Maharaja Institute of Technology Mysore

Department of Chemistry (18CHE12/22)

MODULE *3*: ENERGY SYSTEMS 10 Hours

Chemical Fuels: Introduction, classification, definitions of CV, LCV, and HCV, determination of calorific value of solid/liquid fuel using bomb calorimeter, numerical problems. Knocking of petrol engine – Definition, mechanism, ill effects and prevention. Power alcohol, unleaded petrol and biodiesel

Fuel Cells: Introduction, differences between conventional cell and fuel cell, limitations & advantages. Construction, working & applications of methanol-oxygen fuel cell with H_2SO_4 electrolyte, and solid oxide fuel cell (SOFCs)

Solar Energy: Photovoltaic cells- introduction, construction and working of a typical PV cell, Preparation of solar grade silicon by Union Carbide Process/Method. Advantages & disadvantages of PV cells

Q1. What is a chemical fuel? Give its classification with an example.

Definition: Fuel is any combustible carbonaceous substance, which on burning produces significant amount of heat which can be used economically for industrial and domestic purposes.

Classification on the basis of their origin:

- **Primary or natural fuel** is the one, which occurs naturally and requires no chemical processing before utilization. Ex: wood, coal, peat, crude petroleum and natural gas.
- **Secondary or artificial (derived) fuels** are produced from primary fuels by subjecting them to treatments before utilization. Ex: coke, coal gas and gasoline.

Classification of fuels on the basis of state of aggregation:

State of phase	Primary fuel	Secondary fuel
Solid	Wood, peat, lignite, coal, anthracite	charcoal, coke
Liquid	Crude petroleum	Petrol, kerosene, fuel oil, diesel oil
Gaseous	Natural gas	Coal gas, water gas, producer gas, biogas.

Q2. Mention the characteristics of a good fuel.

- The fuel should have high calorific value.
- It should have a moderate ignition temperature and burn efficiently.
- The fuel should have low moisture content.
- The fuel should leave a low ash content after the combustion.
- The fuel must not produce harmful combustion products such as CO, SO_2, H_2S, NO_2 etc & smoke.
- Fuel must be readily available in abundant amount in natural form or any other form.
- Storage, transportation and handling of the fuel should be easy.
- Combustion rate should be low (combustion should not be rigorous). It should be possible to regulate combustion rate properly.

Q3. What is Calorific Value (CV) of a fuel? Explain the types of calorific value.

Definition: Calorific value of a fuel is defined as the amount heat released/liberated when unit quantity (mass or volume) of a fuel is burnt completely in air or oxygen.

Types of calorific value:

1. **Gross calorific value (GCV) or Higher calorific value (HCV):** GCV is defined as the total amount of heat produced when unit quantity (mass/volume) of the fuel is burnt completely in air or oxygen and the products of combustion are cooled/condensed to room temperature.
2. **Net calorific value (NCV) or Lower calorific value (LCV):** NCV is defined as the amount of heat produced when a unit amount of a fuel is burnt completely in air and the products of combustion are allowed to escape.

NCV = GCV – Latent heat of water vapour formed

= GCV – Mass of hydrogen × 9 × Latent heat of steam NCV = GCV – (9 × % H × Latent heat of steam)/ 100

NCV = GCV – (0.09 × % H × Latent heat of steam)

