10. GROUP 14 ELEMENTS (IV A)

SYNOPSIS:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>At. No</th>
<th>Valence shell configuration</th>
<th>Penultimate shell configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>6</td>
<td>2s² 2p²</td>
<td>C → 2e⁻ s²</td>
</tr>
<tr>
<td>Si</td>
<td>14</td>
<td>3s² 3p²</td>
<td>Si → 8e⁻ s² p⁶</td>
</tr>
<tr>
<td>Ge</td>
<td>32</td>
<td>4s² 4p²</td>
<td>Ge</td>
</tr>
<tr>
<td>Sn</td>
<td>50</td>
<td>5s² 5p²</td>
<td>Si 18e⁻</td>
</tr>
<tr>
<td>Pb</td>
<td>82</td>
<td>6s² 6p²</td>
<td>Pb s²p⁶d₁⁰</td>
</tr>
</tbody>
</table>

They belong to p-block.

**General valence shell configuration:**
Almost all properties will show a normal trend from C to Si. But, beyond Si, the trend or change slows down due to ineffective screening caused by d and f electrons.

**General properties:**
- **Abundance:** Most abundant is Si. Even C is also more abundant. Least abundant is Ge.
- **Density:** It increases down the group. C has higher density than Si due to its diamond form.
- **Order:** Sn < C < Ge < Sn < Pb
- **M.Ps and B.P.s:** They will decrease down the group due to decrease in the inter atomic attraction.
  - C has highest M.P. and B.P. in the entire periodic table.
  - Order of M.P.’s → C > Si > Ge > Sn < Pb
  - Order of B.P.’s → C > Si > Ge > Sn > Pb
    - Sn has least M.P.
    - Pb has least B.P.

**Atomic radius:** Increases down the group.
- Normal increase from C to Si but slow increase from Si onwards. It is due to poor shielding of d e⁻ in Ge and d and f electrons in others.
- Thus, the difference in the atomic radii between Si and Ge is much smaller when compared to that of C and Si.
- Even lanthanide contraction accounts for smaller increase in atomic radii.

**Ionisation potential:** It decreases normally from C to Si.
Thereafter, the decrease is very slow.

**Electronegativity:** It decreases normally from C to Si but there after, it remains constant.

**Metallic nature:** It gradually increases from C to Pb.
- C, Si are non-metals.
- Ge is metalloid
- Sn, Pb are metals
- Because of gradual increase in metallic nature, IVA group is best suitable for the study of periodicity in properties.

**Oxidation states:**
- Common oxidation state is + 4.
Group 14 Elements (IVA)

- Tin and lead will exhibit +2 oxidation state also. +2 is more common and more stable than +4 for Sn and Pb due to inert pair effect.

Valency:
- Common valency is 4.
- Maximum valency of C is also 4 due to the absence of vacant d-orbitals.
- Si and other elements can exhibit a maximum valency of 6 due to the presence of vacant d–orbitals.

Catenation: The ability to form long chains or rings by the atoms of an element is called catenation.
- Catenation ability decreases due to decrease in the bond energy.
- Thus, C has highest catenation than any other element in the periodic table

Comparison of C and Si
Similarities: Due to similar valence shell configuration they have some similarities.
- Both are non-metals.
- Both are abundant in nature.
- Both exhibit tetravalancy.
- Both exhibit common oxidation state of +4
- Both will exhibit allotropy.
- Both will form many similar compounds.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Carbon</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxides</td>
<td>CO₂</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Halides</td>
<td>CCl₄</td>
<td>SiCl₄</td>
</tr>
<tr>
<td>Hydrides</td>
<td>CH₄, C₂H₆, C₃H₈, etc.</td>
<td>SiH₄, Si₂H₆, Si₃H₈, etc.</td>
</tr>
<tr>
<td>Oxyacids</td>
<td>H₂CO₃ (Carbonic acid)</td>
<td>H₂SiO₃ (Silicic acid)</td>
</tr>
<tr>
<td></td>
<td>(COOH)₂ (oxalic acid)</td>
<td>H₂Si₂O₄ (Silico oxalic acid)</td>
</tr>
</tbody>
</table>

Differences: C and Si have some differences due to different (n – 1) shell configuration.

