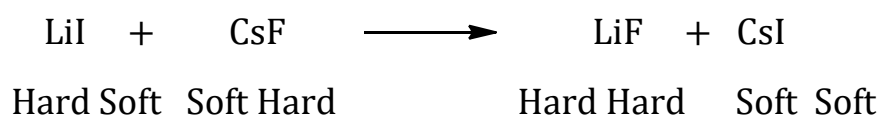
2.) **Occurrence of minerals:** The natural occurrence of ores can also be explained by HSAB Principle. Hard acid metal ion such as Ca^{+2} , Mg^{+2} , Al^{+3} , Fe^{+3} etc frequently occur in nature as their oxides chloride fluorides and carbonates e.g. CaCO_3 , MgCO_3 etc. These metals ions do not occur in nature as their sulphides since S^{-2} is a soft base while soft acids Cu^+ , Ag^+ and Hg^{+2} etc occur in variably in ores as their sulphides due to soft acids-soft base interactions. On the other hand borderline metal ions like Co^{+2} , Ni^{+2} , Pb^{+2} , etc can occur both as sulphides as well as their oxides or carbonates as a result of their intermediate character.

3.) **Prediction of Coordination in complexes of Ambidant Ligand:**

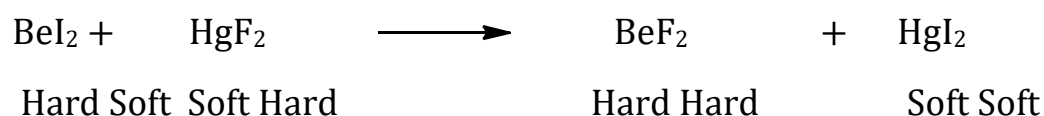
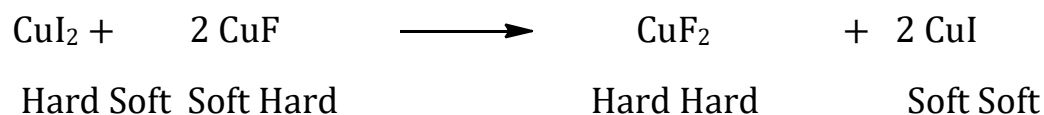
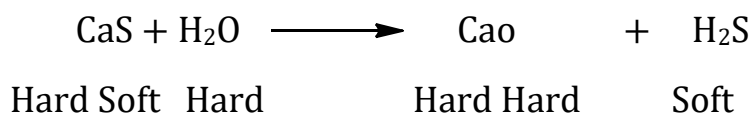
With the help of HSAB Principle we can predict the formation of various metal ion complexes with ambidant ligand. Ambidant ligand is one which although amidentate, may coordinate to the metal ion through either of its two coordinating atoms. For example $[\text{SCN}^-]$ is an ambidant ligand it coordinate through S atom to form the complex as it coordinate through N atom to form the complex $[\text{Co}(\text{NCS})_4]^{-2}$. The reason for the absence is Pd^{+2} is a soft acid so that it prefers to coordinate through the soft atom to form Pd-SCN linkage. Co^{+2} is a hard acid so that it prefers to coordinate through the harder N atom to form the Co-NCS linkage.



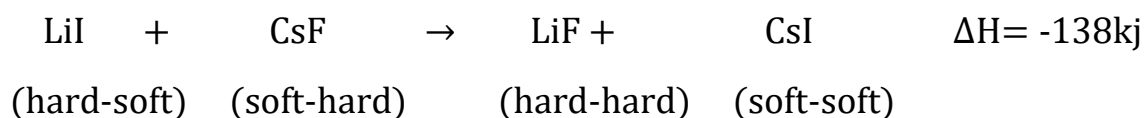
The reaction between LiI and CsF resulting in the formation of LiF and CsI is also an interesting example of HSAB



Other examples which suggest the stability of the Soft-Soft and Hard-Hard interaction are given below:-

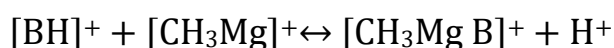


4.) **Predicting Feasibility of a reaction:** The reaction between LiI and CsF to give LiF and CsI is an interesting example of preferential combination of soft –soft and hard – hard species.



Jorgenser has suggested a complex compound will be stable if all the ligands are of the same nature. The complex formed will be unstable. With this, it is easy to understand why the complexes $[\text{Co}(\text{CN})_5\text{F}]^3$ are unstable. It may be recalled that CN^- and I^- are both soft bases while NH_3 and F^- are both hard bases.

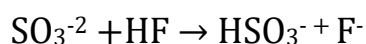
5.) **To find hardness and softness:** to predict hardness and softness of the base B in the following reaction :



If equilibrium shifts towards the right, then B is a soft base because it shows more affinity for the soft acid $[\text{CH}_3\text{Mg B}]^+$ (soft-soft interaction). If the equilibrium shift towards the left, then it is a hard base since it exhibits more affinity for the hard acid H^+ (hard-hard interaction).

