Comprehensive Questions
Part II

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Dear Students,

Comprehensive questions constitute an essential segment of the Chemistry paper, carrying a weightage of 24 marks. Many available textbooks either offer excessively concise answers or include supplementary content not found in the textbook.

In the *Comprehensive Questions Part II*, an endeavor has been made to elucidate the approach for tackling lengthy questions. A compilation of significant long-form questions from past papers is provided. This compilation aims to furnish students with a clear perspective on the most probable long questions expected to come in the final exams. While this book covers the major segments of long questions which have been seen repeatedly in past papers, it is encouraged that students utilize it as a reference to devise their own headings and subheadings for any sections not included herein.

The organic section is not majorly covered as the answers of these questions are quite clear i.e. only equations are needed as answer to questions. Students find theoretical questions challenging to attempt so exclusively that portion is covered in this book.

Wishing you all the best for success in your examinations!

God Bless.

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Ch 1

Periodic Classification of Elements and Periodicity

Defects and Improvements in Mendeleev’s Periodic Table

Defects in Mendeleev’s periodic table

Following are the defects in Mendeleev’s periodic table:

1. Arrangement of elements according to atomic masses

Mendeleev arranged elements in the periodic table in increasing order of their atomic masses.

Mendeleev’s periodic law stated: “If elements are arranged in ascending order of their atomic masses, their chemical properties repeat in a periodic manner”

2. Position of noble gases

The group of noble gases (VIII A) was not in Mendeleev’s periodic table as these gases were not discovered at that time.

3. Wrong position of elements

Elements like Be, Mg, Ca, Sr, Ba and Zn, Cd, Hg were placed in a single vertical group, while according to their properties they belonged to two different categories. The same was true for so many other elements placed in the same vertical group.

Improvements in Mendeleev’s periodic table

In order to make the periodic table more useful and accurate a few improvements were made in Mendeleev’s periodic table:

1. Arrangement of elements according to atomic number

After the discovery of atomic number by Moseley in 1911, it was noticed that elements could be classified more satisfactorily by using their atomic numbers, rather than their atomic masses.

The modern Periodic Law states that: “if the elements are arranged in ascending order of their atomic numbers, their chemical properties repeat in a periodic manner”

2. Position of noble gases

Another improvement was the addition of an extra group (group VIIIA) at the extreme right of the periodic table. This group contains noble gases, which had not been discovered in Mendeleev’s time.

Correct position of elements

In modern periodic table, the confusion of placement of elements was removed by dividing the elements in two types of vertical groups, A and B. In modern periodic table, Be, Mg, Ca, Sr and Ba are placed in group IIA and Zn, Cd, Hg in group IIB.

Groups and Periods

Groups

Definition

Elements with similar properties are placed in vertical columns called Groups. There are eight groups which are usually numbered by Roman numerals I to VIII.

Group I (Alkali metals): Li (3), Na (11), K (19), Rb (37), Cs (55), Fr (87)

Group II (Alkaline Earth metals): Be (4), Mg (12), Ca (20), Sr (38), Ba (56), Ra (88)

Group III (Boron family): B (5), Al (13), Ga (31), In (49), Tl (81)

Group IV (Carbon family): C (6), Si (14), Ge (32), Sn (50), Pb (82)

Group V (Nitrogen family): N (7), P (15), As (33), Sb (51), Bi (83)

Group VI (Oxygen family): O (8), S (16), Se (34), Te (52), Po (84)

Group VII (Halogens): F (9), Cl (17), Br (35), I (53), At (85)

Group VIII (Noble gases): He (2), Ne (10), Ar (18), Kr (36), Xe (54), Rn (86)

Transition elements are present between group II and group III.

Each group is divided into two subgroups, designated as A and B subgroups.

Subgroup A

The subgroups, containing the representative or normal elements are labeled as A subgroups

Subgroup B

B subgroups contain less typical elements, called transition elements, and are arranged in the centre of the periodic table.

Periods

Definition

The horizontal rows of the periodic table are called Periods. There are seven periods in the periodic table numbered by Arabic numerals I to VII.

Shortest period

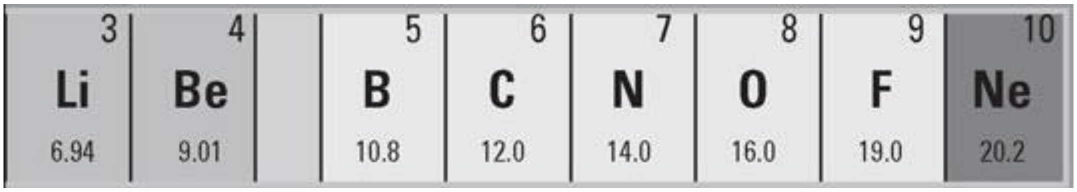
The period 1 contains only two elements, hydrogen (H) and helium (He).

Short periods

The periods 2 and 3 contain eight elements each and are called short periods.

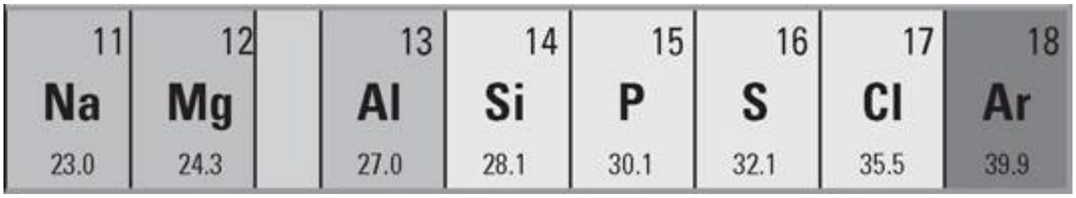
1. All the elements in these periods are representative elements and belong to A subgroup.
2. Every eighth element resembles in properties with the first element.
3. Lithium and beryllium in the 2nd period resemble in most of their properties with sodium and magnesium of the 3rd period, respectively.
4. Boron and aluminium both show oxidation state of +3, fluorine in 2nd period has close resemblances with chlorine of 3rd period.

Members of 2nd period



3	4		5	6	7	8	9	10
Li	Be		B	C	N	O	F	Ne
6.94	9.01		10.8	12.0	14.0	16.0	19.0	20.2

Members of 3rd period



11	12		13	14	15	16	17	18
Na	Mg		Al	Si	P	S	Cl	Ar
23.0	24.3		27.0	28.1	30.1	32.1	35.5	39.9

Long periods

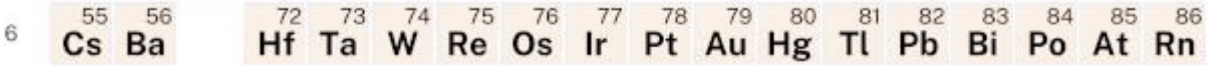
The periods 4 and 5 are called long periods.

1. Each long period consists of eighteen elements.
2. Eight are representative elements belonging to A subgroup similar to second and third periods.
3. The other ten elements, placed in the centre of the table, belong to B subgroups and are known as transition elements.
4. In these periods, the repetition of properties among the elements occurs after 18 elements. As after $_{19}$K (having atomic number 19) the next element with similar properties is $_{37}$Rb.

4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe

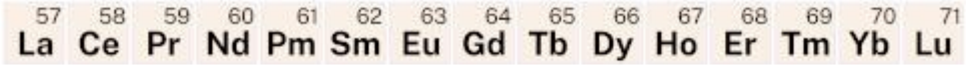
The period 6 is also a long period, which contains thirty-two elements.

1. There are eight representative elements, ten transition elements and a new set of fourteen elements called Lanthanides as they start after $_{57}$La.
2. Lanthanides have remarkably similar properties and are usually shown separately at the bottom of the periodic table.



6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn

Lanthanides



57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

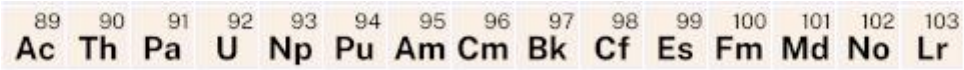
Incomplete Period

The period 7 is incomplete so far.

1. It contains only two normal elements $_{87}$Fr and $_{88}$Ra, ten transition elements and fourteen inner transition elements.
2. The inner transition elements of this period are called Actinides, as they follow $_{89}$Ac.
3. The actinides are also shown at the bottom of the periodic table under the Lanthanides.
4. Due to their scarcity, the inner transition elements are also called rare earth elements.

7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt

Actinides



89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

<u>Periodic Trends</u>

Atomic Size

a. Atomic radius

Definition

Half of the distance between the centres of two bonded atoms of any element is the radius of the atom.

Trend of atomic radius

Down the group

The atomic radius increases from top to bottom within a group. Reasons are:

i. Increase in atomic number.

ii. Increase in shielding effect due to the addition of an extra shell of electrons in each group. As the shielding effect increases the distance between the nucleus and the outer shell electrons increases and the atomic size increases.

iii. Effective nuclear charge decreases so atomic size increases.

Along the period

The atomic size decreases from left to right along the period. Reasons are:

i. The atomic number increases from left to right.

ii. Shielding effect remains constant. The distance between the nucleus and outer shell electrons decreases as with the increase of atomic number the outer shell electrons are pulled closer to the nucleus.

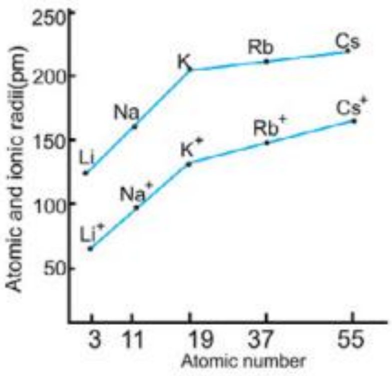
iii. Effective nuclear charge increases.

Lanthanide contraction

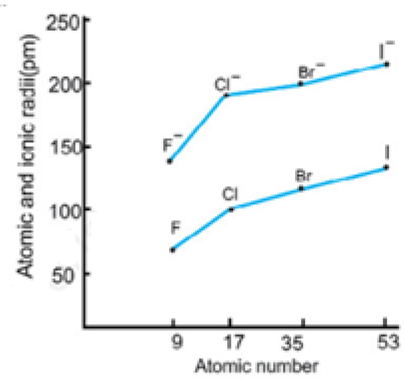
The gradual reduction in the size of lanthanides due to the poor shielding effect of “d” and “f” sub-shells is called Lanthanide contraction.

b. Ionic radius

1. In a group of the periodic table, similar charged ions increase in size from top to bottom.
2. Isoelectronic positive ions show a decrease in ionic radius from left to right because of the increasing nuclear charge.
3. Isoelectronic negative ions of a period decrease in size from left to right.



Atomic and ionic radii of alkali metals



Atomic and ionic radii of halogens

Ionization energy

Definition

The ionization energy of an element is the minimum quantity of energy which is required to remove an electron from the outermost shell of its isolated gaseous atom in its ground state. The ionization energy of sodium is 496 kJ mol^{-1}.

$$\text{Na (g)} \longrightarrow \text{Na}^{+}\text{ (g)} + e^{-} \qquad \Delta H_{i}=496\ \text{kJ/mol}$$

More than one I.E. values

Elements with greater number of electrons have more than one values of ionization energy.

Example

1st I.E. value

For magnesium the first ionization energy value is the energy required to remove the first electron:

$$\text{Mg (g)} \longrightarrow \text{Mg}^{+}\text{ (g)} + e^{-} \qquad \Delta H_{i}=738\ \text{kJ/mol}$$

2nd I.E. value

The second ionization energy value is the energy required to remove the second electron.

$$\text{Mg}^{+}\text{ (g)} \longrightarrow \text{Mg}^{++} + e^{-} \qquad \Delta \text{Hi}=1451\ \text{kJ/mol}$$

Factors affecting ionization energy

The factors upon which the ionization energy of an atom mainly depends are:

i. Magnitude of nuclear charge

ii. Size of the atom

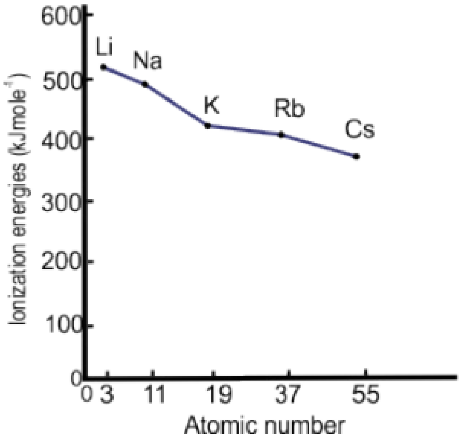
iii. Shielding effect.

Variation within a group

Going down in a group, the effective nuclear charge decreases, shielding effect increases and size of atom increases, therefore, outer shell electrons are held with lesser force with the nucleus. Ionization energy decreases from top to bottom.

Example

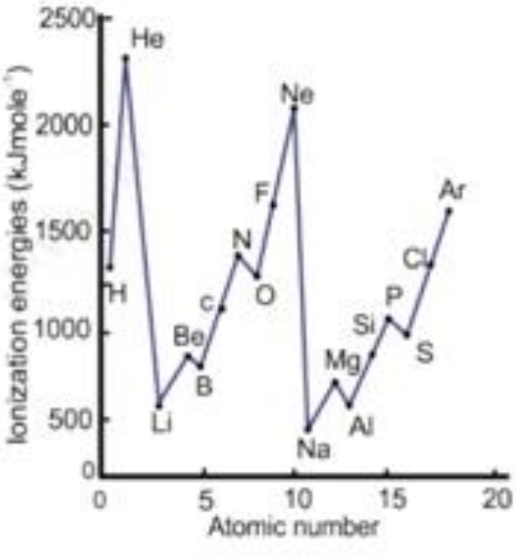
In alkali metals it is easier to remove an electron from caesium atom than from lithium atom.



Ionization energies of alkali metals

Variation across a period

Across a period effective nuclear charge increases, shielding effect remains constant and size of atom decreases. Therefore, there is greater force of attraction between nucleus and outer shell electrons. Ionization energy increases along a period.



Ionization energies of elements of short periods

Ionization energy of inert gases

Inert gases have the highest values of ionization energy because due to complete outermost shell in them, the removal of electron is extremely difficult.

Electron Affinity

Definition

The electron affinity is the energy released or absorbed, when an electron is added to a gaseous atom to form a negative ion.

$$F\,(g) + e^- \longrightarrow F^-\,(g) \qquad E.A = -337\ \text{kJ/mol}$$

First and second electron affinity (E.A.) values

Energy is usually released when electronegative elements absorb the first electron and E.A. in such cases is expressed in negative figures, as in the case of halogens. When a second electron is added to a uni-negative ion, the incoming electron is repelled by the already present negative charge and energy is absorbed in this process.

$$O\,(g) + e^- \longrightarrow O^-\,(g) \qquad E.A_1 = -141\ \text{kJ/mol}$$

$$O^-\,(g) + e^- \longrightarrow O^{2-}\,(g) \qquad E.A_2 = +780\ \text{kJ/mol}$$

Factors affecting electron affinity

Following are the factors affecting electron affinity:

i. Size of the atom

ii. Nuclear charge

iii. Vacancies in the outermost shell.

Relatively smaller atoms with one or two vacancies in the outermost shell show large values of electron affinity.

Variation across period

Electron affinity increases across period because effective nuclear charge increases, shielding effect remains constant and size of atom decreases. Therefore, electrons are held closer to the nucleus.

Variation down the group

Going down in a group, the effective nuclear charge decreases, shielding effect increases and size of atom increases, therefore, outer shell electrons are held with lesser force with the nucleus. Electron affinity decreases from top to bottom.

Metallic and Non-Metallic Character

Metals

Definition

All the elements which have a tendency to form positive ions by losing electrons are considered metals.

Properties

1. All metals are good conductor of heat and electricity.
2. They form basic oxides which give bases when dissolved in water.

$$Na_2O\,(s) + H_2O\,(l) \longrightarrow 2NaOH\,(aq)$$

Periodic trend

1. Metallic character increases from top to bottom in a group as the size of atom increases.
2. Metallic character decreases from left to right in a period as the size of atom decreases. Halogens are least metallic

Non-metals

The elements which gain electrons and form negative ions are called non-metals.

Properties

1. All the gases are non-metals.
2. Poor conductor of heat and electricity.
3. Non-metals form acidic oxides which yield acids on dissolving in water.

$$SO_3\,(g) + H_2O\,(l) \longrightarrow 2H_2SO_4\,(aq)$$

Periodic trend

1. Non-metallic character decreases from top to bottom in a group as the atomic size increases.
   For example,
   In halogens fluorine is the most non-metallic element being the first member. In group VA nitrogen is the most non-metallic and in gaseous state as compared to bismuth which is fairly metallic. In group VIA oxygen is the most non-metallic and in gaseous state compared to polonium which is fairly metallic.
2. Non-metallic character increases from left to right in a period as the atomic size decreases.

Melting and Boiling Points

Melting and boiling points tell about the strength of forces holding atoms or molecules together.

Variation along period

Short periods

1. The melting and boiling points of elements increase with the number of valence electrons up to group IVA and then decrease up to the noble gases.
2. Carbon has the maximum number of binding electrons, thus, it has a very high melting point in diamond in which each carbon is bound to four other carbon atoms.
3. The elements which exist as giant covalent structures have very high melting points.
4. In group IVA, VA, VIA and VIIA the lighter elements of these group exist as small, covalent molecules rather than as three dimensional lattices.
For example,
Nitrogen, oxygen and fluorine exist as individual molecules which have very weak intermolecular forces between them. Their melting and boiling points are extremely low.

IA and IIA

1. The melting points of group IA elements are low because each atom in them provides only one electron to form a bond with other atom.
2. Melting points of group IIA elements are considerably higher than those of group IA elements because each atom in them provides two binding electrons.

Variation in a group

IA and IIA members

1. The melting and boiling points of IA and IIA group elements decrease from top to bottom due to the increase in their atomic sizes.

2. The binding forces present between large sized atoms are relatively weaker as compared to those between smaller atoms.

VIIA members

3. For elements of group VIIA, which exist in the form of molecules, the melting and boiling points increase down the group. Large molecules exert stronger force of attraction due to their higher polarizabilities.

Oxidation State

Definition

The oxidation state of an atom in a compound is defined as the charge (with the sign) which it would carry in the compound.

Oxidation state in ionic compounds

1. In ionic compounds, it is usually the number of electrons gained or lost by the atom.
2. As in the case of sodium chloride, the oxidation states of sodium and chlorine are + 1 and -1, respectively.

Oxidation state in covalent compounds

1. In covalent compounds, oxidation state is based on the difference in their relative electronegativities.
2. For example, $SnCl_4$ is a covalent compound. The oxidation state of tin is + 4 and that of chlorine is -1.

Oxidation state in the free state of elements

The oxidation state of an element is zero in its free state.

Oxidation state and group number

1. The oxidation state of a typical element is directly or indirectly related to the group number to which the element belongs in the periodic table.

   IA to IVA elements
2. The elements of group IA to IVA have the same oxidation states as their group numbers are. It tells about the number of valence electrons.
   For example,
   B, Al and Ga belong to group IIIA, hence, they always show oxidation state of +3.
   VA elements
3. For the elements of group VA, the oxidation states are either the number of electrons present in the valence shell or the number of vacancies available in these shells.
4. N, P, As and Sb frequently show +3 as well as +5 oxidation states.
   VIA elements
5. Elements of group VIA show almost similar behaviour.
   For example,
   In H_2SO_4, sulphur shows the oxidation state of +6, which is the number of electrons in its outermost shell, whereas, its oxidation state is -2 in H_2S, which is the number of vacancies in the shell.
   VIIA elements
6. In group VIIA elements oxidation state is mostly - 1, which is again the number of vacancies in their outermost shells.
   VIIIA elements
7. Group VIIIA elements, which are also called zero group elements, usually show zero oxidation state because there is no vacancy in their outermost shells.
   Transition elements
8. Transition elements also show the oxidation states equal to their group number.
   For example,

Cu(I), Zn(II), V(V), Cr(VI) and Mn (VII).
Due to greater number of valence electrons available in partly filled d-orbitals these elements usually show more than one oxidation states in their compounds.

Electrical Conductance

Electrical conductance of IA and IIA

The electrical conductance of metals in groups IA and IIA, generally increases from top to bottom.

Electrical conductance of IB

Metals of group IB, which are known as coinage metals, have extraordinary high values of electrical conductance.

Electrical conductance of VIA and VIIA

Groups VIA and VIIA show such low electrical conductance that they can be considered as nonconductors.

Electrical conduction of group IVA

1. Carbon, in the form of diamond is non-conductor because all of its valencies are complete.
2. In the form of graphite, carbon is fairly good conductor because one of its four valence electrons is relatively free to move.
3. The lower elements of group IVA, tin and lead, are fairly good conductors and their values of electrical conductivity are comparable with IA.

Electrical conduction of transition metals

In the series of transition metals, the values of electrical conductance vary so abruptly that no general trend can be assigned to them.

Hydration Energy

Definition

The hydration energy is the heat absorbed or evolved when one mole of gaseous ions dissolve in water to give an infinitely dilute solution.

$$H^+ (g) + H_2O (l) \longrightarrow H_3O^+ (aq) \qquad \Delta H_h = -1075 \text{ kJ/mol}$$

Factor affecting hydration energy

Hydration energies highly depend upon charge to size ratio of the ions.

1. For example for group IA, charge to size ratio decreases from top to bottom in a group, the hydration energy also decreases in the same fashion.
2. The hydration energy increases significantly by moving from left to right in a period as the charge to size ratio increases, as found in the metal ions of third period.

Halides

Definition: The binary compounds of halogens with other elements are called halides.
Classification: On the basis of type of bonding there are three types of halides:

1) Ionic halides

2) Polymeric halides
3) Covalent halides

1) Ionic halides: Halides having ionic bond in them are called ionic halides. The metals of the group IA and IIA form ionic halides.

Properties of Ionic halides:

- They are hard crystalline solids.
- They have high melting and boiling points.
- Exist as 3-D crystal lattice structures.
- Fluorides have the highest lattice energies due to small size of fluoride ion.
- Soluble in water.
- Order of melting and boiling points are:
  Fluorides>Chlorides>Bromides>Iodides.

2) Polymeric halides: Those halides which have polymeric structure and have partial ionic bonding with layer or chain lattice. Less electropositive elements like Be, Ga and Al form polymeric halides. The properties of these halides are intermediate between ionic and covalent halides.

3) Covalent halides: Halides having covalent bonds are called covalent halides. Elements of group IVA, VA and VIA give covalent halides.

Properties of covalent halides:

- They are mostly water soluble but less than ionic halides.
- Some of these are gases, some are liquids and majority solids.
- Their melting and boiling points are less than ionic halides.
- Their physical properties are greatly influenced by size and polarizability.
- Iodides have largest size and greater polarizability, hence, higher melting and boiling points.

Trends in a Period: When we move from left to right in a period the percentage of covalent character increases and ionic character decreases.

Trends in a Group: The percentage of ionic character increases down the group and covalent character decreases.

Hydrides

Definition: The binary compounds of hydrogen with other elements are called hydrides.

Classification of hydrides: According to the nature of bonding hydrides may be classified into three classes:

1) Ionic hydrides
2) Covalent hydrides
3) Intermediate hydrides

1) Ionic hydrides: They have ionic bonds in them. These are the hydrides of alkali and alkaline earth metals, except, Be and Mg.

Properties:

- They are white crystalline solids.
- They have high melting and boiling points.
- Conduct electricity in molten state.

2) Covalent hydrides: These hydrides have covalent bonds in them. Elements of group IIIA to VIIA give covalent hydrides.

Properties:

- Usually exist as gases or volatile liquids.
- They are non-conductors.
- Dissolve in organic solvents.
- Their bond energy depends on size and electronegativity of the element.
- Have low melting and boiling points.

3) Intermediate Hydrides: Hydrides of Be and Mg represent the class of intermediate or polymeric hydrides. Their properties are in between the ionic and covalent hydrides. They have polymeric structures and covalent nature.

Trends in the periodic table

Along the period: When we move from left to right the covalent character of the hydrides increases.

Down the group: The ionic character of the hydrides increases down the group.

Oxides

Definition: Binary compounds of oxygen with other elements are called oxides.

Classification: On the basis of their acidic and basic nature they can be classified into three types:

i) Basic oxides
ii) Acidic oxides
iii) Amphoteric oxides

i) Basic Oxides:

- Those oxides which yield bases in water are called basic oxides. These are usually metal oxides.
- The elements of IA and IIA groups except Be form basic oxides.
- They contain O^{2-} ions which have high affinity for proton (H^+) from water, thus, combine with proton and form OH^- ions.

ii) Acidic Oxides:

- Those oxides which when dissolved in water give the acidic solution.
- Oxides of non-metallic elements such as C, N, P and S are acidic in nature.

iii) Amphoteric Oxides:

- Those oxides which have acidic and basic character both are called amphoteric oxides.
- These Oxides:

  Behave as **acids** towards strong **bases**.

  And act as **bases** towards strong **acids**.

- Oxides of relatively less electropositive elements such as BeO, Al_2O_3, Bi_2O_3 and ZnO are amphoteric.

E.g.: $ZnO + H_2SO_4 \Longrightarrow ZnSO_4 + H_2O$

$ZnO + 2NaOH + H_2O \Longrightarrow Na_2[Zn(OH)_4]$

Trends in the Periodic Table

Periods: When we move from left to right in a period the oxides become more and more acidic in nature.

Groups: Down the group increase in basic character of oxides is observed.

The Position of Hydrogen

Position of hydrogen is still undecided because it shows similarities as well as dissimilarities with some groups in the periodic table. Details of it are given below:

Similarities with group IA

1. Like alkali metals hydrogen atom has one electron in Is sub-shell, which it can lose to form H^+.
2. Both hydrogen and alkali metals have a strong tendency to combine with electronegative elements such as halogens.
3. Similar to alkali metals hydrogen also forms ionic compounds, which dissociate in water.

Dissimilarities from group IA

1. Hydrogen is a non-metal in true sense. It does not lose electron as easily as most of the alkali metals do.
2. Unlike alkali metals molecular hydrogen exists in open atmosphere.