C → (n – 1)s² 2e⁻
Si → (n – 1)s²p⁶ 8e⁻

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>It is present in living beings.</td>
<td>It is present in minerals, rocks etc.</td>
</tr>
<tr>
<td>It is hard.</td>
<td>It is soft.</td>
</tr>
<tr>
<td>It has high m.p.</td>
<td>It has low m.p.</td>
</tr>
<tr>
<td>Its catenation ability is maximum.</td>
<td>Its catenation ability is limited.</td>
</tr>
<tr>
<td>Its maximum valency is 4.</td>
<td>Its maximum valency is 6.</td>
</tr>
<tr>
<td>Some allotropes of C are good conductors.</td>
<td>All its allotropes are bad conductors.</td>
</tr>
</tbody>
</table>
## Differences in their compounds:

<table>
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<th>Halides</th>
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<td>CO₂ is gas.</td>
<td>It forms CCl₄.</td>
</tr>
<tr>
<td>CO₂ exist as monomer and only weak Vanderwaal’s forces exists.</td>
<td>As C does not contain vacant d orbitals in its valence shell, it cannot extend its valency beyond 4.</td>
</tr>
<tr>
<td>In CO₂, C is bonded to two ‘O’s by double bonds. O = C = O</td>
<td>As Si contains vacant d-orbitals in its valence shell it can exhibit a valency of 6.</td>
</tr>
<tr>
<td>CO₂ is solube in water .</td>
<td>SiCl₄ is unsaturated and it can form two more bonds.</td>
</tr>
<tr>
<td>SiO₂ is solid.</td>
<td>SiCl₄ is hydrolysed .</td>
</tr>
<tr>
<td>SiO₂ is solid. SiO₂ has giant polymeric structure.</td>
<td>It forms species like SiCl₄.2H₂O, SiCl₆²⁻ .</td>
</tr>
<tr>
<td>SiO₂ is insoluble in water.</td>
<td>SiCl₄ can act as Lewis acid</td>
</tr>
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### Oxides

- CO₂ is gas.
- CO₂ exist as monomer and only weak Vanderwaal’s forces exists.
- In CO₂, C is bonded to two ‘O’s by double bonds. \( O = C = O \)
- CO₂ is solube in water.

### Halides

- It forms CCl₄.
- As C does not contain vacant d orbitals in its valence shell, it cannot extend its valency beyond 4.
- CCl₄ is saturated.
- CCl₄ is not hydrolysed.
- CCl₄ does not form species like CCl₄.2H₂O, CCl₆²⁻.
- CCl₄ cannot act as Lewis acid.

### Hydrides

- It forms large number of hydrides.
- Its hydrides are stable because C – H bond is non polar and it doesnot weaken the adjacent C – C bond.
- Hydrides of C are not hydrolysed due to non-polar nature . These are weak reducing agents.

- It forms very few hydrides.
- Silanes are unstable because Si – H bond is slightly polar and it weakens the adjacent Si – Si bond.
- They are hydrolysed due to polar nature. These are strong reducing agents.
Allotropy:
- The existence of same element in different physical forms is called allotropy.
- Allotrops of an element have similar chemical properties, but different physical properties.
- Allotropic forms may differ in
  1) Crystal structure
  2) Arrangement of atoms
  3) Atomicity
- Carbon has two types of allotropic forms
  1) Crystalline (a) Diamond (b) Graphite
  2) Amorphous (Microcrystalline) coal, coke, charcoal, animal charcoal. Lamp black, carbon black, petroleum coke, gas carbon, sugar charcoal.

Diamond:
Diamonds are measured in carats.
One carat = 0.2 g = 200 mg
- In India, Kohinoor and pitt diamonds are available. Kohinoor is 186 carats and pitt is 136.25 carats.
- Heaviest known diamond in the world is cullinan. It has 3026 carats (S.Africa)

Properties:
- Diamond is the hardest known substance
- It glitters because its refractive index is high i.e., 2.45.
- It has highest m.p. than any other element i.e., 4200 K.
- Diamonds are insulators i.e., bad conductors of electricity.
- It is transparent to light and x-rays.
- It is insoluble in any solvent.
- It is the purest crystalline form of C.
- It is inert form of carbon.
- It is stable upto 1500°C. On heating invacuum above 1500°C, it changes to graphite. [1500 – 800°C]

Structure:
- In diamond, C is sp³ hybridised. Each C is tetrahedrally bonded to four other carbons by strong sigma bonds.
- C – C bondlength is 1.54 Å.
- C – C bond angle is 109°.
- It is three dimensional giant polymeric
- It is the hardest with highest m.p. because of its polymeric structure.
- It is bad conductor as all the four valence electrons are utilised in bonding and number of electrons is left free.