6.) **Solubility of Compounds:** According to Pearson, the compounds formed by hard acid and base or soft acid or soft base are more stable. Thus these compounds will be less soluble e.g. HgS (soft acid-soft base) is more stable than $\text{Hg}(\text{OH})_2$ (soft acid+ hard base) hence $\text{Hg}(\text{OH})_2$ dissolves readily in acidic aqueous solution but HgS does not.

7.) **Limitation of HSAB Principle:** Although (Hard+hard) and (soft+soft) combinations is a useful principle, yet many reactions can not be explained with the help of this principle e.g. in the reaction:

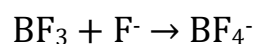


which proceeds towards right, Hard acid (H^+) combine with soft or border line base (SO_3^{2-}) to form $[\text{H}^+][\text{SO}_3^{2-}]$ which is a stable ion [hard acid+ soft base].

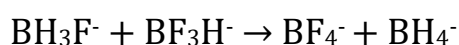
Combination is against the HSAB Principle.

Symbiosis

Jorgensen 1968 observed that the soft ligand have a tendency to combine with a centre already associated with soft ligand and hard ligands have a tendency to combine with a centre already associated with hard ligands. He termed this tendency as Symbiosis. Thus F^- ion had a ligand, readily combine with BF_3 to form a stable complex BF_4^- . Since H^+ ion a soft ligand, readily combines with BH_3 to form a stable complex BF_3H^- BH_4^- :



Mixed substituents are generally not preferred. Thus, compound such as BF_3H^- and BH_3F^- having mixed substituents, interact spontaneously with same substituents



THEORITICAL BASIS OF HARDNESS AND SOFTNESS:

Since hard acids generally have vacant d-orbitals, they can accept electrons from hard bases, so that the bonding between the hard acids and hard bases is predominantly ionic. Interaction between soft acid and soft bases occurs mostly through π bonding so that the bonding between the soft acids and soft bases is largely covalent.

Several views have been put for it to explain the basis of Hard-Hard and Soft-Soft interaction. However, no single view is completely satisfactory. Some of the important theories are as under:

Electrostatic interaction theory:

The electrostatic energy between a positive and negative ion pair is inversely propotional to the inter nuclear distance, therefore smaller the ions the lesser would be the electrostatic attraction between the two ions, consequently, the resulting compound would be highly stable. According to this theory, hard acids and hard bases form purely ionic or electrostatic compounds most of the hard acids such as Li^+ , Na^+ , K^+ etc and hard bases such as O^{2-} , F^- etc are well known to form ionic compounds.

π Bonding Theory:

J.Chatt suggested that electrostatic interactions can not explain the soft – soft interaction because the size of soft species are comparatively very large. The soft acids have loosely held outer d-electrons which can form π bonds by donating to suitable ligands such ligands have empty d-orbitals on the basis atom like P, As, S,I etc. The presence of d-orbitals on the ligands helps to strengthen the π bnding.

Polarisation of the species, also play an important role in explaining their interactions. As already discussed most of the soft acids have 6-10 d-electrons in their electronic configuration. These electrons get easily polarised favouring covalent bonding between them and in the soft bases which are easily polarisable. Thus bonding between soft acids and soft bases is assumed to be largely covalent.

Catalytic poisoning:

Soft metals (e.g. Pd, Pt, v, Cr, Mo, etc) are soft acids and are well known as catalysts. These metal catalyst have been found to be easily poisoned by soft bases, viz. Co unsaturated hydrocarbons (olefins, alkynes, dienes). This is because soft acid- soft base interactions between the metal ions and ligands form the stable complexes and block the activities of catalyst. In other words, the metal atoms lose their activities are said to be poisoned. Thus, soft bases complex with the metals, in atomic state well act as poisoning towards metal catalysts.

Acid and Base Strength of HSAB :

Considering hard-hard interaction as ionic and soft-soft interactions as covalent, Mison and Co-workers (1967) proposed the following relation which can tell whether a given species is hard or soft:

$$PK = -\log K = aX + bY + c$$

Where K is equilibrium constant for the dissociation of the metal-ligand (i.e. acid-bases, complexes are parameters for the metal ions, i.e. acids: a, b are parameters of the ligands i.e. base and C is a constant required to adjust the PK value in such a way that all of these lie on the same scale.

The value of Y parameters for some of the cations are given below :

HARD ACIDS: (Li⁺³ , Al⁺³ , Mg⁺², Na⁺, Ca⁺², Fe⁺², Co⁺², Cs⁺)
(0.36 0.70 0.87 0.93 1.62 2.37 2.56 2.73)

SOFT ACIDS: (Sn⁺² , Tl⁺³, Cu⁺, Pb⁺², Ti⁺, Hg⁺², Au⁺)
(3.17, 3.2, 3.45, 3.58, 3.78, 4.25, 5.95)

If the value is less than 2.8, the acid is hard and if it is more than 3.10 then acid is soft.