Similarities with group VIIA

1. Hydrogen is a gas like most of the halogens and is stable in diatomic form such as F_2, Cl_2 and Br_2.
2. As required by halogens, hydrogen also needs one electron to complete its outermost shell. By accepting one electron hydrogen forms H^- (Hydride ion) similar to F^-, Cl^- and Br^- .
3. Both hydrogen and halogens form stable ionic compounds with alkali metals.

Dissimilarities from group VIIA

1. By losing its only electron, hydrogen forms H^+ but halogens do not form positive ions.

2. Combining with oxygen, hydrogen forms very stable oxides while halogens lack this property.

Similarities with group IVA

1. Valence shell of hydrogen is half-filled like those of group IVA elements.
2. Both, hydrogen and group IV elements combine with other elements through covalent bonding.
3. Like carbon, hydrogen also possesses remarkable reducing properties.

$$CuO\ (s) + H_2O\ (l) \longrightarrow Cu\ (s) + H_2O\ (l)$$

$$SnO_2\ (s) + C\ (s) \longrightarrow Sn\ (s) + CO_2\ (g)$$

Dissimilarities from group IVA

1. Carbon and silicon form long chain compounds, when their atoms combine with each other, while hydrogen do not form such compounds.
2. Similarly, carbon can simultaneously form bonds with more than one elements, whereas, hydrogen due to having only one electron can combine with only one element at a time.

Hydrogen is a unique element whose properties do not match exactly with any of the groups in the periodic table.

Due to partial resemblance in properties with alkali metals and monovalent nature, hydrogen is usually placed at the top of elements in group IA.

Ch 2

s-Block Elements

Peculiar Behaviour of Lithium

Reason for the peculiar behaviour

The deviation shown by lithium can be explained on the basis of:

1. Its small radius

2. High charge density.

The nuclear charge of Li^+ ion is screened only by a shell of two electrons.

3. Lithium is unexpectedly far less electropositive than sodium.

Points of differences

Some of the more important differences of lithium from other alkali metals are listed below:

1. Hardness and lightness

Lithium is much harder and lighter than the other alkali metals.

2. Solubility of lithium salts

The lithium salts of anions with high charge density are generally less soluble in water than those of the other alkali metals, e.g. LiOH, LiF, Li_3PO_4, Li_2CO_3.

3. Lithium complexes

Lithium forms stable complex compounds, although complex formation generally is not a property of alkali metals. One of the stable complexes formed by lithium is $[Li(NH_3)_4]^+$

4. Reaction with water

Lithium reacts very slowly with water, while other alkali metals react violently.

5. Lithium salts with polarizable anions

Lithium salts of large polarizable anions are less stable than those of other alkali metals. Unlike other alkali metals lithium does not form bicarbonate, tri-iodide or hydrogen sulphide at room temperature.

6. Oxides of lithium

When burnt in air lithium forms only normal oxide, whereas the others form peroxides or superoxides.

7. Hydride of lithium

Lithium hydride is more stable than the hydrides of other alkali metals.

8. Covalent nature of lithium compounds

Lithium compounds are more covalent, that is why its halides are more soluble in organic solvents and the alkyls and aryls of lithium are more stable than those of other alkali metals.

9. Reactivity of lithium

Lithium is the least reactive metal of all the alkali metals.

10. Acetylide formation

When acetylene is passed over strongly heated lithium, it does not produce lithium acetylide, but other alkali metals form the corresponding metallic acetylides.

$$2Na_{(s)} + C_2H_{2(g)} \longrightarrow \underset{\text{Sodium acetylide}}{Na^+C^- \equiv C^-Na^+} + H_{2(g)}$$

11. Carbonates and nitrates of lithium

Lithium has low electropositive character, thus its carbonate and nitrate are not so stable and therefore decompose giving lithium oxide. Carbonates of other alkali metals do not decompose. Decomposition of lithium nitrate gives different products than the nitrates of other alkali metals.

$$Li_2CO_3(s) \longrightarrow Li_2O(s) + CO_2(g)$$

$$4LiNO_3(s) \longrightarrow 2Li_2O(s) + 4NO_2(g) + O_2(g)$$

$$2NaNO_3(s) \longrightarrow 2NaNO_2(s) + O_2(g)$$

12. Hydroxide of lithium

Lithium hydroxide when strongly heated, forms lithium oxide but the other alkali metal hydroxides do not show this behaviour.

$$2LiOH \xrightarrow{\text{Red hot}} Li_2O(s) + H_2O(l)$$

13. Nitride of lithium

Lithium reacts with nitrogen to form nitride, while the other members of the group do not give this reaction.

$$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$$

14. Heat of solution

Lithium chloride has an exothermic heat of solution, whereas chlorides of sodium and potassium have endothermic heats of solution.

15. Carbide of lithium

Lithium carbide is the only alkali metal carbide formed readily by the direct reaction.

Peculiar Behaviour of Beryllium

Reason for the peculiar behaviour

This is due to its small atomic size and comparatively high electronegativity value.

1. Hardness of beryllium

Beryllium metal is almost as hard as iron and hard enough to scratch glass. The other alkaline earth metals are much softer than beryllium but still harder than the alkali metals.

2. Melting and boiling points

The melting and boiling points of beryllium are higher than other alkaline earth metals.

3. Beryllium as a reducing agent

As reducing agents, the group IIA metals are all powerful enough to reduce water, at least in principle. However, with water, beryllium forms insoluble oxide coating that protects it from further attack.

4. Oxidation of beryllium

Beryllium in particular is quite resistant towards complete oxidation, even by acids, because of its BeO coating.

5. Reaction with alkalies

Beryllium is the only member of its group which reacts with alkalies to give hydrogen. The other members do not react with alkalies.

$$Be_{(s)} + 2NaOH_{(aq)} \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_{2(aq)}} + H_{2(g)}$$

Commercial Preparation of Sodium by Down's Cell

Significance

1. Most of sodium metal is produced by the electrolysis of fused sodium chloride.
2. The melting point of sodium chloride is 801°C some calcium chloride is added to lower its melting point and to permit the furnace to operate at about 600 ⁰C.

Construction

Anode

In the electrolytic cell the large block of **graphite** at the centre is the anode, above which there is a dome for the collection of chlorine.

Cathode

The cathode is a circular bar of **copper or iron** which surrounds the anode but is separated from it by an iron screen which terminates in a gauze.

Advantage of the arrangement

1. The arrangement permits the electric current to pass freely

2. Prevents sodium and chlorine from mixing after they have been set free at the electrodes

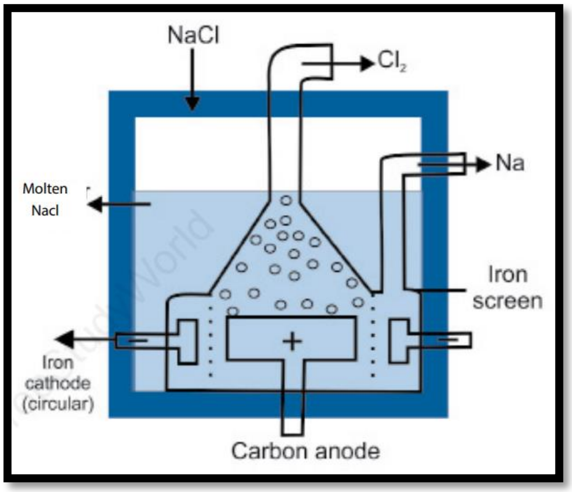


Diagram of Down's Cell

Working

Sodium metal rises in a special compartment from which it is taken out at intervals. The cell produces dry chlorine and 99.9 percent pure sodium. The process is carried out at 600 °C

Advantages

Following are the advantages of Down's cell:

(a) The metallic fog is not produced

(b) Liquid sodium can easily be collected at 600 °C

(c) Material of the cell is not attacked by the products formed during the electrolysis.

Reactions in Down's Cell

$$\mathbf{NaCl \longrightarrow Na^+ + Cl^-}$$

At cathode: $\mathbf{Na^+ + e^- \longrightarrow Na}$

At anode: $\mathbf{Cl^- \longrightarrow \frac{1}{2} Cl_2 + 1e^-}$

Commercial Preparation of Sodium Hydroxide by Diaphragm Cell

Significance

Sodium hydroxide is manufactured on a large scale by the electrolysis of aqueous solution of common salt in a diaphragm cell.

Construction

1. Cell material

The cell is made of steel tank.

2. Cathode

An oblong perforated steel vessel lined inside with asbestos diaphragm serves as a cathode. It is provided with a constant level device to keep the vessel filled to the specified level with brine.

3. Anode

A graphite anode is held within the U shaped diaphragm and it projects into the salt solution.

Working

1. Steam blowing

The steam is blown during the process which keeps the electrolyte warm and helps to keep the perforations clear.

2. Release of gases

The chlorine released at the anode rises into the dome at the top while hydrogen released at the cathode escapes through a pipe.

3. Collection of sodium hydroxide

The sodium hydroxide solution slowly percholates into a catch basin.

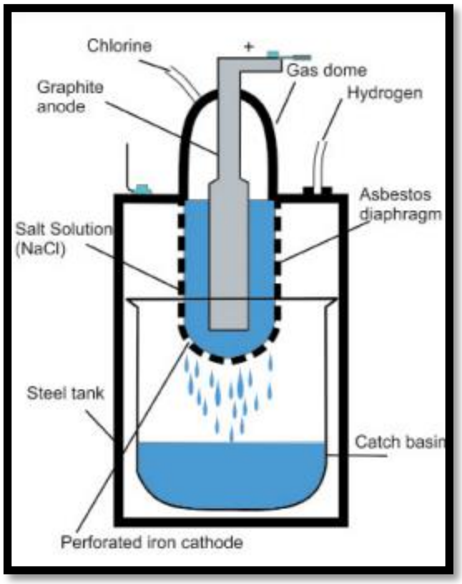


Diagram of Nelson's cell

Reactions taking place in Nelson's Cell

Anode

When the electrolysis takes place chlorine is given off at the anode according to the following reaction:

$$2Cl^- (aq) \longrightarrow Cl_2 (g) + 2e^-$$

Cathode

At the cathode hydrogen is discharged by the reduction of water:

$$2H_2O + 2e^- \longrightarrow 2OH^- (aq) + H_2 (g)$$

The overall result of the above reactions is that the brine loses its chloride ions and the solution turns increasingly alkaline in cathode compartment.

Problems During the working of the Cell

We can face two major problems during the working of the cell.

1. Production of hypochlorite ions

Chlorine produced can react with hydroxide ions in cold giving hypochlorite ions.

$$Cl_2 (g) + 2OH^- (aq) \longrightarrow OCl^- (aq) + Cl^- (aq) + H_2O$$

2. Release of oxygen gas

Hydroxide ions may be attracted towards anode, where they can be discharged releasing oxygen gas. This oxygen gas may contaminate the chlorine and renders it impure.

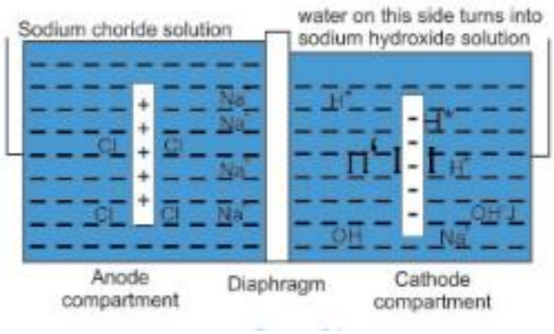
Solution to Problems

1. Use of asbestos diaphragm

The first problem is solved by using asbestos diaphragm. This keeps the two solutions separate while allowing sodium ions to move towards the cathode. This movement of ions keeps the current following through the external current.

2. Leveling of solutions in compartments

The second problem is solved keeping the level of brine in anode compartment slightly higher this keeps the direction of flow of liquid toward the cathode and, thus, preventing the possibility of hydroxides ions to reach the anode.



Output

The solution that flows out of the cathode compartment contains:

1. NaOH (11%)

2. NaCl (16%)

Processing of solution

Evaporation of this solution crystallizes the less soluble NaCl which is filtered off the liquid left contains about 50% NaOH and only 1% NaCl as an impurity.

For commercial purposes this small impurity is not important.

Role of Gypsum in Agriculture and Industry

Role of Gypsum in Agriculture

Gypsum is applied to the soil as a source of calcium and sulphur.

i. Role of calcium

The calcium supplied by gypsum in fertilizers is of importance in crop production in area where soils are subject to extensive leaching.

ii. Role of sulphur

- Sulphur has been recognized as an essential constituent of plants.
- For centuries, sulphur compounds had been applied to soils because of their beneficial effect on plant growth.
- Aside from serving as a constituent of protein and various other compounds in plants, sulphur has an influence on chlorophyll development in plant leaves.
- Although not a constituent of chlorophyll, plants deficient in sulphur exhibit a pale green colour.
- The root system of several plants has been observed to be greatly enlarged by the application of sulphur.
- It has been reported that good crops are produced by the application of sulphur containing materials such as gypsum.

Role of Gypsum in Industries

i. Role of Plaster of Paris

Preparation of Plaster of Paris for use

Plaster of Paris when mixed with half of its weight of water, it forms a plastic type viscous mass and then sets to a hard porous mass. This process is completed within 10 to 15 minutes. During the process expansion about 1% in volume also occurs, which fills the moulds completely and thus a sharp impression is achieved.

1. Plaster of Paris is used for making plaster walls, casts of statuary, coins etc.
2. It is used in surgery. Plaster of Paris bandages are used for holding in place fractured bones after they have been set.
3. Special plasters contain Plaster of Paris and other ingredients which vary with the demands of the use to which they are to be put.

Varieties of Plaster of Paris

Two varieties of plasters are made:

(1) Cement Plaster

Preparation

It is Plaster of Paris to which usually glue or other oils have been added as retarders to prolong the time of setting.

(2) Hard Finish Plasters

Preparation

These are made by the calcination of the anhydrous sulphate with alum or borax. These plasters are set very slowly but give a hard finish.

Uses

When mixed with wood pulp and allowed to set in the form of boards, it forms a material, much used in the construction of buildings as wall boards and partitions.

Other Uses of Gypsum

1. Gypsum is also used as filler in paper industries.
2. Portland cement is made by strongly heating a finely powdered mixture of clay and limestone. The final product, known as clinker, is cooled and then ground into a very fine powder. During the grinding there is added about 2% of gypsum which prevents the cement from hardening too rapidly. The addition of gypsum increases the setting time of cement.

Role of Lime in Agriculture and Industry

Lime, (CaO) is a soft, white compound which is obtained by the thermal decomposition of $CaCO_3$.

Role of Lime in Agriculture

Treatment of acidic soil

Large quantities of calcium oxide are used in agriculture for neutralizing acidic soils. It has been found that application of lime to acidic soils increases the amount of readily soluble phosphorus.

Lime-sulphur sprays

Calcium oxide is also used in large amounts for making lime-sulphur sprays which have a strong fungicidal action.

Slaking of lime

The hydroxide of calcium is obtained when the oxide of the calcium is allowed to react with water. The process is called slaking of lime and it is an exothermic reaction.

$$CaO + H_2O \longrightarrow \underset{\text{Slaked lime}}{Ca(OH)_2}$$

Functions of Calcium in Plant-Growth

i. Development of plants

The presence of calcium is essential for the normal development of plants. The quantity of calcium required by different plants varies considerably.

ii. Development of root hair

An adequate supply of calcium appears to stimulate the development of root hair and, in fact, the entire root system.

iii. Leaf development

Calcium is also necessary for normal leaf development and tends to accumulate in leaves as well as in bark.

iv. Optimum activity of microorganisms

An adequate supply of calcium is also essential for the optimum activity of microorganisms that produce nitrates.

v. Supply of available phosphorus

The effect of calcium on the supply of available phosphorus in the soil is of special significance. Soils containing sufficient calcium are slightly alkaline in nature.

vi. Side-effects of calcium deficiency

When a deficiency of calcium exists various substances such as aluminium and manganese may accumulate in plants in harmful concentrations.

Role of Lime in Industries

1. Refining of metals

Large quantities of lime are used in the extraction and refining of metals.

2. Paper, cement and leather industries

Lime is used in paper, cement and leather industries.

3. Glass manufacturing

The ability of lime to react with sand at high temperature forming calcium silicate ($CaSiO_3$) serves as an important basis for glass manufacture.

4. Ceramic industry

Lime is used in ceramic industry for producing different types of sanitary materials.

5. Lime mortar

Ordinary mortar, also called lime mortar, is prepared by mixing freshly prepared slaked lime (one volume) with sand (three or four volumes) and water to form a thick paste. This material when placed between the stones and bricks hardens or sets, thus binding the blocks firmly together. The equations for the chemical reactions which take place when mortar hardens are:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

$$Ca(OH)_2 + SiO_2 \longrightarrow CaSiO_3 + H_2O$$

6. Refining of sugar

Lime is also used in refining of sugar and other food products.

7. Bleaching powder

Lime is used in the manufacturing of bleaching powder which is used for the bleaching of the fabric and paper pulp.

8. Milk of lime

A suspension of the calcium hydroxide is called milk of lime and is used as a white-wash.

9. Production of acetylene

When lime is heated with coke at about 2800 °C in an electric furnace, calcium carbide is produced, which on hydrolysis yields acetylene (C_2H_2).

$$CaO + 3C \longrightarrow \underset{\text{Calcium carbide}}{CaC_2} + CO$$

10. Dehydrating agent

Lime is often employed as a dehydrating agent, for example, in the preparation of absolute alcohol and the drying of ammonia gas. A mixture of sodium hydroxide and calcium hydroxide (soda lime) is often employed to remove both water and carbon dioxide from certain gases.

Hard Finish Plaster and Cement Plaster

Following are the two varieties of Plaster of Paris:

(1) Cement Plaster

Composition

It is plaster of Paris to which usually glue or other oils have been added as retarders to prolong the time of setting.

(2) Hard Finish Plasters

Composition

These are made by the calcination of the anhydrous sulphate with alum or borax.These plasters are set very slowly but give a hard finish.

Uses

When mixed with wood pulp and allowed to set in the form of boards, it forms a material, much used in the construction of buildings as wall boards and partitions. Gypsum is also used as filler in paper industries.

Chapter 3

Group IIIA and Group IVA Elements

Peculiar Behaviour of Boron

Reason of peculiar behaviour

The difference in the properties of boron and those of the other members of the series is mainly due to the large difference in their sizes and ionization energies.

Points of peculiar behaviour

1. Non-metallic

Boron is the only element in Group IIIA which is non-metallic in behaviour.

2. Electronic arrangement

It is the only element with less than four electrons in the outermost shell which is not a metal.

3. Oxidation states

Boron always uses all the three of its valence electrons for bonding purposes and its common oxidation states are + 3 and -3.

4. Formation of molecular addition compounds

One of the outstanding features of the chemistry of boron is its ability to form molecular addition compounds.

5. Stability of cation

Boron does not form ionic compounds with sulphate, nitrate or other anions because boron does not from a stable cation.

Boric Acids

There are four important boric acids:

(i) Orthoboric Acid, H_3BO_3

(ii) Metaboric Acid, HBO_2

(iii) Tetraboric Acid, $H_2B_4O_7$

(iv) Pyroboric Acid, $H_6B_4O_9$

Orthoboric acid

1. It is a white crystalline chemical substance (triclinic).

2. It is sparingly soluble in cold water (2.6% at 40 ^oC).

3. It dissolves readily in hot water (37% at 107°C).

4. This temperature variation in solubility forms the basis for its separation and purification.

Preparation of boric acid on commercial scale

1. From Colemanite

Colemanite ($Ca_2B_6O_{11}.5H_2O$) is suspended in boiling water while sulphur dioxide is passed through it. Boric acid crystallizes out from the solution while, the other product $CaSO_3$ remains in the solution.

$$\underset{\text{Colemanite}}{Ca_2B_6O_{11}.5H_2O(s)} + 2SO_2(g) + 4H_2O(l) \longrightarrow 2CaSO_3(aq) + 6H_3BO_3(s)$$

2. From Borax

A hot concentrated solution of borax is treated with a calculated quantity of conc. H_2SO_4. On cooling, crystals of boric acid formed separate out.

$$\underset{\text{Borax}}{Na_2B_4O_7(s)} + H_2SO_4(aq) + 5H_2O(l) \longrightarrow Na_2SO_4(s) + \underset{\text{Boric acid}}{4H_3BO_3(s)}$$

Properties of boric acid

1. Physical appearance

Boric acid is a white lustrous crystalline solid having a soft soapy touch, very slightly soluble in cold water but fairly soluble in hot.

2. Volatility

It is volatile in steam.

3. Reaction with ethyl alcohol

It reacts with ethyl alcohol forming ethyl borate.

$$H_3BO_3(s) + 3C_2H_5OH(l) \longrightarrow (C_2H_5)_3BO_3(l) + 3H_2O(l)$$

4. Effect of heat

When heated strongly, it swells to frothy mass losing water molecules. It is first converted into metaboric acid, then to tetra boric acid and finally to boric anhydride.

$$H_3BO_3(s) \xrightarrow{100^\circ\ C} \underset{\text{Metaboric Acid}}{HBO_2}(s) + H_2O(l)$$

$$4HBO_2(s) \xrightarrow{140^\circ\ C} \underset{\text{Tetraboric acid}}{H_2B_4O_7}(s) + H_2O(l)$$

$$H_2B_4O_7(s) \xrightarrow{\text{Red hot}} \underset{\text{Boric anhydride}}{2B_2O_3}(s) + H_2O(l)$$

5. Acidic strength

It is a very weak acid and ionizes to a very limited extent mainly as a monobasic acid.

$$H_3BO_3(s) + H_2O(l) \longrightarrow [B(OH)_4]^-(s) + H^+$$

6. Effect on litmus solution

Its solution has no effect on methyl orange, although it turns blue litmus red.

7. Reaction with NaOH

It is partially neutralized by caustic soda to give borax.

$$4H_3BO_3(aq) + 2NaOH(aq) \longrightarrow Na_2B_4O_7(aq) + 7H_2O(l)$$

8. Reaction with Na_2CO_3

When boric acid is neutralized by soda ash (Na_2CO_3), borax is obtained.

$$4H_3BO_3(aq) + Na_2CO_3(aq) \longrightarrow \underset{\text{Borax}}{Na_2B_4O_7}(s) + 6H_2O(l) + CO_2(g)$$

9. Titration with alkalies

Boric acid being a weak acid, cannot be titrated with alkalies in the usual manner. In the presence of glycerol, however, it can be titrated against a standard alkali using phenolphthalein as an indicator.

Silicates

Definition

The compounds derived from silicic acids are termed as silicates.

Sodium silicate

This is a sodium salt of metasilicic acid H_2SiO_3.It is known as water glass or soluble glass.

Preparation

It is prepared by fusing sodium carbonate with pure sand. The process is carried out in a furnace called reverberatory furnace.

$$Na_2CO_3(s) + SiO_2(s) \longrightarrow \underset{\text{Sodium silicate}}{Na_2SiO_3(s)} + CO_2(g)$$

Properties

Sodium silicate is soluble in water and its solution is strongly alkaline due to the hydrolysis.

Chemical garden

When crystals of soluble coloured salts like nickel chloride, ferrous sulphate, copper sulphate or cobalt nitrate, etc. are placed in a solution of sodium silicate, they produce a very beautiful growth, like plant, which is called chemical garden.

Uses of Sodium silicate

1. Soap filler

It is used as filler for soap in soap industry.

2. Fire proof

It is used in textile as a fire proof.

3. Furniture polish

It is used as furniture polish.

4. Calico printing

It is also used in calico printing.

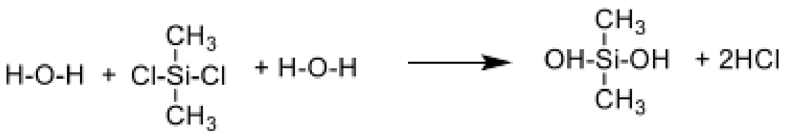
Silicones

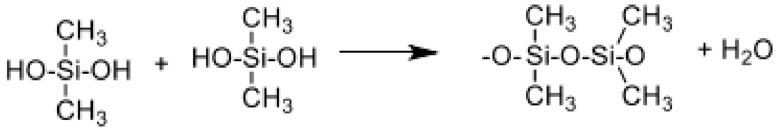
Similarity between silicon and carbon chemistry

Carbon forms carbon dioxide (CO_2), carbon tetrachloride (CCI_4), and methane (CH_4), similarly silicon forms silicon dioxide (SiO_2), silicon tetrachloride ($SiCl_4$), and silane (SiH_4).

Chemistry of Silicones

The silicon atom holds four methyl groups, $Si(CH_3)_4$, just as the carbon atom, $C(CH_3)_4$. If a compound of silicon containing chlorine atoms and methyl groups, $SiCl_2(CH_3)_2$, is allowed to react with water, hydrogen chloride (HCI) comes out, and the silicon atoms join together through oxygen atoms.





This is a methyl silicone. Other alkyl groups may also be substituted for the methyl groups and the molecular chain can be made of various lengths.

Advantage

By this reaction we can make synthetically the silicon oxygen chains found in the mineral silicates.

Difference between silicates and silicones

A difference between silicate and silicone is that -CH_3 groups instead of oxygen atoms are joined to silicon as side chains in silicates.

Properties and Uses of Silicones

Following are the properties and uses of silicones:

Use as lubricants

Some of the methyl silicones are oily liquids and they become more viscous as the chain length increases. They are used as lubricants, either incorporated in greases or as oils, in bearings, gears, etc. They are also used in hydraulic brakes and other hydraulic systems.

Negligible change of viscosity

silicone oil shows very small change in viscosity with change in temperature, compared with the behaviour of other oils of similar viscosity. If the temperature is dropped from 100 °C to 0 °C the viscosity of petroleum oil may increase about one hundred folds, whereas that of silicone oil will increase less than four folds.