Uses:
- In jewellery as precious stones.
- In cutting tools.
- As abrasives.

Graphite:
- It is also known as black lead or plumbago.
• It is thermo dynamically more stable. It is good conductor of heat and electricity because each C is left with one free electron.
• It’s melting point is very high i.e., around 3500°C.

**Preparation of artificial graphite:**
• Graphite is artificially prepared by Acheson’s process. Coke is heated with silica above 3500°C in an electric furnace.
• The SiC is formed and it decomposes to give graphite on further heating
  \[
  \text{SiO}_2 + 3C\text{(coke)} \rightarrow \text{SiC} + 2\text{CO}
  \]
  \[
  \text{SiC}\text{(carborundum)} \xrightarrow{\Delta} \text{Si} + C\text{graphite}
  \]

**Structure of graphite:**
• C is sp² hybridized. Each C is bonded to three other carbons by strong \(\sigma\) bonds. The fourth valence electron of all carbon atoms together will form a delocalised \(\pi\)-electron cloud which is responsible for the conducting nature of graphite.
• Graphite consists of hexagonal rings.
• It has layer lattice structure.
• The layers are bound by Vanderwall forces.
• The distance between the layers is 3.35 Å.
• C – C bondlength is 1.42 Å.
• High meting point of graphite is due to its to two dimensional polymeric structure.
• C – C – C bond angle is 120°.
• The soft and slippery nature of graphite is due to layer lattice structure.

**Uses:**
Used in lead pencils (consists graphite and clay).
• As dry lubricant.
• In making electrodes.
• As moderator in nuclear reactors.
• In painting stoves.
• In electroplating and electrotyping.

**Physical and chemical properties of carbon:**
• Different allotropes of carbon have nearly same reactivity.
• The amorphous forms of C are more reactive due to their increased surface area.
• C reacts with air (or) \(O_2\) and forms \(CO_2\).
• \(C\ (\text{diamond}) + O_2\text{(excess)} \xrightarrow{\text{100°C}} \frac{\text{C}O_2}{\text{Electric furnace}}\)
• \(C\ (\text{white hot coke}) + S\text{(vapour)} \rightarrow \text{CS}_2\)
• Carbon reacts with the oxidizing acids like \(\text{HNO}_3\) and gives acidic oxides.
  \[3C + 4\text{HNO}_3 \xrightarrow{\Delta} 3\text{CO}_2 + 4\text{NO} + 2\text{H}_2\text{O}\]
• Hot \(\text{H}_2\text{SO}_4\) yields \(\text{CO}_2\) and \(\text{H}_2\text{SO}_4\) is reduced to \(\text{SO}_2\).
  \[C + 2\text{H}_2\text{SO}_4\text{(conc)} \xrightarrow{\Delta} \text{CO}_2 + 2\text{SO}_2 + 2\text{H}_2\text{O}\]
C reacts with dil HNO₃ or Conc HNO₃ or Conc H₂SO₄ but not with dil HCl and dil H₂SO₄ because dil / conc HNO₃, Conc H₂SO₄ are oxidizing agents but dil HCl and dil H₂SO₄ are non-oxidizing agents.

C (white, hot coke) + H₂O (steam)

\[ \rightarrow CO \uparrow + H₂ \uparrow \text{ (water gas)} \]

Carbon can act as reducing agent.

\[ SnO₂ + 2C \rightarrow Sn + 2CO \]
\[ CO₂ + C \xrightarrow{\Delta} 2CO \]
\[ Fe₂O₃ + 3C \xrightarrow{250-400^\circ C} 2Fe + 3CO \]

Carbon reduces sodium hydroxide to Na metal.

\[ 2C + 6NaOH \rightarrow 2Na₂CO₃ + 2Na + 3H₂ \]

Carbon reacts with metals or metal oxides to form carbides.

\[ 3Fe + C \rightarrow Fe₃C \]
\[ CaO + 3C \rightarrow CaC₂ + CO \]

Uses of carbon:

i. Mainly C is used as a reducing agent.
ii. It is used in manufacture of CS₂.
iii. In the production of water gas and producer gas.
iv. Activated char coal is used to absorb poisonous gases.

USES OF OXIDES OF CARBON:

Carbon monoxide

- CO is important component of gaseous fuels like producer gas, water gas and coal gas.
- CO is a good reducing agent for many metal oxides to produce metals.
- CO is a good ligand in the metallurgy of Ni by Mond’s process.