The value of b parameters for some of the bases are as under:

OH ⁻	NH ₂	Cl ⁻	Br ⁻	I ⁻	SO ₃ ⁻²
0.40	1.08	2.49	5.58	7.17	12.4
(HARD BASES)			(SOFT BASES)		

From the above data it is clear as the value of b increases softness of the base increases. If this value is less than 3, the base is hard and if it is more than 5 the base is soft.

Electronegativity and Hardness and Softness

Electronegativity value of any species affect the hardness or softness. In brief, highly electronegative species are hard acids and lower electronegative species are soft acids e.g. Li⁺, Na⁺, etc. (highly electronegative ions) are hard acids while transition metal ions like Cu⁺, Ag⁺ etc (low electronegative ions) are soft acids.

If we arrange the donor atoms of the most common lewis bases in an increasing order of their electronegativity value we get:

Donor atom : As, P < C, Se, S, I < Br < N, Cl < O < F

Electronegativity: 2.0, 2.1 < 2.5, 2.4, 2.5, 2.5 < 2.8 < 3.0, 3.0 < 3.5 < 4.0

Soft Lewis acids form metal stable complexes with left hand members of the above series while right hand lewis acids do so with right hand

members. Comparison between acids and bases as defined by Arrhenius,

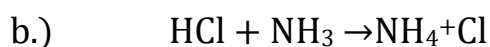
Lowry- Bronsted and Lewis:

1.) Arrhenius acid is a compound that gives H⁺ or H₃O⁺ ions in water and Arrhenius base is compound that furnishes OH⁻ ions in water.

2.) Bronsted acid is a molecule or an ion that can donate one or more protons (H⁺) i.e. Bronsted acid is proton donor. Bronsted acid is a molecule or ion that can accept one or more protons i.e. Base is a proton acceptor.

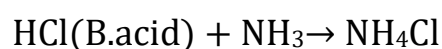
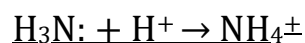
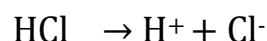
3.) Lewis acid is a molecule or an ion that can accept one or more electron pair and lewis base is molecule or an ion that can donate one or more electron pair i.e. lewis base is and electron pair donor.

4.) Arrhenius acids and lewis acids are the same substance i.e. this can be seen as under:



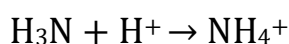
a.) HCl gives H_3O^+ ion in water, it acts as Arrhenius acid in this reaction.

b.) The formation of NH_4^+Cl takes place through the following step:



In this reaction HCl after ionisation gives H^+ and Cl^- ions. H^+ has an empty orbital and hence accept an electron pair from NH_3 and thus form NH_4^+ ion. Thus H^+ ions obtained from HCl accepts an electron pair and hence acts as an lewis acis. This shows that HCl, which acts as Arrhenius acids also behaves as lewis acid.

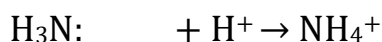
5.) Bronsted Bases and lewis bases are the same substances according to Bronsted concept formation of NH_4^+ ions can be sown as:



(B.base)

In this reaction NH_3 accepts proton (H^+) to form NH_4^+ ions. and act as Bronsted base.

According to Lewis concept the combination of H^+ ions and NH_3 ions takes place as:



(Lewis base)

Hence NH_3 molecule loses one electron pair and hence act as a lewis base. Thus, NH_3 which acts as a bronsted base, also acts as a lewis base.

- Q.1 What is HSAB principle? Discuss some application of this principle.
- Q.2 What do you mean by Symbiosis? Explain with example.
- Q.3 Explain the following on the basis of HSAB principle.
- Reaction between CdSO_4 and Na_2S .
 - AgI_2^- is more stable than silver fluoride ion.
 - Aluminium occurs as sulphide and not as carbonate.
 - Lead occurs both as carbonate and sulphide.
- Q.4 what is the Pearsons HSAB concept? Explain with suitable example.
- Q.5 Classify the following into hard, soft and borderline acid and bases:
 $\text{I}, \text{K}, \text{Cu}, \text{Li}, \text{Ti}, \text{Pd}, \text{Ag}, \text{Ni}, \text{NH}_3, \text{HCl}, \text{CO}, \text{CO}_2$.
- Q.6 What are the theoretical justification of HSAB principle?
- Q.7 On the basis of HSAB explain why $[\text{CoF}_6]^{3-}$ is more stable than $[\text{CoI}_6]^{3-}$.
- Q.8 Explain the stability of minerals obtained in nature and the stability of complexes on the basis of Hard and soft acid base principle.