Non-oxidizable

In the presence of air or oxygen at temperature as high as 300°C, silicone oils remain free from acid formation, oxidation and similar phenomena, which frequently limit the usefulness of petroleum products and other synthetic organic liquids.

Rubber manufacturing and use as insulators

Methyl silicones of high molecular mass resemble rubber and are used in making rubber like tubing and sheets. Silicone molecules can be made in such a way that bridges, or cross linkages bind one long molecule to another at several points along the chain. These compounds have resinous properties and are extensively used in electrical insulation.

Water repellent

A silicone film covers the surface and repels water like a grease film. Much of the leak of electricity through the moisture film on ceramic electrical insulators can be prevented by a silicone film; cloth, plastics, asbestos, glass, leather, and paper. Even filter paper and blotting paper become strongly water repellent when covered with a silicone film.

Semiconductors

Definition

A semiconductor is a substance that has different resistances to the passages of an electric current under different circumstances. They are also called "half-conductors"

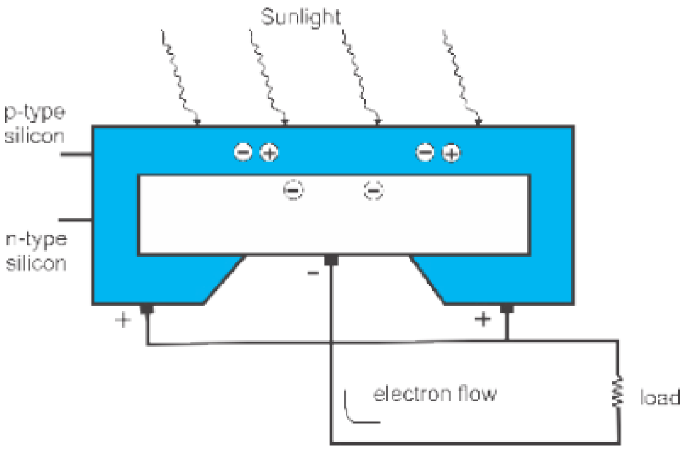
Examples

Elements included:

- Germanium
- Selenium
- Silicon

Compounds included:

- Lead sulphide
- Silicon carbide
- Cadmium sulphide
- Lead telluride
- Gallium arsenide
- Indium antimonide.



Properties of semiconductors

Following are the properties of semiconductors:

1. Conduction of electricity

Semiconductors conduct electricity better than insulators, but not as well as good conductors like metals. When a metal is heated, its resistance increases, when a semiconductor is heated its resistance decreases.

2. Sensitivity to light

Semiconductors are sensitive to light. The greater the intensity of the light that shines on them the better they conduct electricity. The effects that light and heat energy have on semiconductors make them extremely useful.

Use

They are used in photoelectric cells and in solar batteries.

3. Effect of heat or light on conduction of electricity

The electrons of semiconductors do not carry electric current as readily as the electrons of good electric conductors like metals. When the atoms of the material absorb heat or light, the electrons become less tightly bound to their atoms and can conduct electricity.

4. Transistor formation

Semiconductors may be joined with a metal or a different semiconductor to form a junction which allows electricity to pass more properly and is used in transistors which are much smaller and less complicated than electronic tubes.

Use

They are used in radio, television, computers and calculators.

Chapter 4

Group VA and Group VIA Elements

Manufacture of Nitric Acid Birkeland and Eyde’s Process

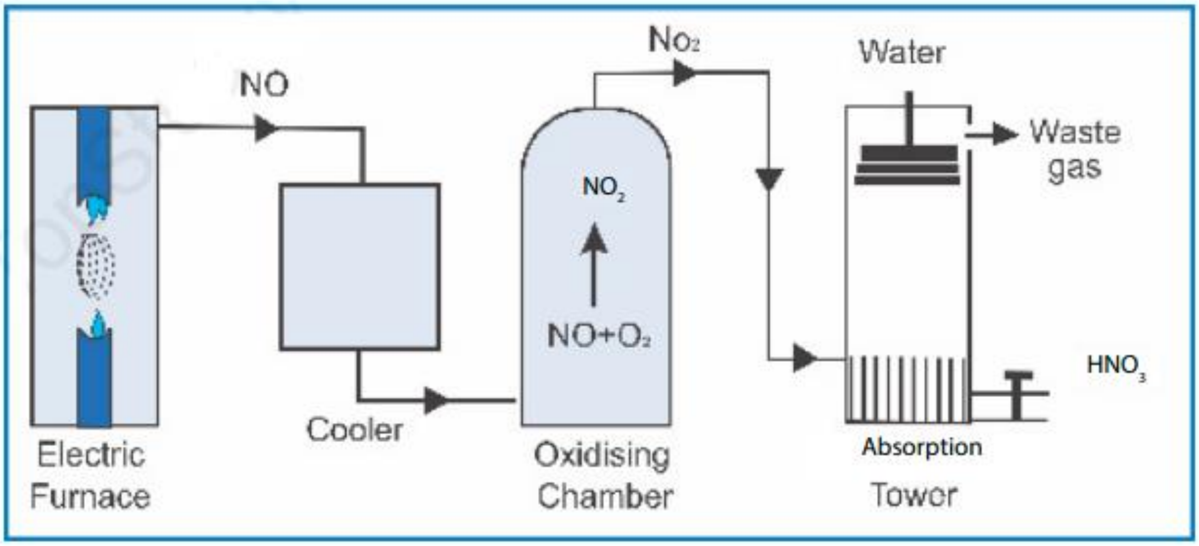
Following steps are involved in the process:

1. Formation of nitric oxide

Atmospheric nitrogen and oxygen are combined to give nitric oxide in an electric arc (3000°C).

$$N_2(g) + O_2(g) \xrightarrow{3000^\circ C} 2NO(g)$$

NO formed is cooled quickly to 1000°C at which it does not decompose.



2. Formation of nitrogen dioxide

At 600 °C, NO combines with O_2 to form NO_2

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

3. Formation of nitrous acid and nitric acid

Nitrogen dioxide is absorbed in water to give dilute HNO_3 along with nitrous acid.

$$2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$$

4. Oxidation of nitrous acid

Nitrous acid is oxidized to nitric acid and nitric oxide which is re-oxidized to NO_2.

$$3\,HNO_2(g) \rightarrow HNO_3(aq) + 2\,NO(g) + H_2O(l)$$

Properties of Nitric Acid

1. Colour

Concentrated nitric acid is a colourless volatile liquid which fumes strongly in air.

2. Smell

It has a pungent smell.

3. Specific gravity

Its specific gravity at 15 °C is 1.53.

Reactions

1. Decomposition

Nitric acid is decomposed in the presence of light even at ordinary temperature.

$$4\,HNO_3(aq) \rightarrow 2H_2O(l) + 4NO_2(g) + O_2(g)$$

2. Acidic behaviour

It is a very strong acid. It reacts in normal way with basic oxides, hydroxides and carbonates forming respective salts.

$$2\,HNO_3(aq) + CaO(s) \rightarrow H_2\,O(l) + Ca(NO_3)_2(aq)$$

$$HNO_3(aq) + NaOH(aq) \rightarrow H_2O(l) + NaNO_3(aq)$$

$$2\,HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2\,NaNO_3(aq) + H_2\,O(l) + CO_2(g)$$

3. Action as an oxidizing agent

It acts as a strong oxidizing agent due to the ease with which it is decomposed.

$$2HNO_3(aq) \rightarrow H_2O(l) + 2NO_2(g) + [O](g)$$

4. Oxidation of non-metals

It oxidizes non-metals to their corresponding oxides.

$$C(s) + 4\,HNO_3(conc.) \rightarrow CO_2(g) + 4\,NO_2(g) + 2\,H_2O(l)$$

$$S(s) + 6HNO_3(conc.) \rightarrow 2H_2O(l) + 6NO_2(g) + H_2SO_4(aq)$$

$$5\,HNO_3(conc.) + P(s) \rightarrow H_3PO_4(aq) + H_2O(l) + 5\,NO_2(g)$$

5. Reaction with metalloids

Metalloids like arsenic and antimony can be oxidized to their corresponding acids.

$$As(g) + 5\,HNO_3(conc.) \rightarrow H_3AsO_4(aq) + 5NO_2(g) + H_2O(l)$$

$$Sb(g) \rightarrow 5HNO_3(conc.) \rightarrow H_3SbO_4(aq) + 5NO_2(g) + H_2O(l)$$

6. Reaction with metals

Nitric acid behaves differently with different metals.

(a) Gold, platinum, iridium and titanium **do not react**.

(b) Iron, cobalt, nickel, chromium, aluminium **are rendered passive** by acid due to the formation of a film of their oxides over them.

(c) Tungsten and uranium are **changed into their oxides**.

(d) Magnesium, calcium and manganese **give hydrogen with dilute nitric acid**.

$$Mg(s) + 2HNO_3(dil) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$$

$$Mn(s) + 2HNO_3(dil) \rightarrow Mn(NO_3)_2(aq) + H_2(g)$$

7. Reaction with copper and lead

Copper and lead give nitric oxide with dilute acid and nitrogen dioxide with concentrated acid.

$$3Cu(s) + 8HNO_3(dil) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

$$Cu(s) + 4\,HNO_3(conc.) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

8. Reaction with mercury

Mercury gives mercurous nitrate and nitric oxide with dilute nitric acid.

$$6Hg(l) + 8\mathrm{HNO_3}(dil) \rightarrow 3Hg_2(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

With concentrated acid, it gives mercuric nitrate and NO_2

$$Hg(l) + 4HNO_3(conc) \rightarrow Hg(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

9. Reaction with silver

$$3Ag(s) + 4HNO_3(aq) \rightarrow 3AgNO_3(aq) + NO(g) + 2H_2O(l)$$

10. Reaction with tin

Dilute nitric acid gives ammonium nitrate, when it reacts with tin. With concentrated acid meta-stannic acid is produced.

$$4Sn(s) + 10HNO_3(dil.) \rightarrow 4Sn(NO_3)_2(aq) + NH_4NO_3(aq) + 3H_2O(l)$$

$$\mathrm{Sn(s)} + 4HNO_3(conc.) \rightarrow H_2SnO_3(aq) + 4NO_2(g) + H_2O(l)$$

11. Reaction with zinc

Zinc gives different products depending upon the concentration of acid and temperature. Very dilute nitric acid gives NH_4NO_3. Moderately dilute nitric acid gives nitrous oxide while concentrated nitric acid gives NO_2.

$$4Zn(s) + 10HNO_3(v.\mathrm{dil.}) \rightarrow 4Z\mathrm{n(NO_3)_2}(aq) + NH_4NO_3(aq) + 3H_2O(l)$$

$$4Zn(s) + 10HNO_3(dil.) \rightarrow 4Zn(NO_3)_2(aq) + N_2O(g) + 5H_2O(l)$$

$$Zn(s) + 4HNO_3(conc.) \rightarrow Zn(NO_3)_2(aq) + 2\,\mathrm{NO_2} + 2H_2O(l)$$

12. Reaction with reducing agents

Reducing agents like $FeSO_4$, H_2S and HI are converted to $Fe_2(SO_4)_3$, S and I_2 respectively, when they react with conc. HNO_3.

$$6FeSO_4(aq)+3H_2SO_4(aq)+2HNO_3(conc.)\rightarrow 3Fe_2(SO_4)_3(aq)+2NO(g)+4H_2O(l)$$

$$2HNO_3(aq)+3H_2S(g)\rightarrow 4H_2O(l)+2NO(g)+3S(s)$$

$$6HI(aq)+2HNO_3(conc.)\rightarrow 4H_2O(l)+2NO(g)+3I_2(s)$$

13. Aqua Regia

Definition

When one volume of concentrated HNO_3 is mixed with 3 volumes of concentrated HCl, aqua regia is formed.

Purpose

It is employed to dissolve gold and platinum.

Reactions Involved

a. Reaction of nitric acid and hydrochloric acid

$$HNO_3(conc.)+3\mathrm{HC1(conc.)}\rightarrow \mathrm{NOC1(aq)}+C1_2(g)+2H_2O(l)$$

b. Decomposition of NOCl

NOCI formed is decomposed giving NO and Cl_2

$$NOC1\rightarrow NO(g)+[C1](g)$$

c. Conversion of noble metals to soluble chlorides

This liberated chlorine gas converts noble metals such as gold and platinum into their water soluble chlorides.

$$Au(s)+3[C1](aq)\rightarrow 2AuC1_3(aq)$$

d. Reaction with glycerine, toluene and phenol

Nitric acid reacts with glycerine, toluene and phenol to prepare materials used as explosives like nitroglycerine, trinitrotoluene (TNT) and picric acid, respectively.

Allotropes of Phosphorus

Phosphorus can exist in at least six different solid allotropic forms. Three are explained below:

1. White phosphorus

It is very reactive.

It is poisonous.

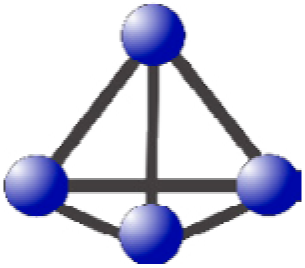
It is volatile.

It is waxy, yellowish white substance.

It is soluble in benzene and carbon disulphide.

It exists in the form of tetra-atomic molecules (P_4) which have a tetrahedral structure.

It boils at 280°C to P_4 vapours which dissociate above 700°C to form P_2 molecules.



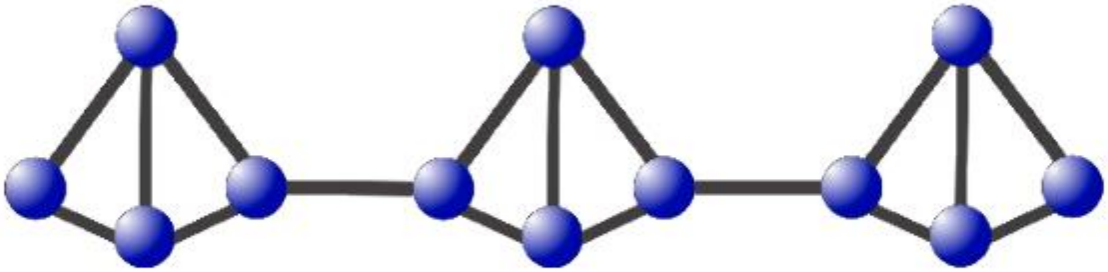
2. Red phosphorus

It is much less reactive than white phosphorus.

It is less poisonous than white phosphorus.

It is prepared by heating white phosphorus in the presence of a little iodine or sulphur as a catalyst up to 250°C in vacuum.

The tetra-atomic molecules of red phosphorus combine to form macromolecules.



3. Black phosphorus

Black phosphorus is the third form which is most stable under ordinary conditions.

Black phosphorus is prepared by heating red phosphorus to high temperature and pressure.

Comparison of Oxygen and Sulphur

Similarities

1. Electronic configuration

Both oxygen and sulphur have same outer electronic configuration of ns^2p^4.

2. Valency

Both oxygen and sulphur are usually divalent.

3. Allotropic forms

Both oxygen and sulphur exhibit allotropic forms.

4. Polyatomic molecules

Both have polyatomic molecules. Oxygen has diatomic O_2, while sulphur has S_2 and S_8 molecules.

5. Combination with metals

Both combine with metals in the form of O^{-2} and S^{-2} with oxidation state -2.

6. Combination with non-metals

Both combine with non-metals and form covalent compounds, e.g, H_2O and H_2S, CO_2 and CS_2 ,etc.

7. Non-metallic nature

Both are typical non-metals.

8. Occurrence

Both are found in free and combined states on earth.

Dissimilarities

Oxygen	Sulphur
Allotropic forms There are two allotropic forms of Oxygen-O_2 and O_3.	**Allotropic forms** There are 3 allotropic forms of sulphur, rhombic, monoclinic and plastic.
Physical state It is gas at ordinary temperature.	**Physical state** It is solid at ordinary temperature.
Solubility in water Oxygen is sparingly soluble in water.	**Solubility in water** Sulphur is not soluble in water.
Combustion Oxygen helps in combustion.	**Combustion** Sulphur is itself combustible.
Magnetic properties It is paramagnetic in nature.	**Magnetic properties** It is diamagnetic in nature.
Reaction with water It does not react with water.	**Reaction with water** When steam is passed through boiling sulphur a little hydrogen sulphide and sulphur dioxide are formed.
Reaction with acids It does not react with acids.	**Reaction with acids** It is readily oxidized by conc. sulphuric acid or nitric acid.
Reaction with alkalies It does not react with alkalies.	**Reaction with alkalies** It reacts with alkali solution and forms sulphides and thiosulphate
Oxidation state It shows -2 oxidation state.	**Oxidation state** It shows oxidation states of -2, +2, +4 and +6.

Manufacturing of Sulphuric acid

Sulphuric acid is being manufactured commonly by contact process.

Contact Process

This method was developed by Knietsch in Germany.

Basic Working

It involves the catalytic combination of sulphur and oxygen to form SO_2 which is then dissolved in water to form H_2SO_4.

Principle

SO_2 obtained by burning sulphur or iron pyrites is oxidized to SO_3 in the presence of V_2O_5 which acts as a catalyst. The best yield of SO_3 can be obtained by using excess of oxygen or air and keeping the temperature between 400-500°C. SO_3 formed is absorbed in concentrated H_2SO_4 and “Oleum” ($H_2S_2O_7$) formed can be converted to sulphuric acid of any strength by mixing adequate quantities of water.

Steps Involved

The process is completed in the steps given below.

a. Sulphur Burners

Sulphur or iron pyrites are burnt in excess of air to produce SO_2.

$$S(s)+O_2(g)\rightarrow SO_2(g)$$

$$4FeS_2(s)+11O_2(g)\rightarrow 2Fe_2O_3(s)+8SO_2(g)$$

b. Purifying Unit

SO_2 is purified from impurities like dust and arsenic oxide, to avoid poisoning of the catalyst. Purifying unit consists of the following parts.

(i) Dust remover

Steam is injected to remove dust particles from the gases.

(ii) Cooling Pipes

The gases are passed through lead pipes to cool them to 100°C.

(iii) Scrubbers

The cooled gases are washed by a spray of water, as SO_2 is not soluble in water at high temperature.

(iv) Drying Tower

The moisture of gases is removed by concentrated H_2SO_4 trickling down through the coke filled in this tower.

(v) Arsenic Purifier

Arsenic oxide is removed by passing the gases through a chamber provided with shelves packed with freshly prepared ferric hydroxide.

(vi) Testing box

In this box a beam of light is introduced which indicates the presence or absence of solid particles. If present the gases are sent back for further purification.

c. Contact Tower

Preheated gases at 400-500°C are passed through vertical iron columns packed with the catalyst V_2O_5. Here SO_2 is oxidized to SO_3.

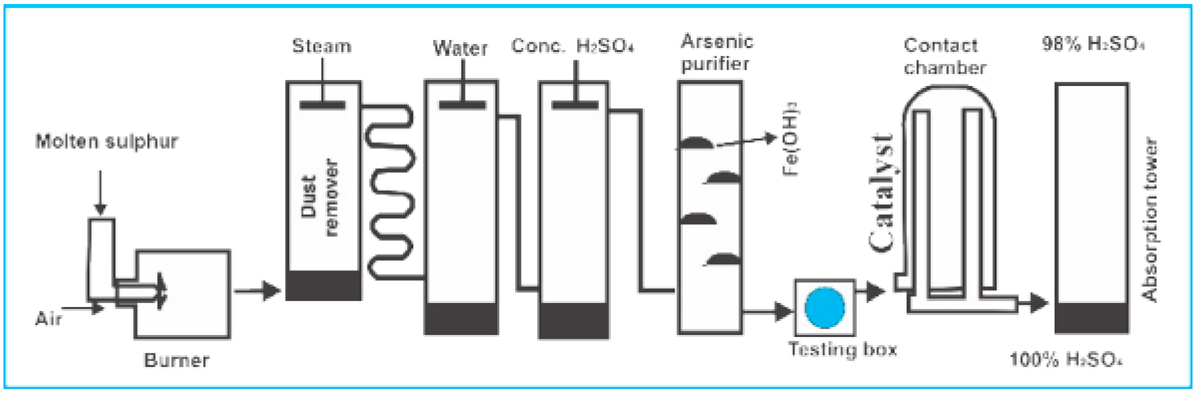
$$2SO_2(g) + O_2(g) \xrightarrow[V_2O_5]{400-500^\circ C} 2SO_3 \qquad \Delta H = -269.3kJ/mol.$$

d. Absorption Unit

The SO_3 obtained from the contact tower is dissolved in 98% H_2SO_4 to form pyrosulphuric acid (oleum), $H_2S_2O_7$. It can be diluted with water to get any required concentration of sulphuric acid.

$$H_2SO_4(aq) + SO_3(g) \rightarrow H_2S_2O_7(l)$$

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(aq)$$



Properties of Sulphuric acid

1. Colour

Pure sulphuric acid is a colourless oily liquid without an odour.

2. Specific gravity

Its specific gravity is 1.834 at 18°C.

3. Freezing point

It freezes at 10.5°C.

4. Boiling point

Its boiling point is 338°C.

5. Dissolution in water

It dissolves in water liberating a lot of heat which raises the temperature of the mixture up to 120°C. H_2SO_4 should always be poured in water in a thin stream to avoid any accident.

6. Non-conductor

Pure acid is a nonconductor of electricity but the addition of a little water makes it a good conductor.

7. Corrosive action on skin

It is extremely corrosive to skin and causes very serious burns to all the tissues.

Reactions of sulphuric acid

1. Stability

It is stable at ordinary temperature but on strong heating it dissociates into SO_3 and H_2O.

$$H_2SO_4 \rightarrow SO_3 + H_2O$$

2. Ionization

It is a strong acid. In an aqueous solution it completely ionizes to give hydrogen, hydrogen sulphate and sulphate ions. The dissociation takes place in two steps:

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(l) + HSO_4^-(aq)$$

$$HSO_4^-(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + H_3O^+(l)$$

3. Reaction as an acid

(i) Reaction with alkalies

$$H_2SO_4(aq) + NaOH(aq) \rightarrow NaHSO_4(aq) + H_2O(l)$$

$$NaHSO_4(aq) + NaOH \rightarrow Na_2SO_4(aq) + H_2O(l)$$

(ii) Reactions with carbonates and hydrogen carbonates

$$Na_2CO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$$

$$2NaHCO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) + 2CO_2(g)$$

(iii) Reaction with salts

$$2NaCl(s) + H_2SO_4(Conc) \xrightarrow{Strong\ heat} Na_2SO_4(aq) + 2HCl(g)$$

$$KNO_3(aq) + H_2SO_4(Conc) \rightarrow KHSO_4(aq) + HNO_3(g)$$

(iv) Reaction with metals

(a) Reaction of cold dilute acid

$$Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$$

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

$$Sn(S) + H_2SO_4(aq) \rightarrow SnSO_4(g) + H_2(g)$$

(b) Reaction of cold concentrated acid

Cold concentrated H_2SO_4 does not react with most of the metals like Cu, Ag, Hg, Pb, Au

(c) Reaction of hot concentrated acid

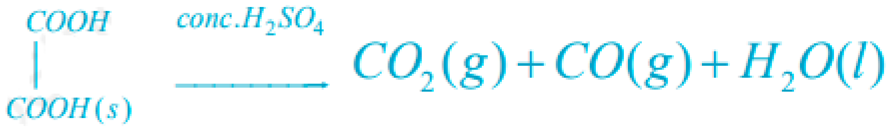
With certain metals hot concentrated sulphuric acid gives metal sulphates, water and SO_2.

$$Cu(s) + 2H_2SO_4(conc) \rightarrow CuSO_4(aq) + 2H_2O(l) + SO_2(g)$$

$$2Ag(s) + 2H_2SO_4(conc) \rightarrow Ag_2SO_4(aq) + 2H_2O(l) + SO_2(g)$$

$$Hg(l) + 2H_2SO_4(conc) \rightarrow HgSO_4(aq) + 2H_2O(l) + SO_2(g)$$

4. Reactions as a Dehydrating agent



$$\begin{array}{c} COOH \\ | \\ COOH(s) \end{array} \xrightarrow{conc.H_2SO_4} CO_2(g) + CO(g) + H_2O(l)$$

$$HCOOH(l) \xrightarrow{conc.\ H_2SO_4} CO(g) + H_2O(l)$$

$$C_2H_5OH(\ell) \xrightarrow[100^\circ C]{Conc.H_2SO_4} C_2H_4(g) + H_2O(\ell)$$

$$C_6H_{12}O_6(s) \xrightarrow{Conc.H_2SO} 6C(s) + 6H_2O(g)$$

$$C_{12}H_{22}O_{11}(s) \xrightarrow{Conc.H_2SO_4} 12C(s) + 11H_2O(g)$$

$$(C_6H_{10}O_5)n \xrightarrow{Conc.H_2SO_4} 6nC + 5nH_2O$$

5. As an Oxidizing agent

$$C(s) + 2\mathrm{H_2SO_4}(conc) \rightarrow \mathrm{CO_2(g)} + 2\mathrm{SO_2(g)} + 2\mathrm{H_2O(g)}$$

$$\mathrm{S(s)} + 2\mathrm{H_2SO_4}(conc) \rightarrow 3\mathrm{SO_2(g)} + 2\mathrm{H_2O(l)}$$

$$H_2S(g) + H_2SO_4(aq) \rightarrow S(s) + SO_2(g) + 2H_2O(g)$$

$$2HBr(aq) + H_2SO_4(aq) \rightarrow Br_2(g) + SO_2(g) + 2H_2O(g)$$

$$2HI(aq) + H_2SO_4(aq) \rightarrow I_2(g) + \mathrm{SO_2(g)} + 2\mathrm{H_2O(g)}$$

6. Reactions with gases

$$\mathrm{H_2SO_4}_{(Conc)} + \mathrm{SO_3(g)} \rightarrow \mathrm{H_2S_2O_7(l)}$$

$$2\,\mathrm{NH_3(g)} + \mathrm{H_2}\,SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$$

7. Reaction with benzene

$$C_6H_6(l) + H_2SO_{4\,(conc)} \rightarrow \underset{Benzenesulphonic\ \mathrm{acid}}{C_6H_5SO_2OH(l)} + H_2O(l)$$

8. Precipitation reactions

$$BaCl_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) \downarrow + 2HCl(aq)$$

$$Pb(NO_3)_2(aq) + H_2SO_4(aq) \rightarrow PbSO_4(s) \downarrow + 2HNO_3(aq)$$

9. Reactions with oxidizing agents

$$\begin{array}{l} 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O] \\ 10FeSO_4 + 5H_2SO_4 + 5[O] \rightarrow 5Fe_2(SO_4)_3 + 5H_2O \\ \hline 2KMnO_{4(aq)} + 8H_2SO_{4(aq)} + 10FeSO_{4(aq)} \rightarrow K_2SO_{4(aq)} + 2MnSO_{4(aq)} + 5Fe_2(SO_4)_{3(aq)} + 8H_2O_{(l)} \end{array}$$

Chapter 5

The Halogens and the Noble Gases

(Any Topic can Come for Long Question)

Commercial Preparation of Bleaching Powder

Main reaction

Bleaching powder can be manufactured by the action of chlorine on dry slaked lime.

$$\underset{\text{Slaked lime}}{Ca(OH)_2} + Cl_2 \longrightarrow \underset{\text{Bleaching powder}}{Ca(OCl)Cl} + H_2O$$

Methods used

(a) Hasenclever’s method (old method)

(b) Beckmann’s method (modern method)

(a) Hasenclever’s Method

Assembly

The apparatus used in this method consists of 4 to 8 iron cylinders placed one above the other horizontally.