Carbon dioxide

- Solid CO₂ is called as dry ice or cardice and used as refrigerant.
- As a coolant in the lab.
- In the manufacturing of urea and in creating inert atmosphere and in neutralizing alkalies.
- As fire extinguisher.
- Used in nitrogenous fertilizer and making urea.
- \[ C₂O₂ \text{ reacts with water and gives malonic acid } CH₂(CHOH)₂ \]

Silica (SiO₂)

- Silica is more abundant in the nature in the form of silicates. Mainly in the form of aluminium silicate.
- SiO₂ exhibits allotropy.
  (1)Crystalline forms: Quartz, trydimite, Crystobalite
At low temperature, α form and at high temperature β form of each crystalline exists. Pure quartz is colourless and impure quartz is coloured

(2) **Amorphous Forms:** Agate, Jaspar, Onyx are the amorphous forms of silica.

- Sand stone consists of sand particles and iron oxide.
- Flint silica consists of both Quartz and amorphous forms.
- Kiesulguhr silica consists of minute sea organisms.

**Preparation of silica:**

1. By burning of Si in O₂
   
   \[ \text{Si} + \text{O}_2 \rightarrow \text{SiO}_2 \]

2. By hydrolysis of SiCl₄ or SiF₄.
   
   \[ \text{SiCl}_4 + 4\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4 + 4\text{HCl} \]
   
   \[ 3\text{SiF}_4 + 4\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4 + 2\text{H}_2\text{SiF}_6 \text{(orthosilicic acid)} \]
   
   \[ \text{H}_4\text{SiO}_4 \rightarrow \text{SiO}_2 + 2\text{H}_2\text{O} \]

- Silica is insoluble in water
- Silica is soluble only in HF among all the acids

**Chemical properties:**

1) **With HF:** It reacts with HF to give SiF₄.
   
   \[ \text{SiO}_2 + 4\text{HF} \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O} \]

2) **With coke:** on heating silica with coke, SiC or carborundum is formed. SiC is very hard substance

   \[ \text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO} \]

3) **Acidic nature:**

   - SiO₂ is slightly acidic in nature.

   \[ \therefore \text{It reacts with bases, basic oxides and basic carbonates to give corresponding silicates.} \]
   
   \[ \text{SiO}_2 + \text{Na}_2\text{O} \rightarrow \text{Na}_2\text{SiO}_3 \]
   
   \[ \text{SiO}_2 + \text{CaO} \rightarrow \text{CaSiO}_3 \]
   
   \[ \text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \]
   
   \[ \text{SiO}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{SiO}_3 + \text{CO}_2 \]
   
   \[ \text{SiO}_2 + \text{CaCO}_3 \rightarrow \text{CaSiO}_3 + \text{CO}_2 \]

**Action of Heat:**

- On heating, one form changes to another form and above 1700°C all the forms change into liquid state.
- Quartz is the purest form of silica.

**Structure of silica:**

- In SiO₂, each Si is tetrahedrally bonded to four oxygen atoms.
- Though Si is bonded to four ‘O’s, the formula is SiO₂ because those four ‘O’s are inturn shared by other silicons.
- It is 3-dimensional giant polymer resembling diamond.
- But, SiO₂ is soft with low m.p. when compared to diamond because Si – O – Si bonds are weak.
There is no direct Si – Si Bond

**SILICONES**

- Silicones are organo silicon polymers containing Si – O – Si bonds.
- Silicones are formed by the hydrolysis of alkyl or aryl substituted chloro silicates and their subsequent polymerization.
- Silicones contain R₂SiO repeating unit.
- The empirical formula of silicone R₂SiO is analogous to that of ketone (R₂CO) and hence are named silicones.

- Alkyl or aryl substituted chlorosilanes are prepared by the reaction of R – Cl with silicon in the presence of metallic copper as a catalyst
  \[ 2RCl + Si \xrightarrow{Cu\text{ powder}} R_2SiCl_2 \]

- Hydrolysis of substituted chlorosilicones yield corresponding silicones which under polymerization.

- Polymerization of dialkyl silane diols yield linear thermoplastic polymers.
- Cyclic or ring silicones are formed when water is eliminated from terminal –OH groups of linear silicones.
- Hydrolysis of RSiCl₃ gives crosslinked silicone.
- Commercial silicone polymers are usually methyl derivatives and to a lesser extent phenyl derivatives.
- Silicones have chemical inertness, water repelling nature, heat resistance and good electrical insulating properties.
- Silicones are used as scalants, greases, electrical insulators in making water – proof cloth & papers and in silicon rubber preparation.
- Silicones are used in paints and enamels.