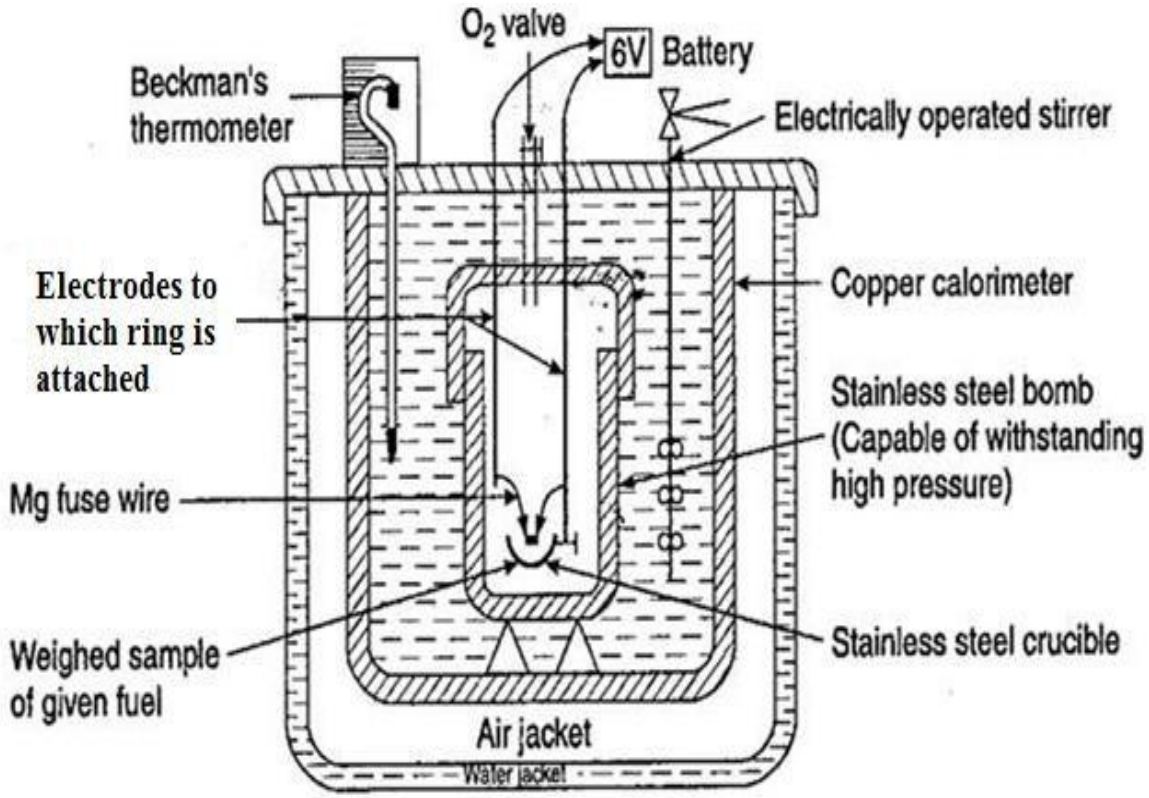
Units of calorific value: The calorific value is generally expressed in joules per kg (J/kg) for solid fuels and joules per cubic meter (J/m^3) for gaseous fuels in SI units.

Q4. Explain the determination of calorific value of a solid/liquid fuel by using Bomb calorimeter.

Principle: A known mass of solid or liquid fuel is completely burnt in excess of oxygen in a bomb calorimeter. The heat liberated is absorbed by surrounding water and calorimeter. Thus the heat liberated by burning fuel is the heat gained by water and copper calorimeter.

Construction: It consists of strong stainless steel bomb having oxygen valve and an electrically operated ignition coil for the combustion. The bomb is place in the copper calorimeter which is surrounded by air jacket and water jacket to prevent the loss of heat in the form of radiation. The calorimeter is provided with an electrically operated stirrer and a Beckman's thermometer.

Working: A known mass of fuel is taken in a crucible; a fine magnesium wire is stretched across the metal electrodes. Oxygen is filled, stirrer is operated and initial temperature is noted. Electrodes are connected to the battery, fuel burns, heat is liberated and a maximum temperature attained is recorded.