They are interconnected and provided with stirrers.

Operation

Addition of slaked lime

The slaked lime is added in through a hopper in the upper cylinder.

It is transported from one cylinder to the other with rotating stirrers.

Addition of chlorine

Chlorine introduced into the lowest cylinder rises up.

It reacts with slaked lime to form bleaching powder.

Bleaching powder is collected through the outlet in the lowest cylinder.

(b) Beckmann’s Method

Assembly

A cast iron tower with eight horizontal shelves is used.

In each shelf there is a rotating rake.

Operation

Addition of slaked lime

Powdered slaked lime is introduced through hopper at the top with compressed air.

Addition of hot air and chlorine

A mixture of hot air and chlorine are introduced from the base of the tower.

Rise of chlorine gas

The slaked lime is pushed down by the rotating rakes while chlorine rises up.

Reaction

Reaction between slaked lime and chlorine produces bleaching powder which is collected at the bottom of the tower.

Principle applied

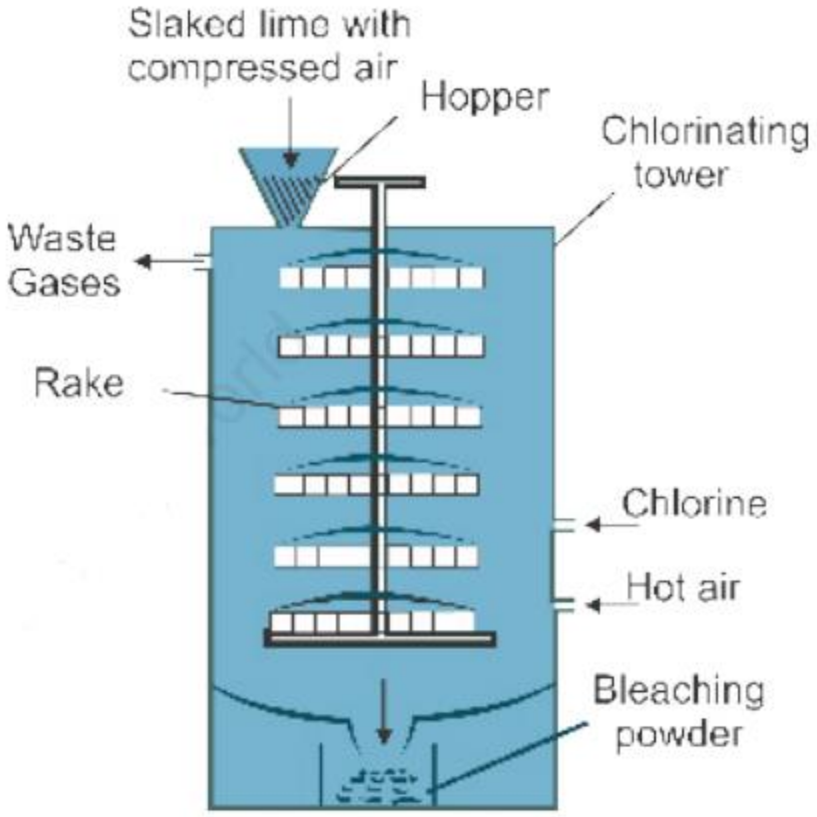
The apparatus works on the countercurrent principle.

Advantage

Thus maximum reaction of slaked lime and chlorine is brought about with very little loss of chorine.

Packaging

Bleaching powder should always be packed in air tight containers to avoid the loss of chlorine.



Commercial Uses of Halogens and their Compounds

Uses of fluorine

1. Freons

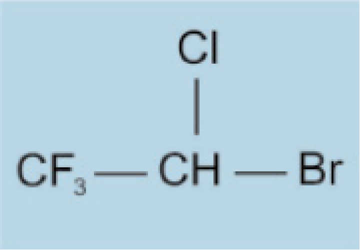
Fluorine is used for the preparation of freons. Freon is the commercial name of low molecular mass fluorochlorocarbons, CCl_2F_2, $CClF_3$. These are being used as refrigerants and aerosol propellants.

2. Teflon

Fluorine is used to prepare Teflon $(-CF_2 — CF_2 -)_n$. It is a polymerized tetrafluoro ethylene compound. It is a valuable plastic which resists the action of oxidants, acids and alkalies. Corrosionproof parts of machinery are made of it. It is used for coating the electrical wiring. Teflon is also used as a non-stick coating for cooking pans.

3. Halothane

Halothane is used as an anaesthetic.



$$CF_3—\overset{\overset{\large Cl}{|}}{C}H—Br$$

4. Toothpastes

Fluorides in toothpastes build a protective coating on teeth.

Uses of chlorine

1. Bleaching powder

Chlorine is used in the manufacture of bleaching powder.

2. Disinfectant

It is used as a disinfectant in swimming pools and water treatment plants.

3. Insecticides and herbicides

A number of antiseptics, insecticides, weedkillers and herbicides are manufactured from chlorine.

4. Hydrochloric acid

It is also used in the manufacture of hydrochloric acid, which is the cheapest industrial acid.

5. PVC plastics

Chlorine is also used in the manufacture of polyvinyl chloride (PVC) plastics.

6. Chloroform and carbon tetrachloride

Chloroform and carbon tetrachloride are prepared from chlorine which are used as solvents.

Uses of bromine

1. Leaded gasoline

Ethylene dibromide ($C_2H_4Br_2$) is added to leaded gasoline to save the engine from lead oxide and lead sulphate deposits.

2. Fungicide

Bromine is also used as fungicide.

3. Photography

Silver bromide is used in photography.

Uses of iodine

1. Disinfectant

It is used as disinfectant and germicide.

2. Iodex and tincture of iodine

Tincture of iodine and iodex are popular preparations of iodine.

3. Iodized salt

Diet with insufficient iodide ions leads to an enlargement of the thyroid (Goiter). To ensure the presence of iodide ion in the diet, sodium or potassium iodide is added to the common salt which is known as iodized salt.

Applications of the Noble Gases

Applications of helium

Helium is used in weather balloons, in welding and in traffic signal light.

A mixture of 80% helium and 20% oxygen is used for breathing by the sea divers.

Helium is used as a cooling medium for nuclear reactors.

Applications of neon

Neon is largely used in making neon advertising signs, in high voltage indicators and TV tubes.

Neon and helium arc is used in making glass lasers.

Applications of argon

Argon is used in electric light bulbs, in fluorescent tubes, in radio tubes, and in Geiger counters (used to detect radioactivity).

Argon is also used for arc welding and cutting.

Applications of krypton

Krypton is used to fill fluorescent tubes and in flash lamps for high speed photography.

Applications of xenon

Xenon is used in bactericidal lamps.

Applications of radon

Radon being radioactive is used in radiotherapy for cancer and for earth quake prediction.

Ch 6

Transition Elements

Properties of Transition Elements

Reason of similarity

Because of a similar electronic configuration, the d-block elements closely resemble one another in their physical and chemical properties.

Points of resemblance

Some of the points of their resemblance are given below:

1. Metals

They are all metals in true sense, some of which play important role in industry, e.g. Ti, Fe, Cr, Ni, Cu, Mo, W, Zr, Nb, Ta, Th, etc.

2. High melting and boiling points

They are all hard and strong metals with high melting and boiling points. They are also good conductors of heat and electricity.

3. Alloy formation

They form alloys with one another and also with other elements.

4. Variable oxidation state

With few exceptions, they show variable valency or oxidation state.

5. Coloured ions

Their ions and compounds are coloured in solid state as well as in solution form at least in one if not all the oxidation states.

General characteristics

(a) Binding energies

Transition metals are tough, malleable and ductile.

Reason

Apart from s-electrons of the outer most shell, the electrons of underlying half-filled d-orbitals also participate in binding. In moving from left to right in any transition series, the number of unpaired electrons increases up to groups VB and VIB, after that pairing takes place and number of unpaired electrons goes on decreasing until it becomes zero at group IIB.

Trend

Binding is stronger up to group VIB and weakens progressively up to group IIB. In the first transition series the general increase in binding energy ends at vanadium.

Reason

This is due to changes in metallic structure, e.g. Mn.

In the third transition series, the increase in binding energy ends at tungsten when all the 5d electrons contribute to binding.

(b) Melting and Boiling Points

Transition metals have very high melting and boiling points.

Reason

Strong binding forces present between their atoms.

Trend

Melting points increase up to the middle of the series and then decrease to a minimum level at the end of the series.

This trend in melting points correlates well with the strength of binding forces.

(c) Covalent Radii and Ionic Radii

Trend of covalent radii

The covalent radii decrease rapidly at the start of the series, then become almost constant and finally begin to increase at the end of the series.

Reason

The increase in covalent radii is possibly due to the fact that the filled 3d orbitals have contracted into the electron core and so shield the outer 4s electrons more effectively from the nucleus.

Trend in ionic radii

Changes in the ionic radii along the series are much less regular, so that periodic trends in the properties of these ions are difficult to rationalize.

(d) Paramagnetism and diamagnetism

Definition

Substances which are weakly attracted by a strong magnetic field are called paramagnetic substances. Those substances which are weakly repelled by a strong magnetic field are called diamagnetic substances.

Reason of paramagnetism

Paramagnetic behaviour is caused by the presence of unpaired electrons in an atom, molecule or ion because there is a magnetic moment associated with the spinning electron.

Unpaired electrons and paramagnetism

It increases with increase in the number of unpaired electrons. When the electrons are paired in an orbital, then magnetic moments are cancelled out and the substances become diamagnetic.

Trend of paramagnetism

The paramagnetic behaviour is the strongest for Fe^{3+} and Mn^{2+} and decreases on both sides of the first transition series.

Reason

Both Mn^{2+} and Fe^{3+} have 5 unpaired electrons each. The number of unpaired electrons decreases gradually to zero on both sides.

(e) Oxidation State

One of the most important properties of the transition elements is the fact that they exhibit variable valency or oxidation state.

Reason

They show variable valencies because of the involvement of the unpaired d electrons in addition to s electrons in bond formation.

Trend

All 3d series elements show an oxidation state of +2 in addition to higher oxidation states.

+2 oxidation state is shown when only the 2s electrons are involved in bonding.

In the highest oxidation states of the first five elements all the s and d electrons are used for bonding.

After Mn, the number of oxidation states decreases as the d-subshells fill up and fewer unpaired electrons are available for bond formation.

(f) Colour

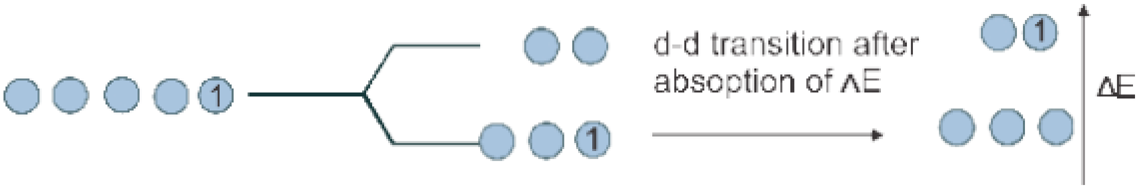
In transition elements, the d orbitals are responsible for the colour development in their compounds.

Reason is d-d transition

When these orbitals are involved in bonding, they split up into two energy levels, one set has a higher energy than the other. The electrons residing in low energy d-orbitals absorb a part of the visible light and jump to high energy d orbitals. The process is called d-d transition.

Example

In $[Ti(H_2O)_6]^{3+}$, yellow light is absorbed, while most of the blue and red lights are transmitted, therefore the solution of $[Ti(H_2O)_6]^{3+}$ ions looks violet in colour.



(g) Interstitial Compounds

When small non-metal atoms like H, B, C, N enter the interstices of transition metals and impart useful features to them, they are called Interstitial compounds.

Characteristics

These are non-stoichiometric compounds.

They are also termed as interstitial alloys.

(h) Alloy Formation

Some transition metal atoms are able to replace one another in the metallic lattice and form substitutional alloys among themselves.

Reason

Similarity in the sizes of atoms.

Examples

Alloy steels are an important example of this type of material in which iron atoms are substituted by chromium, manganese and nickel atoms, etc. to give the steel more useful properties.

Brass, bronze, coinage alloys, etc.

Manufacture of Wrought Iron from Cast Iron

Type of furnace

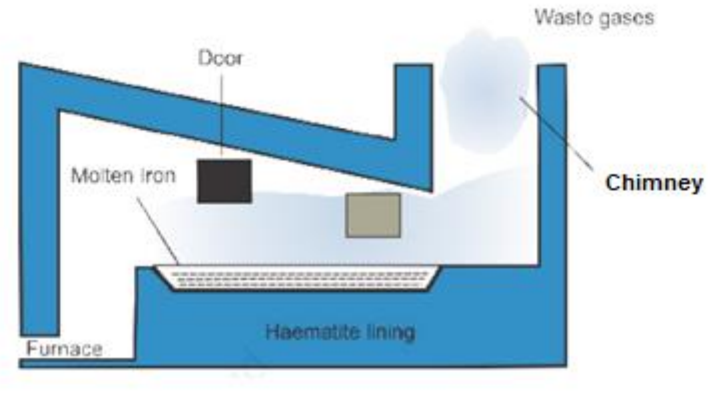
It is manufactured from cast iron by puddling i.e. by heating cast iron in a special type of reverberatory furnace called puddling furnace.

Design of puddling furnace

1. The funance has a low roof to deflect the hot gases and flames downwards and to melt cast iron.
2. The hearth of the furnace is lined with haematite (Fe_2O_3).

Working

1. The cast iron is placed on the hearth.
2. It is melted by hot gases and stirred or puddled with long iron rods called rabbles through the doors to bring it in thorough contact with the lining of the hearth, i.e.Fe_2O_3.
3. The haematite (Fe_2O_3) lining supplies oxygen, necessary for the oxidation of carbon, sulphur, silicon, manganese and phosphorus present in the cast iron.
4. Oxides of carbon and sulphur, being volatile escape out at high temperature.



- **Chemical reactions**

$$3C + Fe_2O_3 \longrightarrow 2Fe + 3CO$$

$$3S + 2Fe_2O_3 \longrightarrow 4Fe + 3SO_2$$

- **Slag formation**

Oxides of manganese, silicon and phosphorus form slags

$$3C + Fe_2O_3 \longrightarrow 2Fe + 3CO$$

$$2Mn + O_2 \longrightarrow 2MnO$$

$$MnO + SiO_2 \longrightarrow MnSiO_3 \text{ (Slag)}$$

$$4P + 5O_2 \longrightarrow 2P_2O_5$$

$$Fe_2O_3 + P_2O_5 \longrightarrow 2FePO_4 \text{ (Slag)}$$

- **Melting point of metal**

With the removal of impurities, the melting point of the metal rises and it becomes a semi-solid mass.

- **Further Purification**

1. Metal is taken out in the form of balls or blooms on the ends of rabbles.
2. While still hot, these balls are subjected to hammering to squeeze out, as much of slag as possible.
3. The product so obtained is known as wrought iron.

Manufacture of Steel

Steel can be manufactured by the following two processes:

1. Open hearth process

Material used

Cast iron, wrought iron or steel scrap

2. Bessemer’s process

Material used

Cast iron only

Other processes

Some other processes are also used to prepare special type of steel from pure wrought iron.

Open Hearth Process

This is the most modern method for the manufacture of steel.

Furnace used

It is carried out in an open hearth furnace.

Construction of furnace

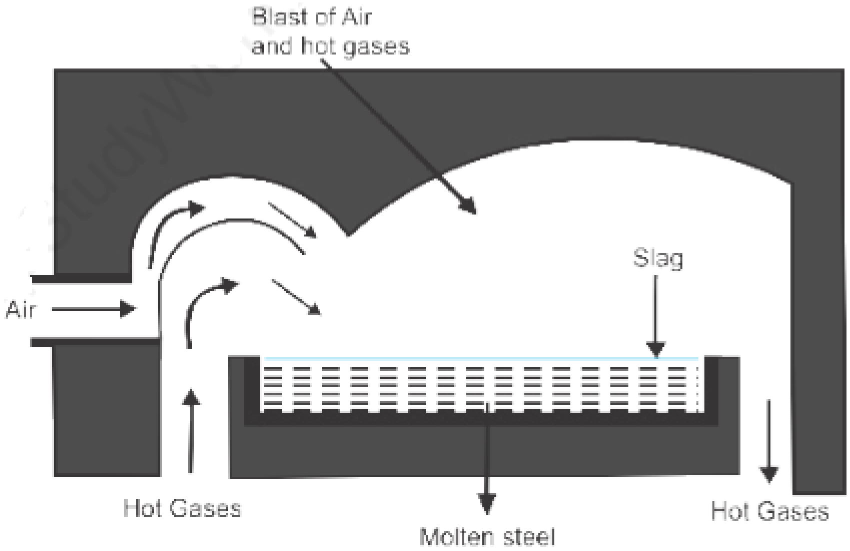
This furnace has a low roof to deflect the hot gases and flames downward to melt the charge.

Principle used

The open hearth furnace works on the regenerative principle of heat economy.

Types of open hearth processes

Open hearth process is of two types:
1. Furnace with acidic lining like SiO_2 is used when the impurities are Mn, Si,etc.
2. Furnace with basic lining like dolomite (CaO, MgO) is used when the impurities are P and S, etc.



Process and chemical reactions

1. A mixture of cast iron, scrap steel and quick lime is charged into the furnace.
2. At about 1600 °C Si, Mn, C, S, and P are burnt out and removed according to the following reactions.

$$C + \frac{1}{2} O_2 \longrightarrow CO$$
$$Si + O_2 \longrightarrow SiO_2$$
$$Mn + \frac{1}{2} O_2 \longrightarrow MnO$$

CO escapes in the flue gases.

- **Slag formation**

Silica (SiO_2) combines with CaO, MnO and FeO to form silicates (slag) which float on the surface of the molten metal.

$$SiO_2 + CaO \longrightarrow CaSiO_3$$
$$SiO_2 + MnO \longrightarrow MnSiO_3$$
$$SiO_2 + FeO \longrightarrow FeSiO_3$$

- **Other reactions**

Phosphorus and sulphur react with Fe_2O_3 to form P_2O_5 and SO_2.

$$2Fe_2O_3 + 3S \longrightarrow 4Fe + 3SO_2$$
$$5Fe_2O_3 + 6P \longrightarrow 10\,Fe + 3P_2O_5$$

- **Slag formation**

The oxides produced react with calcium oxide to form slag again.

$$P_2O_5 + 3CaO \longrightarrow Ca_3(PO_4)_2 \text{ (Fertilizer)}$$

It is ground as powder and sold as a fertilizer

$$SO_2 + CaO \longrightarrow CaSO_3$$

- **Further processing**

Samples are taken at intervals and the percentage of carbon in the steel is determined regularly. When this is reduced to about 0.1%, the calculated weight of ferromanganese (Fe, Mn, C) is added.

Advantage of ferromanganese

Manganese desulphurises the steel. Carbon raises the carbon contents to the required values. After giving time for mixing, a little more ferromanganese is added and the charge is allowed to run into moulds where it solidifies to ingots.

Duration

The whole process takes about 10 hours.

Bessemer's Process

Furnace

The furnace used in this process is called Bessemer's converter.

Furnace design

1. It is a pear shaped vessel made of steel plates.
2. At the bottom the converter is provided with a number of holes through which hot air can be introduced.
3. The converter is held on a central axis so that it can be tilted in any desired position for feeding and pouring out the finished materials.

Working and chemical reactions

1. Molten pig or cast iron (25 to 30 tons) from the blast furnace is fed into the converter
2. Hot air blast is injected through the perforated base. This oxidizes carbon, silicon, and manganese.

$$C + \frac{1}{2} O_2 \longrightarrow CO$$

$$Si + O_2 \longrightarrow SiO_2$$

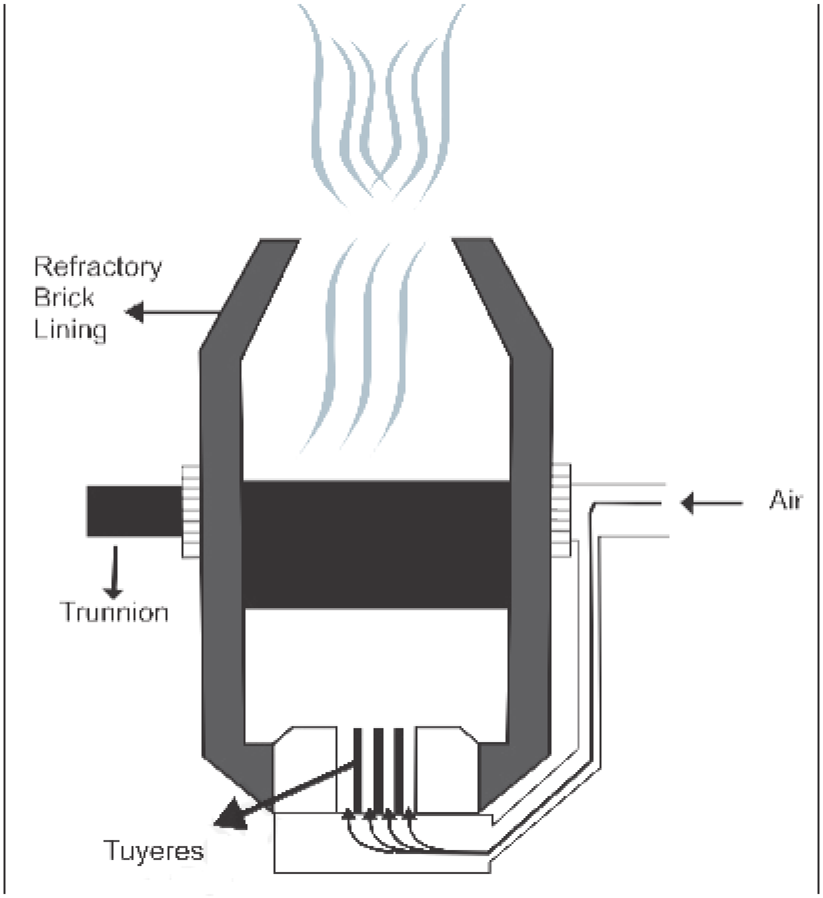
$$2Mn + O_2 \longrightarrow 2MnO$$

- **Slag formation**

The oxides form a slag of $MnSiO_3$.

$$MnO + SiO_2 \longrightarrow MnSiO_3$$

The heat evolved during the oxidation is enough to keep iron in the molten state.



- **Other reactions**

CO produced burns at the mouth of the converter with a blue flame. Iron is partly oxidized to ferric oxide (Fe_2O_3) which also extracts carbon from cast iron to form CO.

$$4Fe + 3O_2 \longrightarrow 2Fe_2O_3$$

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3\,CO$$

Within 10 to 15 minutes the flame due to CO subsides indicating that the carbon is completely oxidized.

- **Addition of ferromanganese**

Ferromanganese is added to correct the proportion of carbon to obtain the desired qualities. A blast of air is continued for a moment to ensure thorough mixing.

Advantage of ferromanganese

The addition of Mn imparts increased hardness and tensile strength.

- **Removal of entrapped gases**

In order to remove entrapped bubbles of gases (blow holes), such as O_2, N_2, CO_2, a little aluminum or ferrosilicon is also added. Aluminum removes nitrogen as nitride.

$$2\,Al + N_2 \longrightarrow 2AlN$$

- **Collection of steel**

1. At the end of the operation, the molten steel is poured out into moulds for casting.
2. Such castings are free from any defect.

Electrochemical theory of corrosion

Definition of corrosion

Any process of chemical decay of metals due to the action of surrounding medium is called corrosion.

Electrochemical Theory

Factor of corrosion

The impurities present in the metal promote corrosion.

Explanation

Consider what happens when copper and aluminium come in contact with one another in moist air. After sometime, we will notice that aluminium gets corroded while copper remains intact. This can be explained by the electrochemical theory. According to this theory, moisture and CO_2 are present on the surface of the metal.

Equation

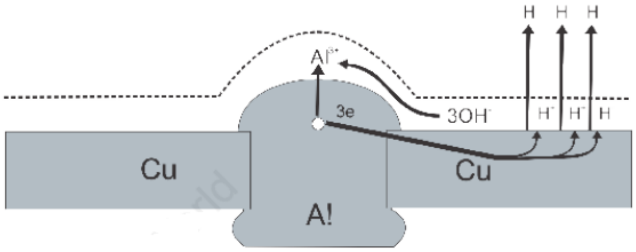
Water ionizes into H^+ and OH^- ions. CO_2 dissolves in water forming H_2CO_3 which ionizes as follows:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

Galvanic cell establishment

Copper and aluminium are immersed in the solution containing H^+, OH^- and HCO_3^- ions. This forms a galvanic cell in which aluminium releases electrons and changes to Al^{3+} ion (being more reactive than Cu) i.e it acts as positive electrode and Cu acts as a negative electrode.