**SILICATES:**

- Many building materials are silicates. Ex: Granites, slates, bricks and cement.
- Ceramics and glass are also silicates.
- The Si-O bonds in silicates are very strong.
- They do not dissolve in any of the common solvents nor do they mix with other substances readily.
The silicates can be divided into six types. They are mentioned here.

i) **Orthosilicates or Nesosilicates**: Their general formula may be \( M^{+2} (SiO_4)^{−4} \).

   Example: Willemite \( Zn_2(SiO_4) \)

ii) **PyroSilicates or SoroSilicates or DiSilicates**: These contain \( SiO_4^{−6} \) units. PyroSilicates are rare.

   Example: Thortveitite \( Ln_2[Si_2O_7] \).

iii) **Chain Silicates**: They have the units \( (SiO_3)_n^{−} \)

   Example: Spodumene \( LiAl(SiO_3)_2 \).

   Amphiboles are one type chain Silicates. Generally double chains are formed in them.

iv) **Cyclic Silicates**: They are silicates having ring structures. They may be formed of general formula \( (SiO_3)_n^{−} \) . Rings containing three, four, six and eight tetrahedral units are known. But rings with three and six are the most common.

   Ex: Beryl \( Be_3Al_2[Si_6O_{18}] \)

   v) **Sheet Silicates**: When SiO4 units share three corners the structure formed in an infinite two dimensional sheet. The empirical formula \( (Si_2O_3)_n^{2−} \). These compounds appear in layer structures. They can be cleaved. Ex: Kaolin \( Al_2(OH)_4 Si_2O_5 \).

   Example: Kaolin \( Al_2(OH)_4 Si_2O_5 \).

   vi) **Frame work silicates or three dimensional silicates**: Sharing all the four corners of a SiO4 tetrahedron results in three dimensional lattice of formula SiO4.

   Example: Quartz; Tridymite; Cristobalite; Feldspar and Ultramarine (\( Na_8[Al_6Si_6O_{24}]S_2 \)), Zeolites

### Uses of Silicates

i) Clay minerals are used for absorbing chemicals.

ii) Micas (i.e. sheet silicates) are used for electrical insulation.

iii) Asbestos is used for thermal insulation.

iv) Agate and flint are used as hard or sharp surfaces.

v) Variety of silicates used for ornaments and jewellery.

vi) Cement, ceramics and glass are all useful material to the man.

- Simple ortho silicates contain discrete SiO4 units Eg: olivine-, Zircon - \( ZrSiO_4 \), phenacite - \( Ba_2SiO_4 \), willimitc \( Zn_2SiO_4 \), \( Mg_2SiO_4 \).
- Pyrosilicates are formed when two SiO4 tetrahedral share a corner.
- Pyrosilicates contain units \( SiO_3^{−} \).
- Examples for Pyrosilicates thortveitite \( Sc_3SiO_3^{−} \), Hemimorphite \( Zn_xSi_2O_6 Zn(OH)_2 2H_2O \).
When SiO$_4$ units share two oxygen atoms with each other cyclic and linear single chain silicates having the empirical formula \[\left[\text{SiO}_4\right]^{2n-}\].

- **Beryl** - \(\text{BeAlSi}_2\text{O}_6\) is cyclic silicate.
- **1 linear silicate chain is present in Diopside** - \(\text{MgCu}\left(\text{SiO}_4\right)_2\) or \(\text{MgCaSi}_2\text{O}_6\).
- If two linear chains are cross-linked, the resulting double stranded silicates have the composition \(\left[\text{Si}_{1}\text{O}_{1}\right]^{2n-}\) and are called amphiboles.

**ZEOLITES:**
- Aluminium silicates are called Zeolites Eg. \(\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8\cdot x\text{H}_2\text{O}\)
- (sodium aluminium orthosilicate)
- If aluminium atoms replace few silicon atoms in 3-D net work of silica \(\text{SiO}_2\) the overall structure know as alumunium is formed and it acquires negative charge.
- Cations such as Na$^+$, K$^+$, Ca$^{2+}$ etc. balance the negative charge.
- Eg: Feldspar & zeolites.
- These have honey comb like structure and have the general formula \(M_n\left(AIO_2\right)_{3/2}\left(SiO_2\right)_x\cdot H_2O\) \((M = \text{Na}^+ , K^+ \text{ or Ca}^{2+})\) \( (n = \text{charge on metalion})\)
- These act as ion exchanger and molecularsieves
- Artificial Zeolites can be prepared by heating chain clay silica & \(\text{Na}_2\text{CO}_3\)
- Eg of artificial zeolite is permutite, \(\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8\cdot x\text{H}_2\text{O}\) used in the softening of hard water.