Aluminium ions attract OH^- ion to form, $Al(OH)_3$ i.e it starts dissolving. The H^+ ions present on the Cu receive the electrons and released as H_2. Aluminium corrodes rapidly when in contact with copper which is lower in electrochemical series.



Conclusion

When an active metal Al (higher in the electrochemical series) comes in contact with less active metal Cu (lower in the electrochemical series) a galvanic cell is established. Active metal corrodes rapidly, while the other remains intact.

$KMnO_4$ as an Oxidizing Agent

(a) Reaction with H_2S

It oxidizes H_2S to sulphur.

$$\begin{array}{c}
2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O] \\
5H_2S + 5[O] \longrightarrow 5H_2O + 5S \\
\hline
2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 5S + 8H_2O
\end{array}$$

(b) Reaction with $FeSO_4$

It oxidizes $FeSO_4$ to $Fe_2(SO_4)_3$

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

(c) Reaction with Oxalic Acid

It oxidizes oxalic acid to CO_2 and H_2O

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

(d) Reaction with KOH

When an alkaline solution of $KMnO_4$ is heated, O_2 is evolved.

$$4KMnO_2 + 4KOH \rightarrow 4K_2MnO_4 + 2H_2O + O_2$$

Chapter 7

Fundamental Principles of Organic Chemistry

Organic Compounds and their properties

Definition

Organic chemistry is that branch of chemistry which deals with the study of compounds of carbon and hydrogen (hydrocarbons) and their derivatives.

Some Features of Organic Compounds

Following are the features of organic compounds:

1. Peculiar nature of carbon

Carbon forms a large number of compounds due to its unique property of linking with other carbon atoms to form long chains or rings. This self-linking property of carbon is called catenation. Carbon also forms stable single and multiple bonds with other atoms like oxygen, nitrogen and sulphur, etc. It can form numerous compounds of various sizes, shapes and structures.

2. Non-ionic Character of Organic Compounds

Organic compounds are generally covalent compounds and do not give ionic reactions.

3. Similarity in Behaviour

There exists a close relationship between different organic compounds which has reduced the study of millions of compounds to only a few homologous series.

4. Complexity of Organic Compounds

Organic molecules are usually large and structurally more complex. For example, starch has the formula $(C_6H_{10}O_5)_n$ where n may be several thousands. Proteins are very complex molecules having molecular masses ranging from a few thousands to a million.

5. Isomerism

Organic compounds are represented by the same molecular formula but different structural formulas called isomerism.

6. Rates of Organic Reactions

The reactions involving organic compounds are slow and in general the yields are low. The slow rate of the organic reactions is due to the molecular nature of organic compounds.

7. Solubility

Most organic compounds are insoluble in water and dissolve readily in non-polar organic solvents, such as, benzene, petroleum ether, etc.

Classification of Organic Compounds

They may be broadly classified into the following classes:

1. Open chain or Acyclic compounds.

2. Closed chain or Cyclic (or ring) compounds.

(1) Open Chain or Acyclic Compounds

This type of compounds contains an open chain of carbon atoms. The chains may be branched or non-branched (straight chain). The open chain compounds are also called aliphatic compounds.

Straight Chain (or non- branched) Compounds

Those organic compounds in which the carbon atoms are connected in series from one to the other.

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$

n-Butane

$H_2C{=}CH\text{-}CH_2\text{-}CH_3$

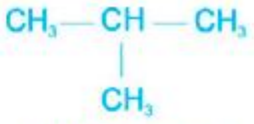
1-Butene

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$

1-Butanol

Branched chain compounds

Those organic compounds in which the carbon atoms are attached on the sides of chain.

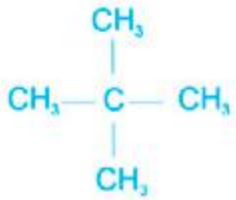


$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

2-Methylpropane
Isobutane

$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH_2$$

2-Methylpropene
(Isobutylene)



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

2.2 Dimethylpropane(neo-Pentane)

(2) Closed Chain Compounds or Cyclic Compounds

These compounds contain closed chains or rings of atoms and are known as cyclic or ring compounds. These are of two types:

(a) Homocyclic or carbocyclic compounds

(b) Heterocyclic compounds

(a) Homocyclic or Carbocyclic Compounds

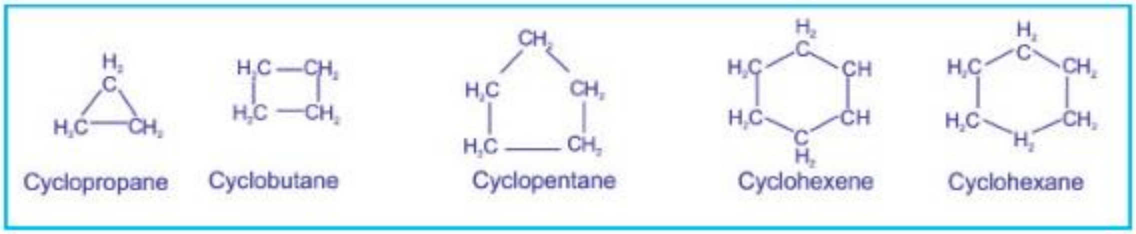
The compounds in which the ring consists of only carbon atoms, Homocyclic or carbocyclic compounds. Homocyclic compounds are further classified as:

1. Alicyclic compounds

2. Aromatic compounds

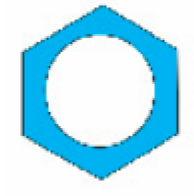
(1) Alicyclic Compounds

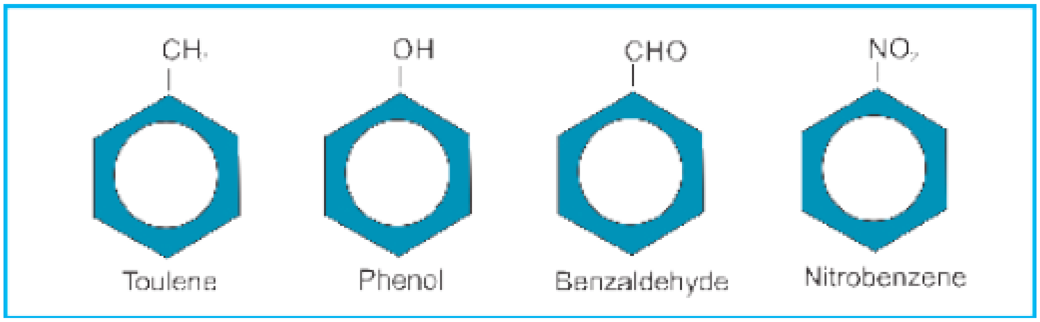
The homocyclic compounds which contain a ring of three or more carbon atoms and resembling aliphatic compounds are called alicyclic compounds. The saturated alicyclic hydrocarbons have the general formula C_nH_{2n}.



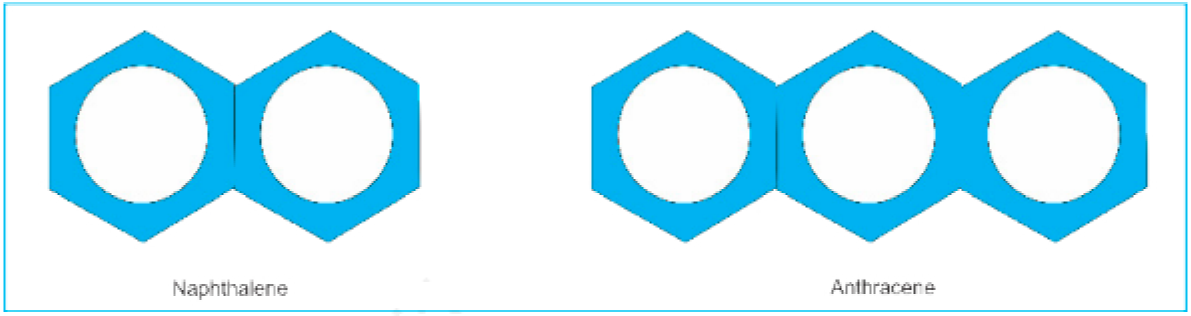
(2) Aromatic Compounds

These carbocyclic compounds contain at least one benzene ring. The aromatic compounds may have a side-chain or a functional group attached to the ring.



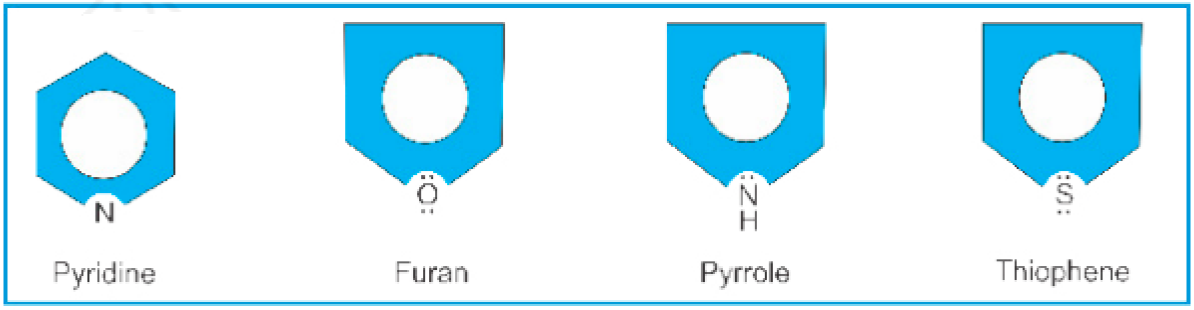


The aromatic compounds may also contain more than one benzene rings fused together.



(b) Heterocyclic Compounds

The compounds in which the ring consists of atoms of more than one kind are called heterocyclic compounds or heterocycles. The atom other than carbon viz, N, O, or S, present in the ring is called a hetero atom.



Cracking of Petroleum

Need of Cracking

The fractional distillation of petroleum yields only about 20% gasoline. Due to its high demand this supply is augmented by converting surplus supplies of less desirable petroleum fractions such as kerosene oil and gas oil into gasoline by a process called cracking.

Definition

It is defined as breaking of higher hydrocarbons having high boiling points into a variety of lower hydrocarbons, which are more volatile (low boiling).

Example:

A higher hydrocarbons $C_{16}H_{34}$ splits according to the following reaction:

$$\underset{\text{Alkane}}{C_{16}H_{34}} \xrightarrow[700^{o}]{\text{Heat}} C_7H_{16} + 3CH_2{=}CH_2 + CH_3\text{-}CH{=}CH_2$$

In cracking C-C bonds in long chain alkane molecules are broken, producing smaller molecules of both alkanes and alkenes.

Types of Cracking

Following are the types of cracking:

1. Thermal cracking

2. Catalytic cracking

3. Steam cracking

1. Thermal Cracking

Definition

Breaking down of large molecules by heating at high temperature and pressure is called Thermal Cracking.

Products

It is particularly useful in the production of unsaturated hydrocarbons such as ethene and propene.

2. Catalytic Cracking

Definition

Higher hydrocarbons can be cracked at lower temperature (500°C) and lower pressure (2 atm), in the presence of a suitable catalyst. This is called catalytic cracking.

Products

A typical catalyst used for this purpose is a mixture of silica (SiO_2) and alumina (AI_2O_3). Catalytic cracking produces gasoline of higher octane number and, therefore, this method is used for obtaining better quality gasoline.

3. Steam Cracking

Definition

In steam cracking higher hydrocarbons in the vapour phase are mixed with steam, heated for a short duration to about 900 °C and cooled rapidly.

Products

The process is suitable for obtaining lower unsaturated hydrocarbons.

Other Advantages of Cracking

1. Besides increasing the yield of gasoline, cracking has also produced large amounts of useful by-products, such as ethene, propene, butene and benzene.
2. These are used for manufacturing drugs, plastics, detergents, synthetic fibres, fertilizers, weed killers and important chemicals like ethanol, phenol and acetone.

Reforming

Cause of Knocking in Engine

The gasoline fraction present in petroleum is generally not of good quality. When it burns in an automobile engine, combustion can be initiated before the spark plug fires. This produces a sharp metallic sound called knocking which greatly reduces the efficiency of an engine.

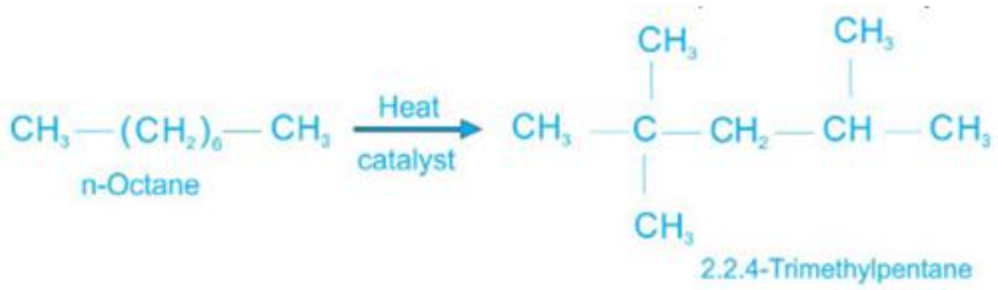
Importance of Octane Number

1. The quality of a fuel is indicated by its octane number.
2. As the octane number increases, the engine is less likely to produce knocking.
3. Straight- chain hydrocarbons have low octane numbers and make poor fuels.
4. Experiments have shown that isooctane or 2,2,4-trimethyl pentane burns very smoothly in an engine and has been arbitrarily given an octane number of 100.

Definition

The octane number of gasoline is improved by a process called reforming. It involves the conversion of straight chain hydrocarbons into branched chain by heating in the absence of oxygen and in the presence of a catalyst.

Chemical Equation



Catalyst Used

Tetraethyl lead $(C_2H_5)_4Pb$, is an efficient antiknock agent

Disadvantage of Tetraethyl lead

Lead oxide is reduced to metallic lead which is discharged into the air through the exhaust pipe and causes air pollution.

Hybridization

Definition

Hybridization is the concept in which atomic orbitals of different energy and shape intermix to form a new set of orbitals of same shape and energy.

OR

Atomic orbitals differing slightly in energy intermix to form new orbitals, which are called hybrid atomic orbitals. They differ from the parent atomic orbitals in shape and possess specific geometry.

Types

There are three basic types of hybridization:

1. sp^3
2. sp^2
3. sp

sp^3 Hybridization

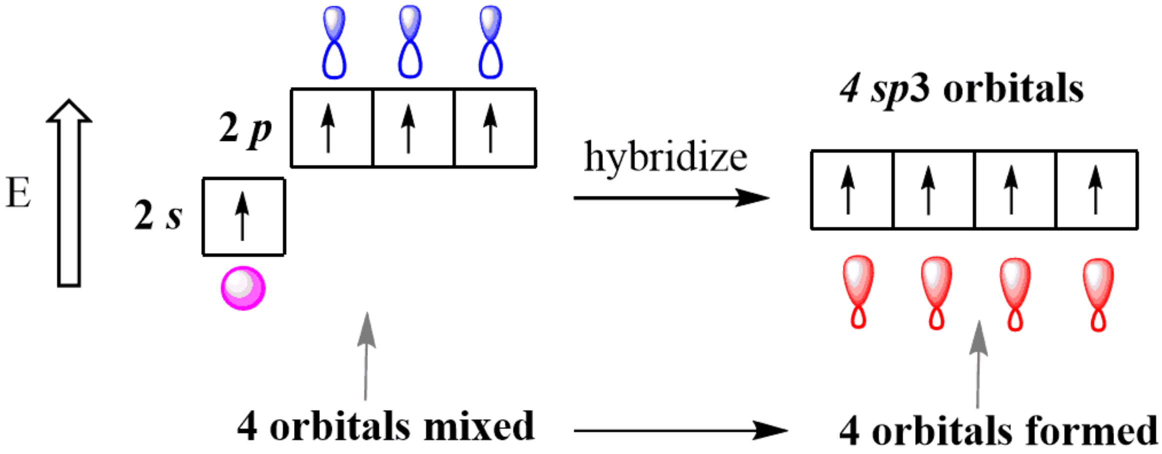
Definition

One s and three p orbitals intermix to form a set of four equivalent sp^3 hybrid orbitals.

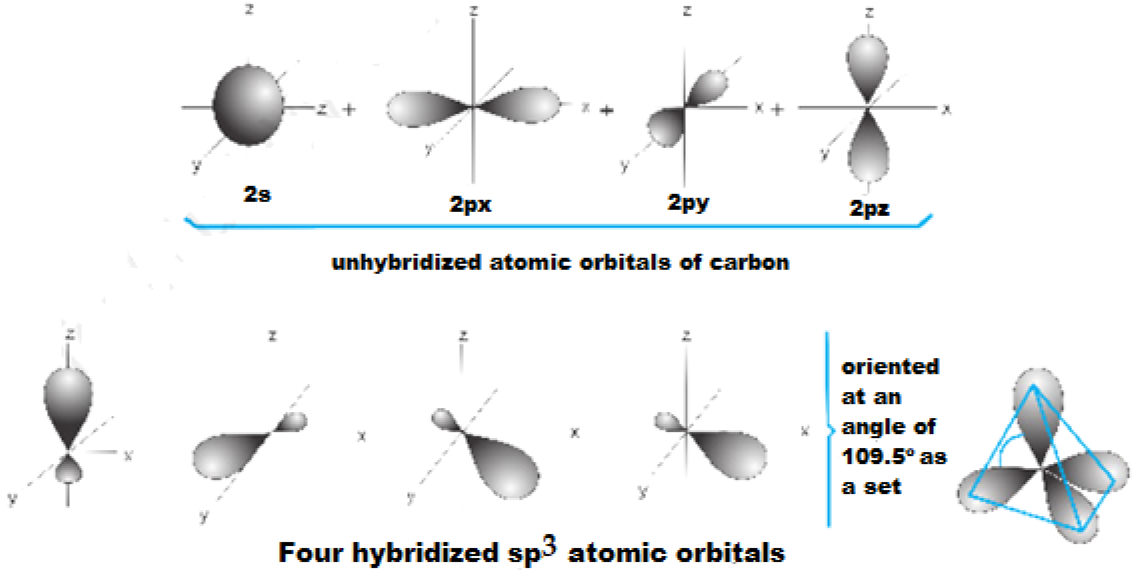
Examples

CH_4, C_2H_6, NH_3 and H_2O

Methane



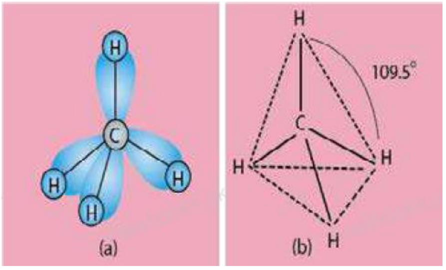
Energy for excitation
Before excitation the carbon should make two covalent bonds releasing an adequate amount of energy. After excitation, however, it will form four covalent bonds releasing almost double the amount of energy. This excess energy is more than that needed to excite the carbon atom. Electron from 2s jumps to empty $2p_z$ giving a total of four unpaired electrons.



Explanation

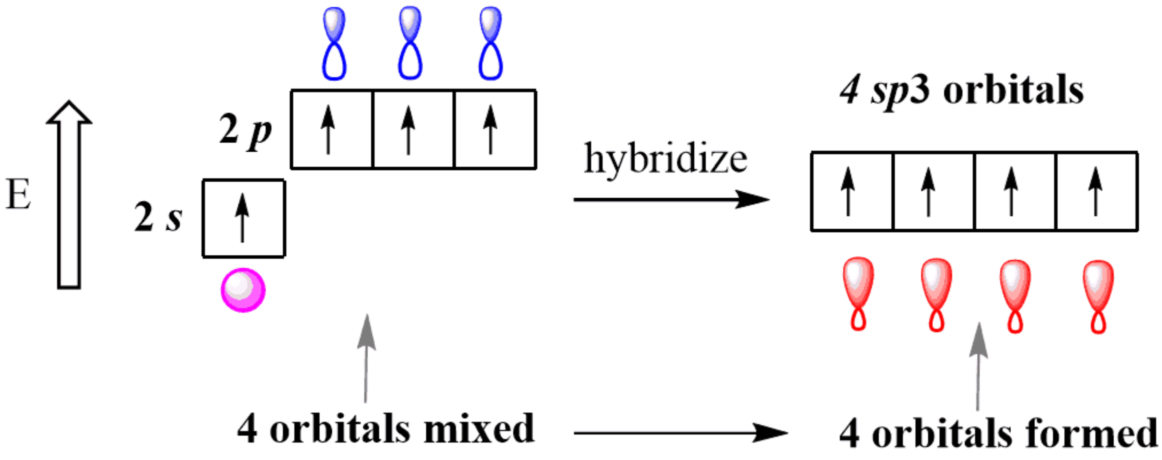
Hydrid orbitals: Four sp^3 hybrid orbitals consisting of two lobes formed due to overlap of one s and three p orbitals. Each orbital has one larger lobe and the other smaller lobe.
Overlap of orbitals: Each sp^3 hybrid orbital combines with s orbital of hydrogen to give sp^3-s sigma bonds.
Geometry: Tetrahedral geometry with carbon at center.
Bond angles: Total six bond angles of 109.5°.
Total bonds: Four sigma bonds formed by the overlap of sp^3 hybrid orbitals of carbon with 1s orbitals of four hydrogen atoms.
Arrangement of bonds: The four C-H bonds which result from sp^3-s overlap are directed towards the corners of a regular tetrahedron. All the four hydrogen atoms do not lie in the same plane.

Faces, corners, edges: The tetrahedral structure of CH_4 has four faces, four corners and six edges.



Structure of methane

Ethane



Explanation

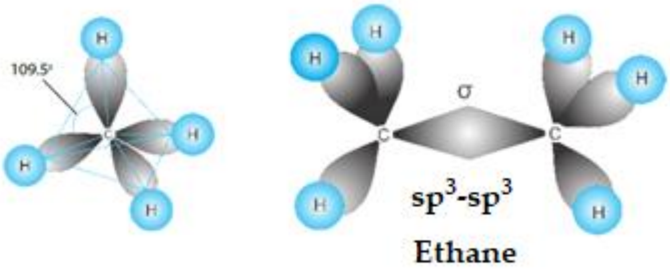
Hybrid orbitals: Each carbon in ethane is sp^3 hybridized. The four sp^3 hybrid orbitals are formed due to overlap of one s and three p orbitals.

Overlap of orbitals: The two tetrahedrons of each carbon are joined together by sp^3-sp^3 sigma bond. The other three sp^3 orbitals of each carbon overlap with s orbital of each hydrogen to form sp^3-s sigma bonds.

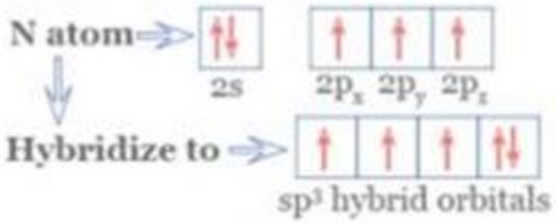
Geometry: Each carbon is hybridized to give a tetrahedron.

Total bonds: One sp^3-sp^3 sigma bond and six sp^3-s sigma bonds.

Bond angles: Bond angle in each tetrahedron is 109.5°.



Ammonia



Explanation

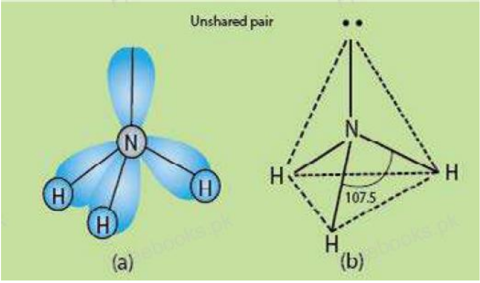
Hybrid orbitals: One s and three p orbitals of nitrogen atom hybridize to form four sp^3 hybrid atomic orbitals.

Overlap of orbitals: Three sp^3 orbitals overlap with three s-orbitals of hydrogen atoms.

Geometry: One corner of the tetrahedron is occupied by lone pair of electrons. The other three corners have single electron. Shape of ammonia is a pyramidal molecule due to repulsion of bond pairs by lone pair of electrons.

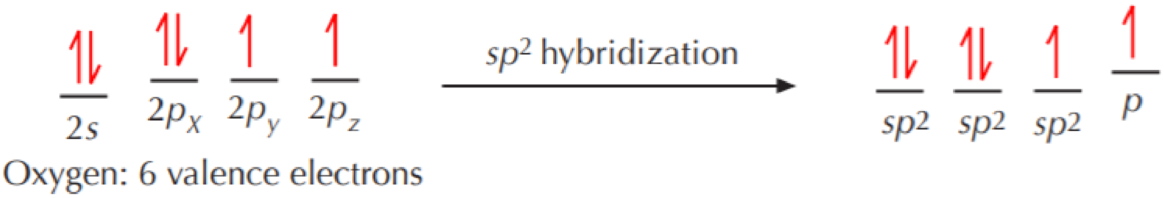
Total bonds: Three sigma bonds formed by sp^3-s orbital overlap.

Bond angle: The bond angle in ammonia is 107.5°.



Structure of ammonia

Water



Explanation

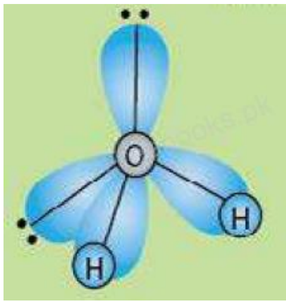
Hybrid orbitals: 2s and three 2p orbitals of oxygen hybridize to form four sp^3 hybrid orbitals.

Overlap of orbitals: The sp^3 orbitals overlap with s orbital of H atoms to form two sigma bonds.

Geometry: The hybrid orbitals will have a tetrahedral arrangement. The two corners of the tetrahedron are occupied by lone pair of electrons and the other two corners by single electron. The molecule of water has bent or angular structure (distorted tetrahedron) because of the repulsion of lone pairs on bond pairs.

Total bonds: Two sigma bonds formed by sp^3-s orbital overlap.

Bond angle: The bond angle in water is 104.5°.



Structure of water

sp^2 hybridization

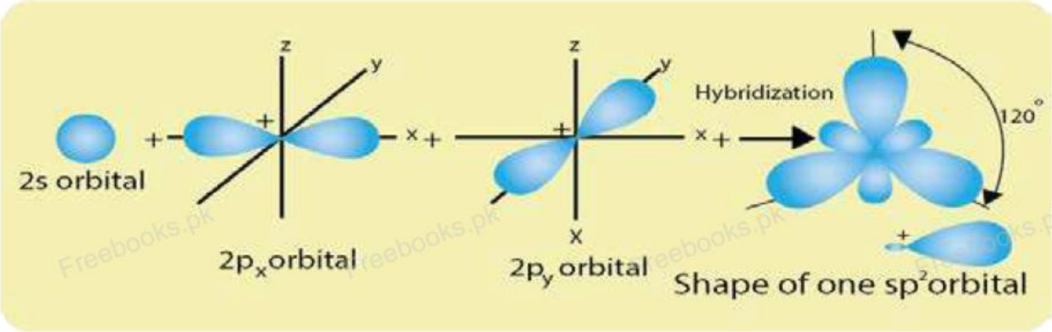
Definition

In sp^2 hybridization, one ‘s’ and two ‘p’ atomic orbitals of an atom intermix to form three orbitals called sp^2 hybrid orbitals.

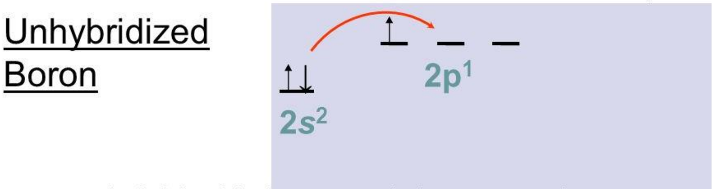
Examples

BF_3

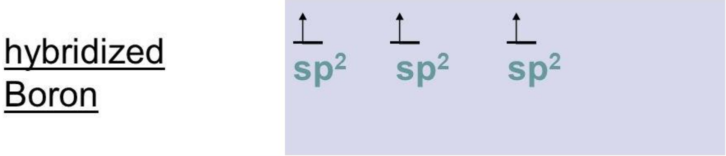
Ethene (ethylene)



Boron Trifluoride



For BF_3, 3 hybrid orbitals are needed, so 3 atomic orbitals are required as follows: $(s + p + p) = sp^2$



Explanation

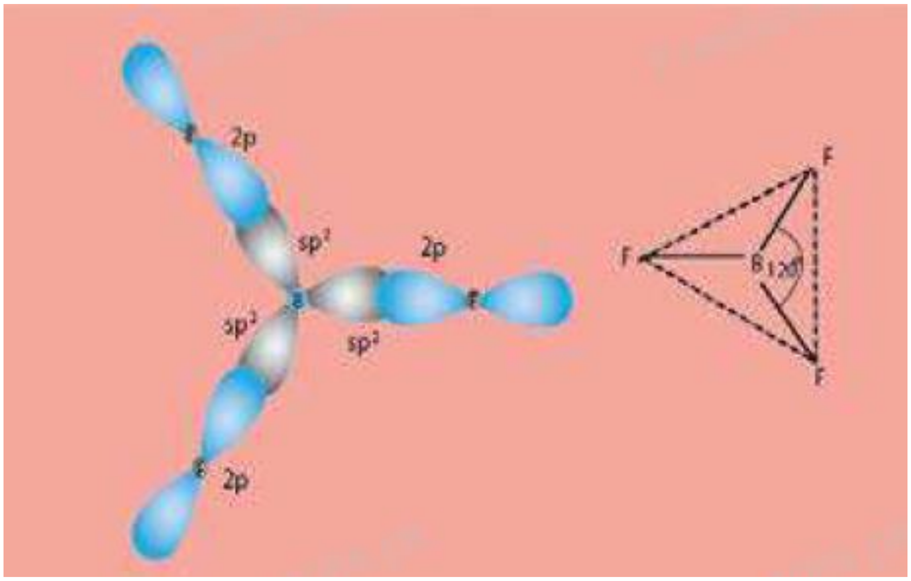
Hybrid orbitals: One s and two 2p atomic orbitals of boron overlap to form three sp^2 hybrid orbitals.

Overlap of orbitals: BF_3 is formed by the overlap of three half-filled sp^2 hybrid orbitals of boron with $2p_z$ orbitals of three fluorine atoms.

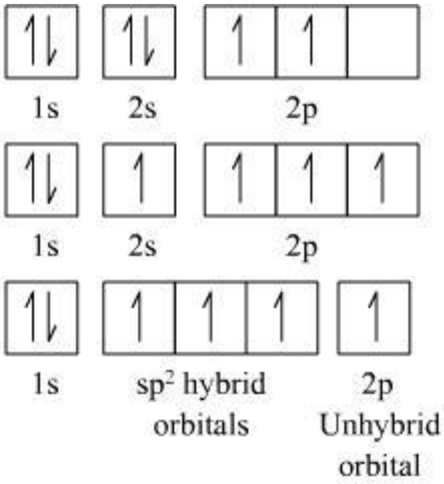
Geometry: The structure is triangular planar.

Total bonds: Three bonds formed by sp^2-$2p_z$ orbital overlap.

Bond angle: The three bond angles are each of 120°.



Ethene/Ethylene $H_2C=CH_2$



Explanation

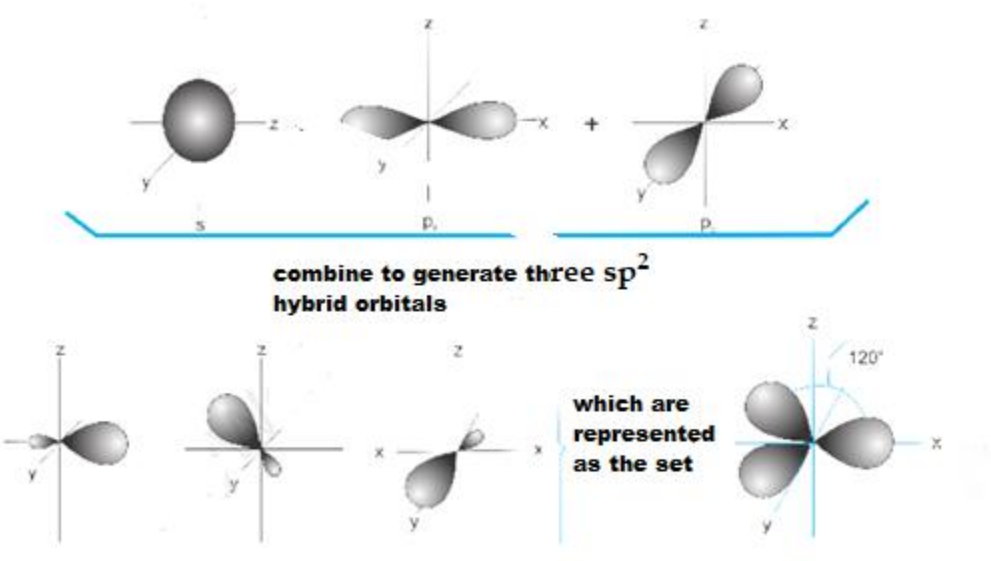
Hybrid orbitals: Three sp^2 hybrid orbitals formed by one s and two 2p orbitals of carbon.

Unhybridized orbitals: The unhybridized 2p$_z$ orbital will remain perpendicular to the hybridized orbitals.

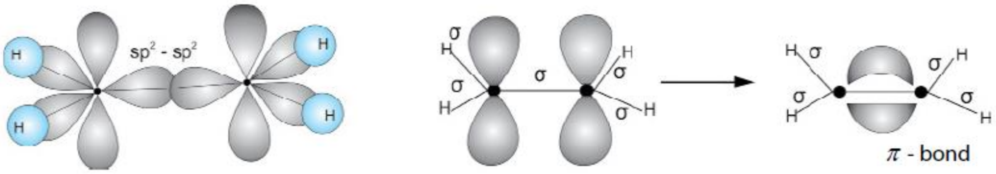
Overlap of orbitals: sp^2 hybrid orbital of each carbon overlaps to give sp^2-sp^2 sigma bond and the other two sp^2 orbitals overlap with 1s orbitals of hydrogen to give sp^2-s sigma bonds. The unhybridized 2p$_z$ orbitals overlap sideways to give a π-bond.

Geometry: Trigonal planar.

Bond angle: The bond angle between any two sp^2 hybrid orbitals is 120°.



Total bonds: One sp^2-sp^2 sigma bond and two sp^2-s sigma bonds. One $2p_z$-$2p_z$ π-bond.



Structure of ethene

sp hybridization

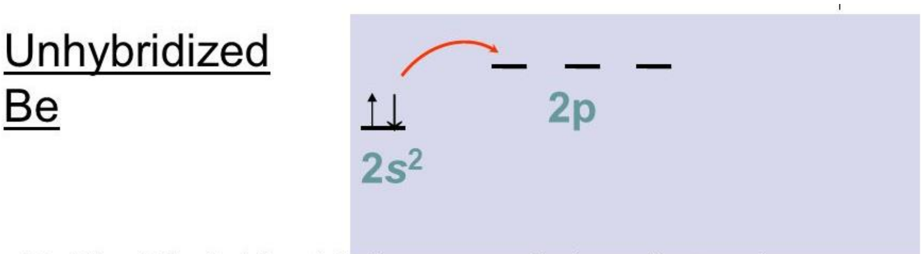
Definition

In sp hybridization, one ‘s’ and one ‘p’ orbitals intermix to form two sp-hybrid orbitals called sp hybrid orbitals.

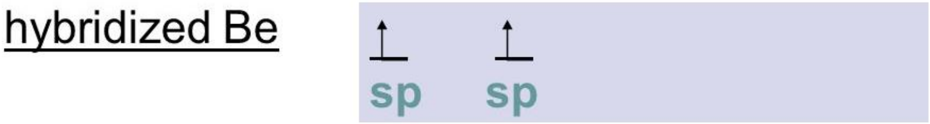
Examples

Ethylene, $BeCl_2$

Beryllium Dichloride

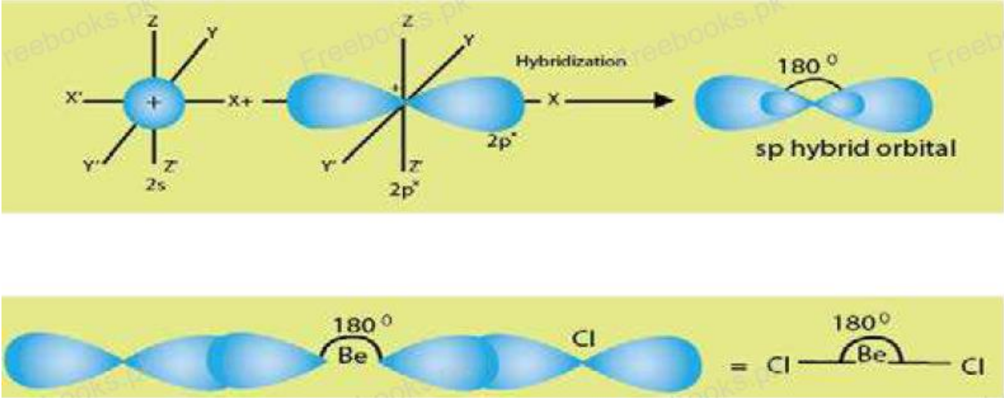


For $BeCl_2$, 2 hybrid orbitals are needed, so 2 atomic orbitals are required as follows: (s + p) = sp



Explanation

- **Hybrid orbitals:** One s and one p orbital of Be overlap to give two sp hybrid orbitals.
- **Overlap of orbitals:** Two sp hybrid orbitals of Be atom overlap with the half-filled $3p_z$-orbitals of chlorine atoms.
- **Geometry:** Linear shape.
- **Total bonds:** Two sp-$3p_z$ sigma bonds.



Structure of Beryllium dichloride

- **Bond angle:** The Cl-Be-Cl bond angle is 180°.

Ethyne/Acetylene HC≡CH

Hybrid orbitals: One 2s and one 2p orbitals of the carbon atom mix together to give rise to two degenerate sp hybridized atomic orbitals.

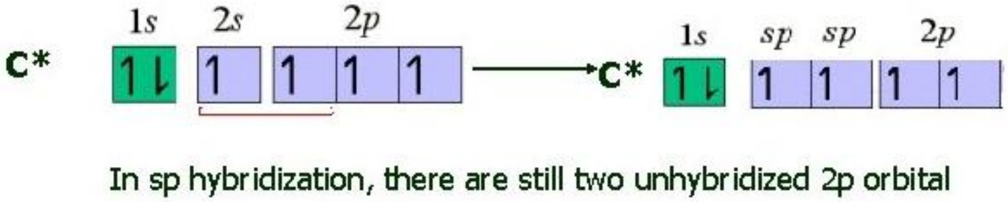
Unhybridized orbitals: The unhybridized 2py and 2pz orbitals are perpendicular to the hybridized orbitals.

Overlap of orbitals: Two sp hybridized carbon atoms join together to form a sigma bond by sp-sp overlap. The other sp orbital forms a sigma bond with 1s orbital of hydrogen atom. The two unhybridized p orbitals on each carbon atom overlap sideways give two π -bonds.

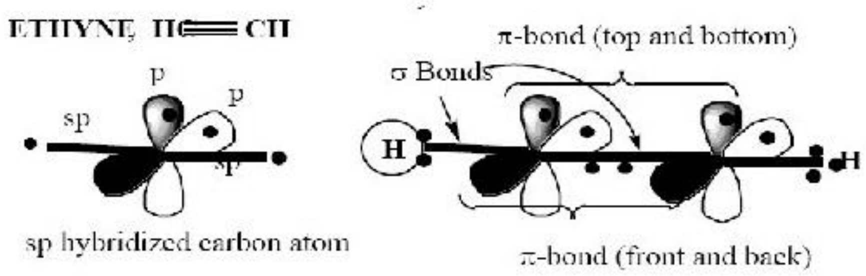
Geometry: Linear shape.

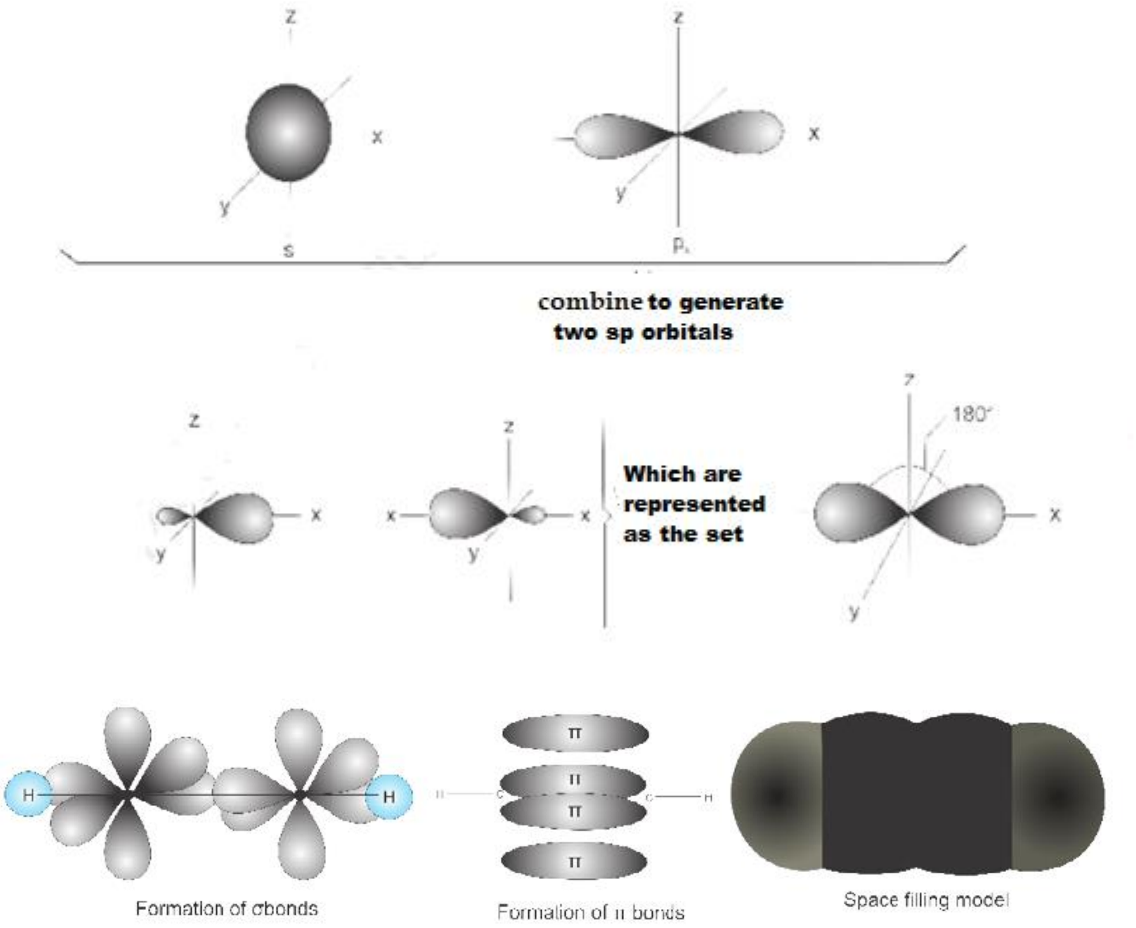
Total bonds: One sp-sp sigma bond and two sp-s sigma bonds. Two, $2p_y$-$2p_y$ and $2p_z$-$2p_z$, π-bonds.

Bond angles: These orbitals have a bond angle of 180°.



In sp hybridization, there are still two unhybridized 2p orbital





Isomerism

Definition

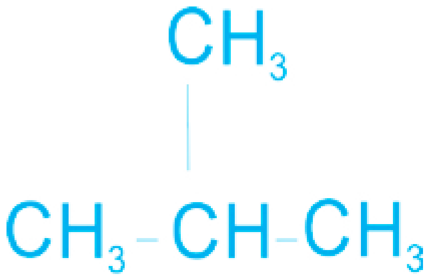
Two or more compounds having the same molecular formula but different structural formulas and properties are said to be isomers and the phenomenon is called isomerism.

Example

Butane (C_4H_{10}) has two isomers.

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$

n-Butane



$$\overset{\displaystyle CH_3}{\overset{|}{}} \quad CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3$$

Isobutane

Types of Isomerism

(1) Structural Isomerism

The structural isomerism arises due to the difference in the arrangement of atoms within the molecule.

Types of structural isomerism

The structural isomerism can be exhibited in five different ways.

(i) Chain Isomerism

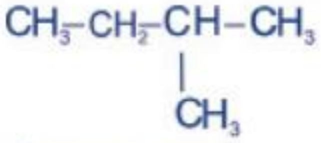
This type of isomerism arises due to the difference in the nature of the carbon chain.

Example

Pentane (C_5H_{12}), has following arrangements possible.

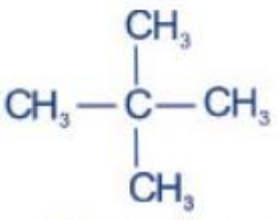
$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$

n-Pentane



$CH_3\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_3$

Isopentane



$CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}\text{—}CH_3$

Neopentane

(ii) Position Isomerism

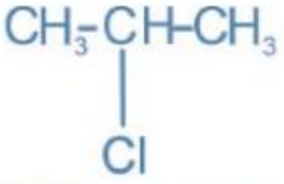
This type of isomerism arises due to the difference in the position of the same functional group on the carbon chain.

Examples

Chloropropane has two positional isomers.

$CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl$

1-Chloropropane



$CH_3\text{-}\underset{\displaystyle Cl}{\underset{|}{CH}}\text{-}CH_3$

2-Chloropropane

Butene (C_4H_8) has two positional isomers.

$CH_3\text{-}CH_2\text{-}CH{=}CH_2$

l-Butene

$CH_3\text{-}CH{=}CH\text{-}CH_3$

2-Butene

(iii) Functional Group Isomerism

The compounds having the same molecular formula but different functional groups are said to exhibit functional group isomerism.

Example

There are two compounds having the same molecular formula C_2H_6O, but different arrangement of atoms.

$CH_3\text{-}O\text{-}CH_3$

Dimethyl ether

$CH_3\text{-}CH_2\text{-}OH$

Ethyl alcohol

(iv) Metamerism

This type of isomerism arises due to the unequal distribution of carbon atoms on either side of the functional group.

Example

Diethyl ether and methyl n-propyl ether.

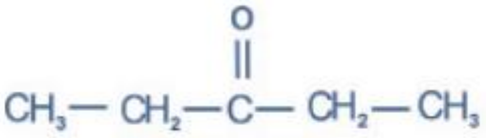
$CH_3 - CH_2 - O - CH_2 - CH_3$

Diethyl ether

$CH_3 - O - CH_2 - CH_2 - CH_3$

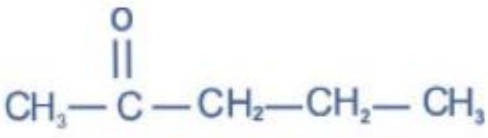
Methyl n-propyl ether

For a ketonic compound $C_5H_{10}O$, the two metamers are possible.



$CH_3 - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2 - CH_3$

Diethyl ketone

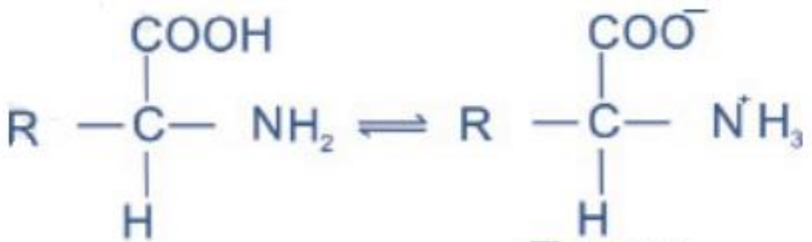


$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2 - CH_2 - CH_3$

Methyl n-propyl ketone

(v) Tautomerism

This type of isomerism arises due to shifting of proton from one atom to other in the same molecule.



$$R - \underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle COOH}{|}}{C}} - NH_2 \rightleftharpoons R - \underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle COO^-}{|}}{C}} - \overset{+}{N}H_3$$

Zwitterion

(2) Cis-trans Isomerism or Geometric Isomersim

Definition

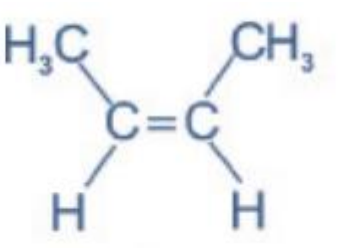
Such compounds which possess the same structural formula, but differ with respect to the positions of the identical groups in space are called cis-trans isomers and the phenomenon is known as the cis-trans or geometric isomerism.

Conditions

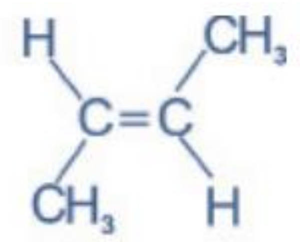
The necessary and sufficient condition for a compound to exhibit geometric isomerism is that the two groups attached to the same carbon must be different.

Examples

2-Butene can exist in the form of cis and trans isomers.

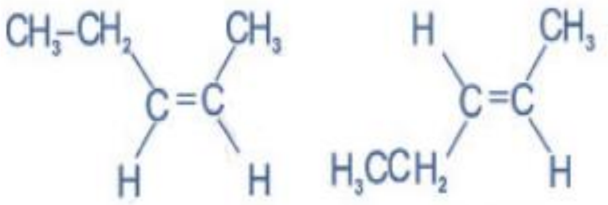


Cis



Trans

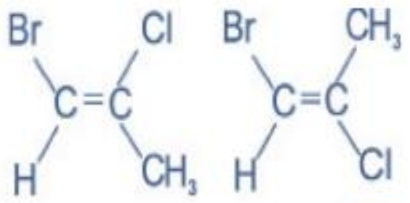
Similarly 2-pentene and l-bromo-2-chloropropene also show cis-trans isomerism.



Cis

Trans

2-Pentene



Cis

Trans

1-bromo-2-chlororpopene

In the cis-form, the similar groups lie on the same side of the double bond.

In the trans-form, the similar groups lie on the opposite sides of the double bond.

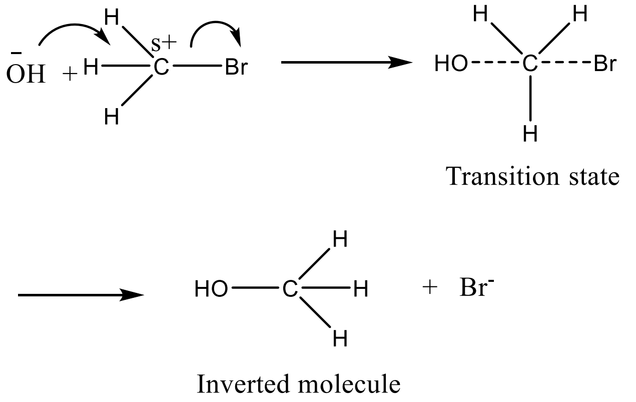
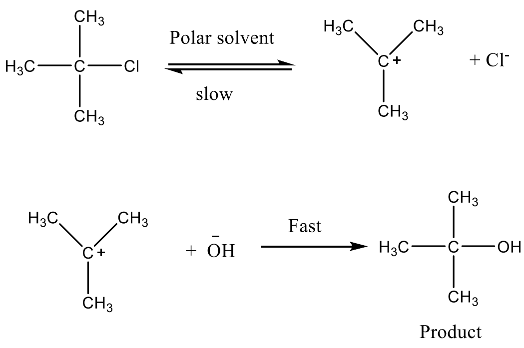
No free rotation

Two carbon atoms joined by a single bond are capable of free rotation about it. When two carbon atoms are joined by a double bond, they cannot rotate freely. The relative positions of the various groups attached to these carbon atoms get fixed and gives rise to cis- trans isomers. The rotation of two carbon atoms joined by a double bond could happen only if the π bond breaks. This costs too much energy making geometric isomers possible.