**USES OF ZEOLITES:**

As catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation eg: (A type of zeolite) used to convert alcohols directly into gasoline hydrated zeolites are used as ion exchangers of hard water.

**SILICON TETRACHLORIDE:**

1. SiCl$_4$ is know as tetrachlorosilico methane.
2. It is used.
   (i) To make ultra pure Si for transistors.
   (ii) SiCl$_4$ mixed with ammonia is used in warfare for the production of smoke screens.
   (iii) SiCl$_4$ is hydrolysed at high temperature to give fine SiCl$_2$. This SiCl$_2$ is used in epoxy paints and resins.
   (iv) SiCl$_2$ obtained as above is used as an inert filler in silicons rubber.
3. SiCl$_4$ does not form \([\text{SiCl}_6]^{2-}\). Because
   (i) Si$^{+4}$ is small in size. Six Cl$^{-1}$ ions cannot be accommodated around Si$^{+4}$ ion.
   (ii) The interaction of the lone pairs on Cl$^{-1}$ ion and the Si$^{+4}$ particle is weak.
Uses of Silica:
- As building material.
- Quartz glass is used to prepare glass to work with u, v radiation.
- In the preparation of sand bricks used for lining of furnaces.
- Coloured quartz is used in making lenses, optical instruments.
- As acid flux in metallurgy.

Fuel gases:
- Fuels burn in air and produce heat energy.
- Calorific value can be expressed as the heat energy released per gram.
- Calorific value is also expressed as kJ/m³ for gaseous fuels.
- Out of solid, liquid and gaseous fuels, the gaseous fuels are more advantageous because of:
  a) High calorific value
  b) No ash and no smoke.
  c) Easy to transport.

Producer gas:
- It is the mixture of CO(33%) + N₂(64%).

Manufacture:
- It is manufactured in a furnace named as gas producer by the incomplete combustion of coal.
- The furnace is filled with coal and air is sent into it through its bottom.
- Some of the coal is burnt to give CO₂, which rises up through hot beds of coal and gets reduced to CO.
  \[
  C + O₂ \rightarrow CO₂
  \]
  \[
  CO₂ + C \rightarrow 2CO
  \]
- Through the exit at the top, producer gas is collected.
- Its calorific value is very low because N₂ is non-combustible.
- It should be used on the spot to avoid loss of heat.

Uses:
- As fuel in steel and glass industries
- As fuel in gas engines.
- As fuel in the manufacture of ammonia

Water gas:
- It is the mixture of CO and H₂ in 1 : 1 ratio by volume. It is also known as blue gas as both components burn with blue flame.
- It is also called synthesis gas.

Manufacture:
- By passing steam over white hot coke water gas is prepared.
  \[
  C + H₂O \overset{>1000{^\circ}C}{\rightarrow} CO + H₂ - \text{heat}
  \]
- The above reaction is endothermic and hence the coke becomes cold after some time. If steam is passed over cold coke, unwanted reaction occurs.
  \[
  C + 2H₂O \rightarrow CO₂ + 2H₂
  \]
- To maintain required temperature air is supplied for some time. Thus, steam and air are supplied alternately over coke to produce water gas.
- Water gas has high calorific value.

Uses:
• As fuel in various industries.
• In the manufacture of ammonia by Haber’s process.

**Semiwater Gas:** (Thin producer gas)
• It is the mixture CO, H₂ and N₂ (CO + H₂ + N₂)
• The order of their volumes in semiwater gas.
  N₂ > CO > H₂
  55%, 25%, 10%
• Semi-water gas is obtained by passing steam and air simultaneously over white hot coke.
• Its calorific value is less than that of water gas.

**Uses:**
• As fuel in steel industry.
• In internal combustion engines.

**Carburetted water gas:**
• It is mixture of water gas and hydro carbons.
• The order of volumes of various gases in the carbureted water gas: H₂ > CO > Saturated hydrocarbons > Unsaturated hydrocarbons
• Its calorific value is very high.
• It is also used as industrial fuel.
• For the above fuel gases, the order of calorific values is

Carburetted water gas > water gas > semi water gas > producer gas