Chapter 10

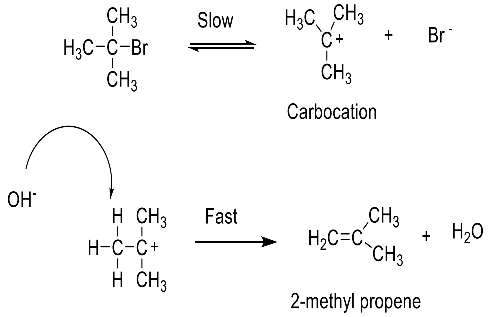
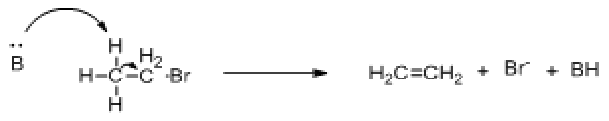
Alkyl halides

Comparison of S_N1 and S_N2 reactions

Sr No	S_N2	S_N1
1.	**Name** It is called nucleophilic substitution bimolecular	**Name** It is called nucleophilic substitution unimolecular
2.	**Number of steps** This is a single step mechanism	**Number of steps** This is a two step mechanism
3.	**Extent** The extent of bond formation is equal to the extent of bond breakage	**Extent** The extent of bond formation is not equal to the extent of bond breakage
4.	**Mechanism**  Transition state Inverted molecule	**Mechanism**  50% inversion
5.	As soon as the nucleophile starts attacking the electrophilic carbon of the substrate, the bond with which the leaving group is attached starts breaking	The first step is the reversible ionization of the alkyl halide in the presence of an aqueous ethyl alcohol. This step provides a carbocation as an intermediate. In the second step this carbocation is attacked by the nucleophile to give the product
6.	**Direction of attack of nucleophile** Nucleophile attacks from the side which is opposite to the leaving group	**Direction of attack of nucleophile** The intermediate carbocation is a planar specie allowing the nucleophile to attack on it from both the directions with equal ease
7.	**Configuration of product** 100% inverted product	**Configuration of product** 50% inversion of configuration and 50% retention of configuration in product
8.	**Hybridization** The substrate carbon atom changes its state of hybridization from tetrahedral sp^3 to planar sp^2 for a short time	
9.	**Molecularity** Two molecules are participating in this step so it is called a bimolecular reaction Molecularity= 2	**Molecularity** Only one molecule participates in the rate determining step (slow step) so it is unimolecular reaction.

		Molecularity=1
10.	**Rate of Reaction** Rate=k[Alkyl halide]^1[Nucleophile]^1	**Rate of Reaction** Rate=k[Alkyl halide]^1
11.	**Order of Reaction** 1+1=2 Second order reaction	**Order of Reaction** First order reaction
12.	Primary alkyl halides give SN2	Tertiary alkyl halides give SN1
	Secondary alkyl halides give both SN1 and SN2 depending on conditions	

Difference between E1 and E2 Reactions

Sr No	E1	E2
1	It is a two step elimination reaction	It is a one step elimination reaction
2	It is unimolecular reaction	It is bimolecular reaction
3	It is carried out along with S_N1	It is carried out along with S_N2
4	It is given by tertiary alkyl halides	It is given by primary alkyl halides
	Secondary alkyl halides give both E1 and E2	
5		
	Nature of the product in both the cases is an alkene	
6	Molecularity of the reaction is 1	Molecularity of the reaction is 2
7	Rate=k[Alkyl halide]	Rate=k[Alkyl halide][Base]
8	Order of the reaction is 1	Order of the reaction is 2

Common points between E1 and E2 reactions

- In both elimination reactions a new C-C π bond is formed and a C-H bond and a C-leaving group bond is broken.
- In both elimination reactions a species acts as a base to remove a proton to form the new π bond.
- With increase of temperature we get elimination reactions.

Chapter 15

Commom Chemical Industries in Pakistan

Fertilizers

Definition

Fertilizers are the substances added to the soil to make up the deficiency of essential elements like nitrogen, phosphorus and potassium (NPK) required for the proper growth of plants. Fertilizers enhance the natural fertility of the soil or replenish the chemical elements taken up from soil by the previous crops.

Elements essential for plant growth

Following are the two types of plant nutrients:

Micro-nutrients (Trace elements)

Definition

The nutrients which are required in a very small amount for the growth of plant, are called micro-nutrients.

Examples

These include Boron, Copper, Iron, Manganese, Zinc, Molybdenum and Chlorine.

Quantity required

Only minute amounts of these elements are needed for healthy plant growth and it may be dangerous to add too much quantity because they are poisonous in larger quantities. These are generally required in quantities ranging from 6 grams to 200 grams per acre.

Macro-nutrients

Definition

The nutrients which are required in a large amount for the growth of plants, are called macro-nutrients.

Examples

These include Nitrogen, Phosphorus, Potassium, Calcium, Magnesium, Sulphur, Carbon, Hydrogen and Oxygen.

Quantity required

These are generally required in quantities ranging from 5 kg to 200 kg per acre.

Requirement of a Fertilizer

Following are the basic requirements of a fertilizer:

1. The desired elements should be present in the compound in a water soluble form readily available to the plants.
2. The compound employed as fertilizer should be stable in soil as well as in storage.
3. It should not be deliquescent or set to hard stony materials with time.
4. It should be cheap to manufacture.

Essential Qualities of a Good Fertilizer

The essential requisites of a good fertilizer are:

1. Nutrient availability

The nutrient elements present in it must be readily available to the plant.

2. Solubility in water

It must be fairly soluble in water so that it thoroughly mixes with the soil.

3. Plant health

It should not be injurious to plant.

4. Price

It should be cheap.

5. Stability

It must be stable so that it is available for a longer time to the growing plant.

6. pH of soil

It should not alter the pH of the soil.

7. Assimilation by plant

By rain or water, it should be converted into a form, which the plant can assimilate easily.

Classification of Fertilizers

The classification gives the following types of fertilizers:
i) Nitrogeneous fertilizers
ii) Phosphatic fertilizers
iii) Potassium fertilizers

Nitrogenous fertilizers

Definition

These fertilizers supply nitrogen to the plants or soil.

Benefit of nitrogen to plant

Nitrogen is required during the early stage of plant growth for the development of stems and leaves.
It is the main constituent of protein.
It imparts green colour to the leaves.
It enhance the yield and quality of the plants.

Examples

Some of the examples of nitrogen fertilizers are: -
ammonium sulphate
calcium ammonium nitrate
basic calcium nitrate
calcium cyanamide
ammonia
ammonium nitrate
ammonium phosphate
ammonium chloride
urea

(i) Ammonia (NH_3) as a Fertilizer

Physical state

Ammonia is used in liquid state while all the other fertilizers are used in the solid form.

Controlling soil acidity

All the nitrogen fertilizers except calcium nitrate, sodium nitrate and potassium nitrate make the soil acidic but this acidity can easily be controlled through liming of the soil (by the addition of lime) at regular intervals.

Application to soil

Liquid ammonia has become an important fertilizer for direct application to soil.

Composition

It contains 82% nitrogen and it is injected about 6 inches under the surface of soil to avoid it from seeping out.

(ii) Urea ($NH_2 - CO - NH_2$)

Urea is a high quality nitrogeneous fertilizer. It is the most widely used nitrogen fertilizer in Pakistan.

Composition

It contains about 46% nitrogen and is the most concentrated solid nitrogen fertilizer.

Manufacturing Process

Urea is produced by the reaction of liquid ammonia with gaseous carbon dioxide.

Steps Involved

Following steps are involved in the manufacture of urea:
i) Preparation of Hydrogen and Carbon dioxide
ii) Preparation of Ammonia
iii) Preparation of Ammonium Carbamate
iv) Preparation of Urea

v) Concentration of Urea
vi) Prilling

Preparation of ammonium carbamate

Gaseous CO_2 is mixed with ammonia in the volume ratio of 1:2 in a reactor to produce ammonium carbamate.

$$CO_2(g) + 2NH_3(g) \longrightarrow NH_2-\overset{\overset{O}{||}}{C}-ONH_4$$

Preparation of urea

Dehydration of ammonium carbamate gives urea.

$$NH_2-\overset{\overset{O}{||}}{C}-ONH_4 \longrightarrow NH_2-\overset{\overset{O}{||}}{C}-NH_2 + H_2O$$

Concentration of Urea Solution

The urea solution is concentrated in an evaporation section where water is evaporated by heating with steam under vacuum in two evaporation stages whereby 99.7% urea melt is obtained. It is then pumped to prilling tower.

Prilling

The molten urea is sprayed at the prilling tower by means of prilling bucket where it is cooled by the air rising upward. Molten droplets solidify into the form of prills.

Bagging

Urea prills thus produced are either sent to the bagging section or to the bulk storage.

(iii) Ammonium Nitrate (NH_4NO_3)

Reaction

It is manufactured by the neutralization reaction between ammonia and nitric acid as given below:

$$NH_3(g) + HNO_3(g) \rightarrow NH_4NO_3(s)$$

Evaporation

After neutralization, the water is evaporated.

Melting process

The solid ammonium nitrate is melted and then sprayed down from a tall tower.

Drying process

The falling droplets are dried by an upward current of air.

Prills

The fertilizer solidifies as tiny, hard pellets called prills.

Nature of prills

Prills of fertilizers are free of dust, easy to handle and easy to spread on the field.

Percentage composition

Ammonium nitrate contains 33-33.5% nitrogen.

Application and limitations

It is a useful fertilizer for many crops except paddy rice because the microbial bacteria in flooded fields decomposes it to nitrogen gas.

Usage

It is also used in combination with limestone.

Nature

It is hygroscopic in nature.

Phosphatic Fertilizers

These fertilizers provide phosphorus to the plants or soil.

Role of phosphorus

Phosphorus is required to stimulate early growth
To accelerate the seed and fruit formation during the later stages of growth.
It also increases resistance to diseases.

Solubility in water

The various phosphatic fertilizers have different compositions, due to which they have different solubilities.

Examples

The two most important water soluble fertilizers are super phosphate (calcium super phosphate) $Ca(H_2PO_4)_2$ and triple phosphate (diammonium- phosphate $(NH_4)_2HPO_4$).

(i) Diammonium Phosphate $(NH_4)_2HPO_4$

This compound of fairly high purity is prepared by continuous process

Reaction

Reaction between anhydrous ammonia gas and pure phosphoric acid at 60 - 70 °C and pH 5.8 - 6.0.

$$2NH_3(g) + H_3PO_4(l) \rightarrow (NH_4)_2HPO_4 + \text{heat}$$

It is an exothermic reaction.

Evaporation

The heat of reaction vaporizes water from the liquor and the crystals of diammonium phosphate are taken out, centrifuged, washed and dried.

Composition and usage

It contains 16% nitrogen and 48% P_2O_5. This product contains about 75% plant nutrients and is deemed suitable for use either alone or mixed with other fertilizers.

Potassium Fertilizers

Definition

These fertilizers provide potassium to the plant or soil.

Benefits of potassium for plant

Potassium is required for the formation of starch, sugar and the fibrous material of the plant.
It increase resistance to diseases and make the plants strong by helping in healthy root development.
It also helps in ripening of seeds, fruits and cereals.
Potassium fertilizers are especially useful for tobacco, coffee, potato and corn.

(i) Potassium Nitrate (KNO_3)

Reaction

On industrial scale it is prepared by the double decomposition reaction between sodium nitrate and potassium chloride.

$$NaNO_3(aq) + KCl(aq) \rightarrow NaCl(aq) + KNO_3(aq)$$

Preparation of sodium nitrate solution

A concentrated hot solution of sodium nitrate is prepared

Addition of potassium chloride

Solid potassium chloride is added into it.

Effect of heat

On heating, the potassium chloride crystals change into sodium chloride crystals, and the hot potassium nitrate is run through the sodium chloride crystals at the bottom of the kettle.

Addition of water

A little water is added to prevent further deposition of sodium chloride as the solution is cooled, which results into a good yield of pale yellow solid potassium nitrate.

Composition

It contains 13% nitrogen and 44% potash.

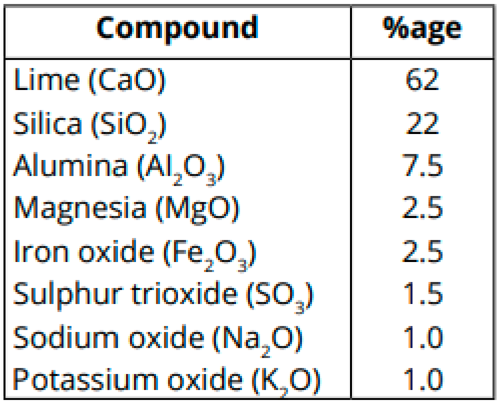
Cement Industry

Definition

Cement is the material obtained by burning an intimate mixture of calcarious and argillaceous materials at sufficiently high temperature to produce clinkers. These clinkers are then ground to a fine powder.

Essential constituents

The essential constituents are lime (obtained from limestone) silica and alumina (present in clay).



Compound	%age
Lime (CaO)	62
Silica (SiO_2)	22
Alumina (Al_2O_3)	7.5
Magnesia (MgO)	2.5
Iron oxide (Fe_2O_3)	2.5
Sulphur trioxide (SO_3)	1.5
Sodium oxide (Na_2O)	1.0
Potassium oxide (K_2O)	1.0

Raw Materials

1. Calcarious material

Limestone, marble, chalks, marine shell as source of CaO.

2. Argillaceous material

Clay, shale, slate, blast furnace slag. They provide acidic components such as aluminates and silicates.

3. Other raw material being used is gypsum.

Manufacturing Process of Cement

The manufacturing process of cement involves either a dry process or a wet process:

Factors

The choice of dry or wet process depends on the following factors.

1. Physical condition of the raw materials.
2. Local climatic conditions of the factory.
3. The price of the fuel.

Comparison of dry and wet process

Dry process needs excessive fine grinding and it is more suited for the hard material.

Wet process is free from dust, grinding is easier and the composition of the cement can easily be controlled.

Wet Process

In this process grinding is done in the presence of water.

Stages

There are five stages in the manufacture of Portland cement:

1. Crushing and grinding of the raw material.
2. Mixing the material in correct proportion.
3. Heating the prepared mixture in a rotary kiln.
4. Grinding the heated product known as clinker.
5. Mixing and grinding of cement clinker with gypsum.

1. Crushing and Grinding

Soft raw materials are first crushed into a suitable size, often in two stages, and then ground in the presence of water, usually in rotating cylindrical ball or tube mills containing a charge of steel balls.

2. Mixing of Raw Material

The powdered limestone is then mixed with the clay paste in proper proportion (limestone 75%, clay 25%).

The mixture is finely ground and made homogeneous by means of compressed air mixing arrangement. The resulting material is known as slurry.

The slurry, which contains 35 to 45% water, is sometimes filtered to reduce the water content from 20 to 30%.

The filler cakes are stored in storage bins.
This reduces the fuel consumption for heating stage.

3. Heating the Slurry in a Rotary Kiln

Raw meal or slurry is introduced into the rotary kiln with the help of a conveyer.

Assembly

The rotary kiln consists of a large cylinder 8 to 15 feet in diameter and 300-500 feet in length.
It is made of steel and is lined inside with firebricks.

Operation

The kiln rotates horizontally on its axis at the rate of 1-2 revolution per minute and it is inclined a few degree.
As the kiln rotates, the charge slowly moves downward due to the rotary motion.
Now the charge is heated by burning coal, oil or natural gas.
In the rotary kiln the charge passes through the different zones of temperature where different reactions take place.
The charge takes 2-3 hours to complete the journey in the kiln.

(a) Drying or Pre-heating Zone (Minimum temperature zone)

Temperature

In this zone the temperature is kept at 500°C.

Products

The moisture is removed.
The clay is broken into AI_2O_3, SiO_2 and Fe_2O_3.

(b) Decomposition Zone (Moderate temperature zone)

Temperature

Here the temperature goes up to 900°C.

Products

In this zone the limestone ($CaCO_3$) decomposes into lime (CaO) and CO_2.

$$CaCO_3(s) \xrightarrow[900°C]{} CaO(s) + CO_2(g)$$

(c) Burning Zone (Maximum tem perature zone)

Temperature

The temperature goes up to 1500°C

Products

The oxides, e.g. CaO, SiO_2, AI_2O_3 and Fe_2O_3 combine together and form calcium silicate, calcium aluminate and calcium ferrite.

(d) Cooling Zone

Temperature

This is the last stage in the kiln where the charge is cooled up to 150-200°C.

(iv) Clinker Formation

The resulting product obtained from the kiln is known as cement clinker.

Appearance of clinker

This has the appearance of greenish black or grey coloured balls varying in size from small nuts to peas.

(v) Grinding the Clinkers with Gypsum

Cooling

The cement clinkers are then air-cooled.

Addition of gypsum

The required amount of gypsum (2.0%) is first ground to a fine powder and then mixed with clinkers.

Storage and packing

At this stage finished cement is pumped pneumatically to storage silos from where it is drawn for packing in paper bags or for dispatch in bulk containers.

Setting of Cement

The use of cement in the construction of building is based on its property of setting to a hard mass when its paste with water is allowed to stand for some time.

Reactions Involved

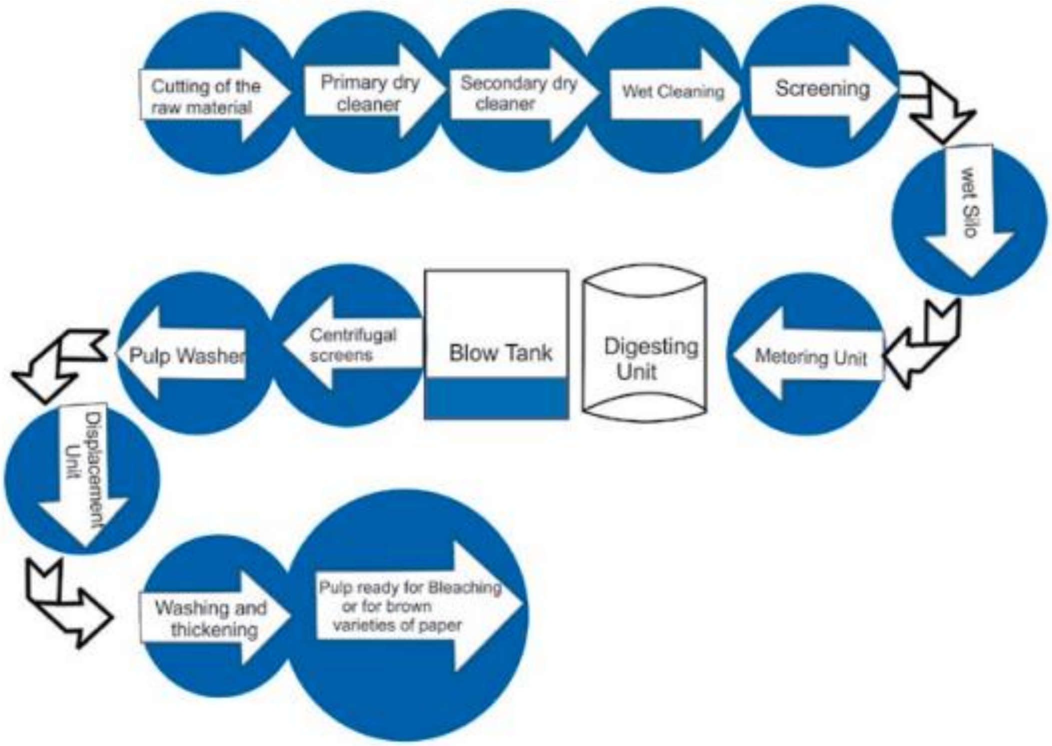
The reactions involved in the setting of cement are described as follows:

(i) Reactions Taking Place in First 24 Hours

Absorption of water by tricalcium aluminate

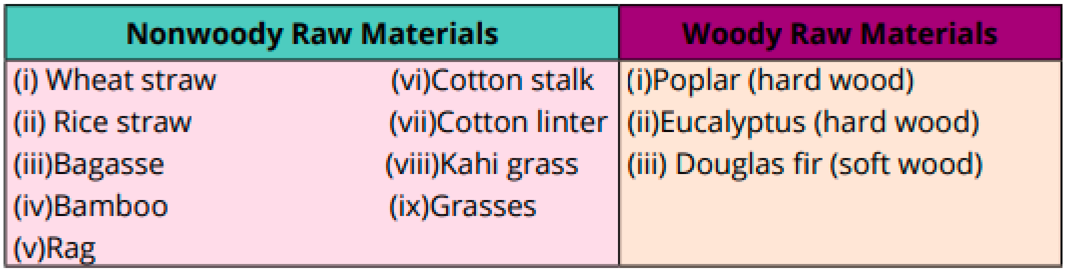
A short time after the cement is mixed with water, tri-calcium aluminate absorbs water (hydration) and forms a colloidal gel of the composition, $3\ Ca.\ Al_2O_3.\ 6H_2O$ (hydrated tricalcium aluminate).

Crystallization of gel
This gel starts crystallizing slowly, reacts with gypsum ($CaSO_4.\ 2H_2O$) to form the crystals of calcium sulpho-aluminate ($3CaO.Al_2O_3.3CaSO_4.2H_2O$).
(ii) Reactions Taking Place Between 1 to 7 Days
Production of calcium hydroxide and aluminium hydroxide
Tricalcium silicate ($3CaO.SiO_2$) and tri-calcium aluminate ($3CaO.Al_2O_3$) get hydrolyzed to produce calcium hydroxide and aluminium hydroxide.
Formation of needle-shaped crystals
The calcium hydroxide starts changing into needle-shaped crystals, which get studded in the colloidal gel and impart strength to it.
Filling of interstices
Aluminium hydroxide fills the interstices resulting in hardening the mass.
Loss of water by gel
The gel formed starts losing water partly by evaporation and sets to a hard mass.



Paper Industry

Definition
Paper is defined in term of its method of production that is a sheet material made up of a network of natural cellulosic fibres which have been deposited from an aqueous suspension. The product obtained is a network of interwinning fibres.
Brief Description of the Process
Raw Material
The main raw materials used in the production of pulp and paper in Pakistan is of two types:
Non-woody
Woody



Nonwoody Raw Materials		Woody Raw Materials
(i) Wheat straw	(vi)Cotton stalk	(i)Poplar (hard wood)
(ii) Rice straw	(vii)Cotton linter	(ii)Eucalyptus (hard wood)
(iii)Bagasse	(viii)Kahi grass	(iii) Douglas fir (soft wood)
(iv)Bamboo	(ix)Grasses	
(v)Rag		

Pulping Processes

The following are three principal methods of chemical pulping and are used for the production of paper pulps.

1. Kraft process (Alkaline)
2. Sulphite process (Acidic)
3. Neutral sulphite semi-chemical process (NSSC)

Advantages of NSSC

The neutral sulphite semi chemical process has come to occupy the dominant position because of the advantages in chemical recovery and pulp strength.

Neutral Sulphite Semi Chemical Process

Process Description

Buffering medium

This process utilizes sodium sulphite cooking liquor which is buffered with sodium carbonate or NaOH to neutralize the organic acid liberated from the raw materials.

Material used

The non-woody raw materials which are used in this process are wheat straw, rice straw, bagasse, cotton linter and rags. Wheat straw may be used alone or combined with other materials in different proportions.

Steps Involved

The essential steps in the process are:

i. Cutting of the raw materials
ii. Dry cleaning
iii. Wet cleaning
iv. Screening
v. Digestion
vi. Blow tank
vii. Pulp washing
viii. Bleaching
ix. Paper making machine
x. Stock preparation plant

(i) Cutting of Raw Materials

Non-woody

The non-woody raw materials come in the precut state and are processed as such.

Woody

In the case of wood based raw materials big logs are cut into small chips before further processing.

(ii) Dry Cleaning

Wheat straw is collected from the storage and is then sent for dry cleaning.

Air blow

Air is blown into the raw material which removes unwanted particles.

(iii) Wet Cleaning

Dry wheat straw is then subjected to wet cleaning, which not only removes the remaining dust particles, but the soluble materials also get dissolved in water.

(iv) Screening

In most pulp and paper processes some type of screening operation is required to remove the over sized troublesome and unwanted particles.

Magnetic separators

Magnetic separator removes iron pieces like nails and bolts, etc. Stones and other oversized pieces are removed by centricleaners.

Chest screens

The major types of chest screens are vibratory, gravity, and centrifugal.

The material is then sent to wet silo.

(v) Digestion

From wet silo, the material is sent to digester.

Dimensions of digester

The digester is usually 10 meters in length and 2 meters in diameter.
It is made of steel and wrought iron.
This is the main unit of the process.

Process of digestion

The digestion process can be either batch or continuous. In our country batch process is mostly used.

Introduction of steam

As the raw material enters into the digester, steam is introduced at the bottom.

Injection of sodium sulphite

Liquor containing sodium sulphite is injected simultaneously to cover the raw material.

Buffering of sodium sulphite

Sodium sulphite used is buffered with sodium carbonate or sodium hydroxide to maintain its pH 7-9.

Closing and revolving the digester

The digester is closed carefully. It is revolved at 2.5 RPM and a temperature of 160- 180°C is maintained.

Time duration

The digester takes 45 minutes to attain the desired temperature after which it gets switched off automatically and pressure is released.

(vi) Blow Tank

The cooked material from the digester is blown into a blow tank and then pumped to a centrifugal screen for the separation of cooked from uncooked materials.

(vii) Pulp Washing

The cooked material from the blow tank is washed thoroughly with water using 80 mesh sieve to remove the black liquor that would contaminate the pulp during subsequent processing steps.

Removal of lignin

The pulp is washed with required amount of water to remove soluble lignin and coloured compounds. Lignin is an aromatic polymer and causes paper to become brittle.

Storage

It is then thickened and finally stored in high-density storage tower.

(viii) Bleaching

The colour of the pulps is mainly due to residual lignin. These pulps are then sent to bleaching unit

Chlorine or sodium hypochlorite

In Pakistan, bleaching is done with chlorine or sodium hypochlorite and hydrogen peroxide. After washing, the unbleached pulp is sent to the chlorinator where chlorine at 4 - 5 bar pressure is injected from chlorine tank.

Reaction of chlorine

The chlorine react with unbleached pulp at about 45°C for 45-60 minutes to give the good results.

Neutralization with water

The residual chlorine is neutralized with water which act as antichlor. The correct dosage is important and calculated amount of chlorine is needed to achieve the required brightness.

Washing with hot water

After chlorination pulp is washed with hot water at 60°C and is then sent to the storage tank.

Drying with hot air

Pulp is dried with hot air supply.

After drying the pulp is ready for manufacturing of paper.

Stock Preparation Plant

Stages Involved

There are three important stages in the treatment of the pulp prior to its delivery to the paper making machine.

The first is the dispersion of the pulp as a slurry in water.

The second is the mechanical refining or beating of the fibres to develop appropriate physical and mechanical properties for the product being made.

The third is the addition of chemical additives end recycled fibres from the waste paper plant.

Wet end chemistry of paper

(x) Paper Making Machine

A basic Fourdrinier type machine is used for paper making.

(a) Flow Spreader

The flow of spreader takes the plup and distributes it evenly across the machine from back to front.

Consistency

Consistency of the stock is below 1%.

(b) Head Box

The pressurized head box discharges a uniform jet of pulp suspension on a fabric.

Suction devices

Special suction devices work for the removal of water.

(c) Fourdrinier Table

The endless, moving fourdrinier fabric forms the fiber into a continuous matted web while the fourdrinier table drains the water by suction forces.

(d) Press Section

The paper sheet is conveyed through a series of roll presses where additional water is removed and the web structure is consolidated (i.e the fibres are forced into intimate contact).

(e) Dryer Section

Rotary drum

Wet sheet of paper so formed is dried in the dryer section of the machine with the help of rotary drum.

Separation of water

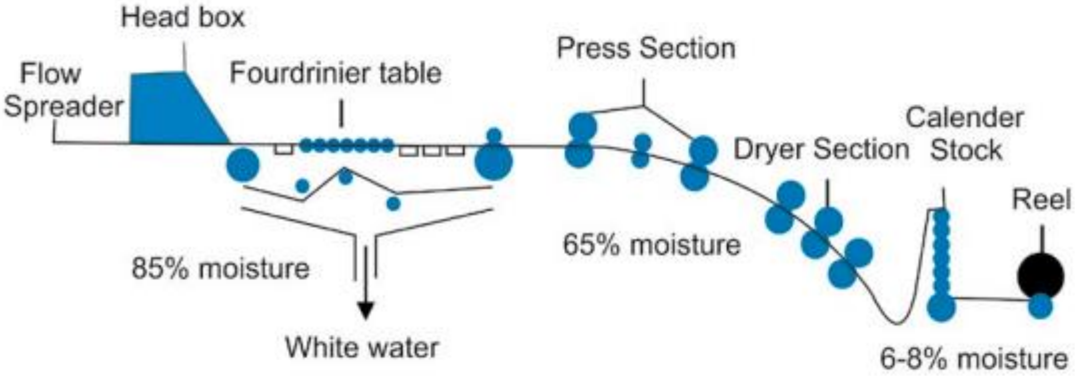
Water is separated from the fiber either by gravity, by suction or by pressing and by heating.

(f) Calendar Stock

The sheet is calendered through a series of roll nips to reduce thickness and smooth the surface.

(g) Reel

The dried paper is wound in the form of a reel having final moisture of about 6-8%.



Chapter 16

Environmental Chemistry

Components of the Environment

The environment consists of the following components:
(i) Atmosphere
(ii) Hydrosphere
(iii) Lithosphere
(iv) Biosphere

(i) Atmosphere

Definition

The layer of gases surrounding the earth is called atmosphere.

Thickness

Its thickness is about 1000 km above the surface of the earth and half of its mass is concentrated in the lower 5.6 km.

Function

The gases in the atmosphere absorb most of the cosmic rays and the major portion of the harmful electromagnetic radiation coming from the sun.

The absorption of these harmful radiations protects the life on the earth.

The gases present in the atmosphere are essential for sustaining life on earth i.e., O_2 is required for breathing.

CO_2 is required for plant photosynthesis.

N_2 is used by nitrogen fixing bacteria and water vapours are responsible for sustaining various forms of life on the earth.

Atmosphere also maintains the heat balance of the earth.

Composition

It consists of various gases in different proportions i.e., N_2 (78%), O_2 (21%), Ar (0.9 %), CO_2 (0.03 %) and trace amounts of H_2, O_3, CH_4, CO, He, Ne, Kr and Xe. It also contains varying amounts of water vapours.

(ii) Hydrosphere

Definition

The hydrosphere includes all water bodies, mainly oceans, rivers, streams, lakes, polar ice caps, glaciers and ground water reservoirs (water below earth surface).

Percentage distribution

Oceans contain 97% of earth’s water but because of high salt contents this water cannot be used for human consumption.

The polar ice caps and glaciers consist of 2% of the earth’s total water supply.

Only 1% of the total earth’s water resources are available as fresh water i.e., surface water; river, lake, stream and ground water.

The fresh water is being used by agriculture (69%), industry (23%) and for domestic purposes (8%).

(iii) Lithosphere

Definition

It consists of rigid rocky crust of earth and extends to the depth of 100 km.

The mantle and core are the heavy interior of the earth, making up most of the earth’s mass.

Percentage composition

The 99.5 % mass of the lithosphere is made of 11 elements, which are oxygen (~ 46.60 %), Si (~27.72 %), Al (8.13 %), Fe (5.0 %), Ca (3.63 %), Na (2.83 %), K (2.59 %), Mg (2.09 %) and Ti, H_2 and P (total less than 1 %). The elements present in trace amounts (0.1 to 0.02 %) are C, Mn, S, Ba, Cl, Cr, F, Zr, Ni, Sr and V. These elements mostly occur in the form of minerals.

(iv) Biosphere/Ecosphere

Definition

Biosphere is the region of earth capable of supporting life.

Composition

It includes lower atmosphere, the oceans, rivers, lakes, soils and solid sediments that actively interchange materials with all types of living organisms i.e., human beings, animals and plants.

Ecosystem

Ecosystem is a smaller unit of biosphere which consists of community of organisms and their interaction with environment i.e., animals, plants and microorganisms which lie in a definite zone and depend on the physical factors such as soil, water, and air.

Effects of pollution on ecosystem

Any substance in the environment which adversely affects the human health, quality of life and the natural functioning of ecosystem, is known as environmental pollutant.

With continuous rapid growth in population, urbanization, industrialization and transportation, environmental pollution is spreading in almost every city of the world.

The quantity of pollutants affecting the environments have increased rapidly in the last half century and they have adversely affected human health and eco-system.

Nitrogen Oxides (NO_x)

(a) Natural Sources

Bacterial action produces NO_x mainly NO

(b) Human Activities

Nitrogen oxides are generally produced by combustion of coal, oil, natural gas and gasoline. Both oxides result from the oxidation of nitrogeneous compounds present in fossil fuel. The burning of fuel in the presence of air in internal combustion engine also produces NO.

$$N_2 + O_2 \xrightarrow{\text{high temperature}} 2NO$$

Nitrogen dioxide is produced when nitric oxide reacts with oxygen.

$$2NO + O_2 \rightarrow 2NO_2$$

Residence time

The residence time of NO and NO2 in the atmosphere are 4 and 3 days respectively.

Photochemical reactions

Due to photochemical reactions, NO_x are converted to HNO_3 which is carried down in either rain fall or as dust.

Sulphur Oxides, SO_2

(a) Natural Sources

On global scale most of sulphur dioxide is produced by volcanoes (67%) and by oxidation of sulphur containing gases produced by decomposition of organic matter.

(b) Human Activities

Air is polluted with SO_2 due to combustion of coal (containing 1-9%S), crude oil and other fossil fuel in power plants and petroleum industry, etc.

$$S + O_2 \rightarrow SO_2$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

Side effects

These gases (SO_2 and SO_3) because of their pungent odour are very irritant and suffocating.

Through various reactions in the atmosphere they form sulphate aerosols.

These aerosols cause severe respiratory troubles particularly among older people.

Sulphur dioxide is the major source of acid deposition in the atmosphere.

Acid Rain

Definition

Acid rain also as acid deposition, was discovered by Angus Smith in Great Britain in the mid seventeenth century but this phenomenon gained importance as a serious environmental problem in 1950's. Initially it was referred to the precipitation which was more acidic than natural rain.

Reactions Involved

Due to the presence of CO_2 in the atmosphere the natural rain itself forms carbonic acid.

$$CO_2(g) + H_2O(aq) \rightarrow H_2CO_3(aq)$$

$$SO_2 + 1/2O_2 + H_2O \xrightarrow{\text{(hydrocarbon,smoke,metal oxides)}} H_2SO_4$$

In the atmosphere SOz and NOx are transformed by reactions with oxygen and water into H_2SO_4 and HNO_3 respectively. These acids get mixed with rain. The acid deposition includes both wet (rain, snow, fog) and dry acidic deposition.

pH

The pH of unpolluted rain water should be 5.6. The rain water has pH less than 5 is considered truly acidic.

Temporary acid rain

In some countries due to release of HCI by volcanic eruption there is temporary acid rain.

Side Effects of Acid rain

Acidification of soil

Acidification of the soil and rocks can leach metals like aluminium, mercury, lead and calcium and discharges them into water bodies.

Human and Marine health

These heavy metals are accumulated in the fishes and are health hazards for humans and birds as they eat these fishes.

The elevated concentration of aluminium is harmful for fish as it clogs the gills causing suffocation. Acidification of the soil can also leach nutrients thus damaging leaves and plants and growth of forest.

Damage to buildings

It also damages building materials such as steel, paint, plastic, cement, masonry work and sculptural materials especially of marble and limestone.

Smog

Definition

The word smog is a combination of smoke and fog.

Reducing smog

If it contains high contents of SO_2 it is chemically reducing in nature and is known as 'reducing smog'.

Cause of reducing smog

The main cause of reducing smog is combustion of coal.

Photochemical smog

Photochemical smog consists of higher concentrations of oxidants like ozone and is also termed as oxidizing smog.

Physical characteristics of photochemical smog

It is a yellowish brownish grey haze which is formed in the presence of water droplets and chemical reactions of pollutants in the air.

It has unpleasant odour because of its gaseous components.

Main components

The main reactants of photochemical smog are nitric oxide NO and unburnt hydrocarbons.

Nitric oxide is oxidized to nitrogen dioxide within minutes to hours depending upon the concentration of pollutant gas.

The yellow colour in photochemical smog is due to the presence of nitrogen dioxide.

Conditions for smog formation

The following conditions are required for the formation of smog:

1. There must be sufficient NO ,hydrocarbons and volatile organic compounds (VOC) emitted by the vehicular traffic.

2. Sunlight, so that some of the chemical reactions may occur at a rapid rate.
3. The movement of air mass must be little so that reactions are not disturbed.

Ultimate outcome of photochemical smog

The overall result of photochemical smog in afternoon is the built up of oxidizing agents such as H_2O_2, HNO_3, peroxyacetyl nitrate (PAN) and ozone in the air.

PAN is an eye irritant and is also toxic to plants.

Harmful effects of ozone depletion

Ozone Hole

The thickness of the ozone layer has been decreasing over Antarctic during the spring time since the mid 1970's. By the mid 1980's loss in ozone at some altitudes over Antarctica resulted in about 50% depletion of the total overhead amount. The region in which ozone depletes substantially in every year during Sep-Nov is now termed as "ozone hole".

Depletion of ozone in stratosphere

The concentration of ozone in the stratosphere is being depleted through various chemical reactions not only above Antarctica but worldwide.

Purification of water

Methods

Water is purified through the following methods:
1. Aeration
2. Coagulation
3. Chlorination

Chlorination

Chlorine is frequently used to disinfect water.

Advantage

Chlorine treatment is very effective in killing the pathogens that may cause serious water-borne diseases such as typhoid and cholera which have killed many thousands of people around the world.

Commonly used chlorinating agents

The most commonly used disinfecting agent is hypochlorous acid HOCI.

Function of HOCl

This neutral covalent compound kills microorganisms readily by passing through their cell membranes.

Generation of HOCl

The hypochlorous acid is not stable thus it cannot be stored, it is therefore generated by either dissolving molecular chlorine gas or sodium and calcium hypochlorites in water.

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

Cheapness

Disinfection by chlorine is inexpensive.

Harmful effects of chlorination

Harmful effects of chlorination of water are due to its reactions with dissolved ammonia and organic matters present in water.

The hypochlorous acid reacts with dissolved ammonia to form chloramines NH_2Cl, $NHCl_2$ and especially nitrogen trichloride NCI_3 which is a powerful eye irritant.

$$NH_3 + 3HOCl \rightarrow NCl_3 + 3H_2O$$

The alkaline pH can prevent the formation of chloramines.

Chlorination of organic matter

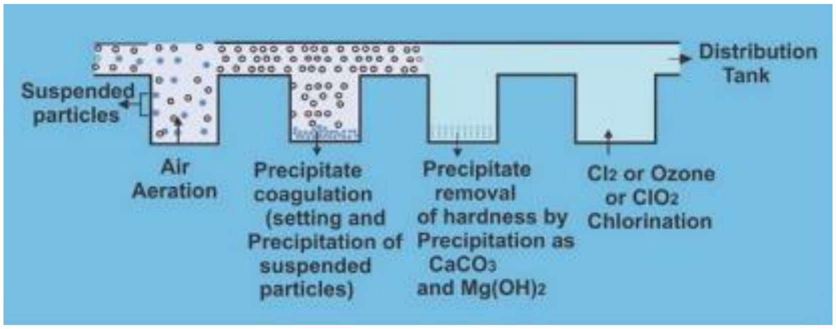
Chlorination of water containing organic materials also forms some organic compounds which are toxic. If phenol is present in water then chlorinated phenols are formed which have offensive odour and taste and are toxic.

Chloroform $CHCl_3$ is formed when hypochlorous acid reacts with organic matter (humic acid) dissolved in water.

Harmful effects of chloroform
Chloroform is suspected liver carcinogen and also has negative reproduction and development effects in humans.

Harmful effects of chlorinated water
The risk of bladder and rectal cancer increases by drinking chlorinated water.

Safe alternatives
To avoid the formation of toxic compounds with chlorine, ozone or chlorine dioxide is used for the disinfection of water.



Incineration of the Muncipal Solid Waste

Definition
Incineration is a waste treatment process in which solid waste is burned at high temperatures ranging from 900 to 1000 °C.

Process
The burning of the solid waste in the incinerator consumes all combustible materials leaving behind the non-combustible materials and the ash residues.

Landfills
The ash residues of the incinerator are disposed off on the land or landfills.

Reduction in waste volume
The incineration may reduce the volume of the waste by two third.

Fire fuel
The combustible components of garbage such as paper, plastics and wood provide fuel for the fire.

Electricity generation
In incineration the heat of combustion may be used in producing steam which runs the turbines to produce electricity.

Incineration of Industrial and Hazardous Waste

Assembly
A rotary kiln which accepts all types of wastes including liquid, solid or sludge.

Operation

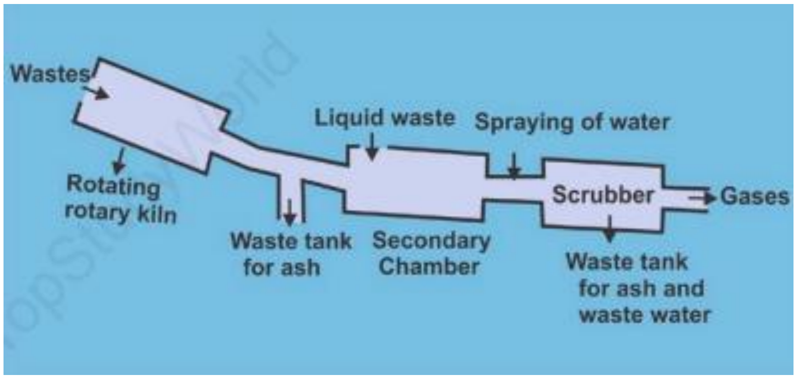
Temperature
The wastes are burned at temperatures between 650° to 1100 °C.

Collection of ash
Ash from the rotating chamber is collected at waste tank and the remaining liquid gaseous materials are passed to the secondary chamber. This chamber is non-rotating and hence the temperature range of 950° to 1300°C is maintained. In this chamber organic molecules are completely destroyed.

Water spray
The gases produced are then cooled to 230 °C by evaporating water spray.

Scrubber system
The cooled gases are then passed through scrubber system which eliminates the surviving particulates and acid forming components like CO_2.

Landfills
Ash residues and waste water produced in the rotating and secondary chambers are disposed off in the landfills.



Drawbacks of incineration

Not clean

It is not a clean process of the disposal of solid wastes.

Pollution

It produces air pollution and also toxic ash.

Dioxin production

Significant source of dioxins which is a class of carcinogen compounds.

Acid rain

Smoke stacks from incineration may emit oxides of nitrogen and sulphur which lead to acid rain.

Heavy metals

Heavy metals such as lead, cadmium, mercury, etc., may also be present in the leachate of the incinerators.

Important Long Questions from Past Papers

Chapter 1

1. Mention the improvements made in Mendeleev's periodic table?
2. Define ionization energy. Give its units. Explain its trend in the periodic table.
3. Explain trend in the periodic table of the following:
    a. Ionization potential b. Electrical conductivity c. Atomic radius
    d. Electron affinity
4. Define hydration energy. Explain it.
5. What are hydrides? Describe them.
6. What are halides? Explain them.
7. What are halides? Classify and discuss covalent halides in details.
8. Explain position of hydrogen in the periodic table.

Chapter 2

1. Write eight properties of lithium in which it behaves differently from its group members.
2. Show four reactions in which lithium behaves differently from its own group.
3. Explain Peculiar behaviour of beryllium.
4. Explain the commercial preparation of sodium by Down's cell. What are the advantages of this process?
5. Write commercial method for the preparation of NaOH.
6. Write eight points to describe the role of lime in industries.
7. Describe the role of gypsum in agriculture.
8. Complete and balance the following equations.
    a. $Be + NaOH \longrightarrow$
    b. $Be + O_2 \longrightarrow$

    c. $SiO_2 + Ca(OH)_2 \longrightarrow$
    d. $Mg(NO_3)_2 \xrightarrow{heat}$

    e. $Li_2O + H_2O \longrightarrow$
    f. $Na_2O_2 + H_2O \longrightarrow$
    g. $Mg(OH)_2 \xrightarrow{heat}$
    h. $NaNO_3 \xrightarrow{heat}$
9. Discuss hard finish plasters and cement plasters.

Chapter 3

1. What are silicates? How is sodium silicate prepared? Give its two uses.
2. Give methods for the preparation of H_3BO_3. How does it react with:
    a. $NaOH$
    b. Na_2CO_3
    c. C_2H_5OH

Chapter 4

1. Explain the manufacture of Nitric acid through Birkland and Eyde's Process.
2. How does Nitric acid react with Cu, Hg, Zn, Mg and Sn?
3. Give suitable examples to explain that sulphuric acid is good acid, oxidizing agent and dehydrating agent.
4. Differentiate between oxygen and sulphur.
5. Explain the contact process for the manufacture of sulphuric acid.
6. Exercise Questions 11 & 12.

Chapter 5

Any topic can come for long question.

Chapter 6

1. Define corrosion? Explain electrochemical theory of corrosion.
2. Explain Bessemer's process for formation of steel.
3. Describe the manufacture of wrought iron from cast iron.
4. Explain the following:
   a. Ligands b. Coordination number c.Chelates d.Coordination sphere
   e. Colour c. Paramagnetism d. Oxidation states
5. Describe general characteristics of transition metals.
6. Write down any four properties of transition elements.
7. $KMnO_4$ acts as oxidizing agent. Give four reactions as an example.

Chapter 7

1. Define organic compound. Give any three features of organic compounds.
2. Write a note on classification of organic compounds.
3. Explain Cracking of petroleum.
4. Explain reforming of petroleum.
5. Define hybridization. Explain sp^2 OR sp^3 OR sp hybridization.
6. Define isomerism. Explain any four types of structural isomers.
7. Explain geometrical/cis-trans isomerism.

Chapter 8

1. Convert a.Ethane to Methane b. Methane to ethane

2. How would you prepare alkane from carbonyl compounds?

3. Give one method each for preparation of Ethane, Ethene and Ethyne.
4. Explain acidic nature of alkynes with examples.
5. Convert (i) acetic acid into methane (ii)1-Propanol to 1-Chloro-2-propanol.
6. Convert i. 2,3-Dibromo butane into 2-Butene ii. Acetone into propane
7. Convert acetylene to:
   i. Vinyl acetylene
   ii. Divinyl acetylene
   iii. Benzene
   iv. Acetaldehyde

   - v. Oxalic acid
   - vi. Disilver acetylide
8. Convert propyne into acetone.
9. How will you distinguish between Ethane, Ethene and Ethyne through chemical reactions?
10. Prepare Ethane OR Ethene OR Ethyne from Kolbe's electrolysis?
11. Give mechanism of Halogenation of alkanes.
12. Give the chemical reactions of Ethene with the following.
   - i. H_2SO_4/HCl ii. Br_2 iii. O_3 iv. HOX
13. What are the rules for naming alkanes OR alkynes?

Chapter 9

1. Write down the classification of aromatic hydrocarbons giving one example in each.
2. Discuss atomic orbital treatment to explain the structure of benzene.
3. Describe the structure of Benzene on the basis of resonance method.
4. Write four methods of preparation of benzene.
5. What is meant by orientation in Benzene? Why certain substituents are ortho-para directive and others meta directive? Give one example of each.
6. Write a note on Friedal-crafts reactions.
7. What happens when toluene is reacted with i. Cl_2 in sunlight ii. $KMnO_4$ in presence of H_2SO_4.
8. Convert benzene into:
   - i. Cyclohexane ii. Maleic acid iii. Glyoxal iv. Benzene sulphonic acid
9. Give the mechanisms of nitration and sulphonation of benzene.
10. Write down two reactions in which benzene behaves as saturated hydrocarbon and two reactions in which as unsaturated hydrocarbon.
11. Give mechanism of halogenation of benzene**.**

Chapter 10

1. What are β-Elimination reactions? Differentiate between E1 and E2 reactions**.**
2. Convert ethyl bromide into:
   - a. Ethane b. Propane c. Ethyl alcohol d. n-Butane
3. Give all methods of preparation of alkyl halides.
4. Write reactions of Grignard's reagent with following.
   - a. Water b. Ammonia c. CO_2 d. Alcohol e. HCHO f. CH_3-CHO g. $(CH_3)_2CO$ h. Cl-CN i. CO_2 j. CH_3-CHO k. H_2O l. CH_3OH
5. Discuss S_N2 reaction of alkyl halide in detail.
6. Describe S_N1 reaction of alkyl halide in detail.
7. Differentiate between S_N1 and S_N2 reactions.
8. How will you bring about the following conversions from an alkyl halide?
   - a. Diethyl ether b. Ethyl thioalcohol c. Ethyl acetate d. Nitroethane

Chapter 11

1. Write industrial preparation of Methanol.
2. How is ethyl alcohol prepared by the fermentation of molasses and Starch?

3. Write the two reactions of alcohols in which O-H bond breaks and two reactions in which C-O bond breaks.
4. Discuss the acidic behavior of phenol.
5. Write two methods of preparation of Phenol.
6.
7. Give two methods of preparation of ethers.
8. Convert phenol into:
   a. Picric acid b. Cyclohexanol c. Bakelite
9. Write the chemical reaction of phenol with following:
   i. NaOH ii. Zn iii. CH_3-COCl iv. H_2
   v. HNO_3 vi. CH_3-CO-CH_3 vii. CH_3-COCl viii. Br_2

Chapter 12

1. What are Aldols? Describe with mechanism aldol condensation**.**
2. What types of aldehydes give Cannizzaro's reaction? Give its mechanism.
3. Discuss Haloform reaction with one example.
4. Describe the mechanism of reaction of sodium bisulphite with acetone.
5. Write a note on oxidation of aldehydes and ketones?
6. Discuss the reaction of Ethanal and Propanone with: a. Hydroxyl amine b.Phenyl hydrazine
7. Distinguish:
   a. Acetaldehyde and propanone b. Formaldehyde and acetaldehyde
8. Prepare following compounds from carbonyl compounds:
   a. Lactic acid b. Paraldehyde c. Ethanal Oxime d. Croton aldehyde
9. How does acetaldehyde react with following reagents:
   a. C_2H_5MgI b. HCN c. $NaHSO_3$ d. I_2/NaOH
10. Write any four uses of acetaldehyde OR formaldehyde.
11. Describe any four tests for the identification of carbonyl compounds.

Chapter 13

1. Define Zwitter ion. Discuss effect of acidic and basic medium on the dipolar ionic structure of amino acid.
2. Convert acetic acid into i. Methane ii. Acetyl chloride
3. Complete the following reactions of acetic acid with:
   a. $SOCl_2$ b. HI/P c. Na_2CO_3

Chapter 15

Any topic can come for long question.

Chapter 16

1. Name the components of the environment. Give approximate composition of atmosphere and lithosphere.
2. What is Acid Rain, how does it affect our environment?
3. Write a note on smog?
4. Describe the natural and human sources of Nitrogen oxides and sulphur oxides**.**
5. Write methods for the purification of water. Explain the process of disinfection of water by chlorine.
6. What will happen when the concentration of ozone will decrease?

7. Explain the process of incineration of industrial wastes.

GOOD LUCK
FOR YOUR
Exam
AND
do the best