Calculation:

Mass of the fuel sample taken in the crucible = 'm' g

Mass of water in the calorimeter = W_1 g

Water equivalent of calorimeter, stirrer, thermometer, bomb, etc. = W_2

Initial temperature of water in calorimeter = t_1 ^{0}C

Final temperature of water in calorimeter = t_2 ^{0}C

S = Specific heat; kJ/ kg / ^{0}C

Higher calorific value of the fuel = Q kJ/kg

Heat liberated by burning 'm' Kg of fuel = mQ kJ/ kg

Heat absorbed by water & equipment = $(W_1 + W_2) \times S \times (t_2 - t_1)$ KJ Kg^{-1}

But, heat liberated by the fuel = heat absorbed by water

i.e., $mQ = (W_1 + W_2) \times S \times (t_2 - t_1)$ KJ Kg^{-1}

$$\therefore GCV = Q = \frac{(W_1 + W_2) \times S \times (t_2 - t_1)}{m} \frac{KJ}{Kg}$$

NCV = GCV – (0.09 x %H x Latent heat of steam) KJ Kg^{-1}

Q5. Define Knocking. Explain Knocking mechanism in a petrol (IC) engine.

Definition: Knocking may be defined as the production of shock waves in an IC engine as a result of explosive combustion of air-petrol vapour mixture (due to increase in compression ratio beyond a certain value) which hit the cylinder wall and piston, creating rattling sound.

Mechanism of knocking

The efficiency of an IC engine depends mainly on the compression ratio. It is the ratio of the initial volume of the petrol air mixture to the volume at the end of compression. Increase of compression ratio (to a certain limit) not only increases the efficiency of the engine but also saves the fuel which dependent on the nature of constituents present in the gasoline used. Under normal conditions slow oxidation of the fuel takes place. The oxygen combines with few hydrocarbons and activates those forming peroxides. The activated molecules in-turn combine with other hydrocarbon molecules resulting in smooth combustion.

However, beyond a particular compression ratio, knocking occurs because the chain reaction proceeds in a very fast rate. The unstable peroxides formed decompose giving a number of gaseous compounds. These gaseous products formed ignite

instantaneously and produce shock wave which dissipates its energy by hitting the cylinder wall and piston. As a result, rattling sound is heard.

$C_2H_6 + 3\ ½\ O_2 \rightarrow 2CO_2 + 3H_2O$ ..... Normal combustion

$C_2H_6 + O_2 \rightarrow CH_3O\text{-}OCH_3$

$CH_3O\text{-}OCH_3 \rightarrow CH_3CHO +$

H_2O

$CH_3CHO + 1\ ½\ O_2 \rightarrow HCHO + CO_2 + H_2O$ **Explosive combustion**

$HCHO + O_2 \rightarrow CO_2 + H_2O$

Adverse effect of knocking:1) Knocking increases fuel consumption, 2) reduces engine power and efficiency 3) damages the engine parts like spark plug, piston due to overheating of the cylindrical parts, 4) It produces undesirable rattling noise, 5) The driving becomes rather unpleasant.

Note: Chemical structure and knocking: The tendency of fuel constituents to knock is in the following order: Straight-chain alkanes > branched-chain alkanes > olefins > cyclo alkanes > aromatics.

Q6. Write a note on antiknocking agents or How do you prevent knocking

1. **Leaded petrol or Ethylated petrol:** Knocking can be reduced by adding small amounts of antiknocking agents like TEL (tetra ethyl lead), TML (tetra methyl lead) or a mixture of TEL and TML. These compounds react with peroxy compounds and decomposes them immediately forming lead oxide and lead. These may damage the exhaust pipe. Therefore they are mixed with ethylene dichloride or di bromide which converts lead oxide to lead chloride and lead bromide which are volatile and escapes easily into the atmosphere.

2. **Unleaded petrol:** Unleaded does not contain any lead compounds (like TEL) but mixed with higher octane number compounds like ***isooctane, isopentane, ethyl benzene, etc. Further they are mixed with MTBE*** (methyl tertiary butyl ether $[(CH_3)_3OCH_3]$ or ETBE which contains oxygen for the combustion of petrol, thereby reducing the extent of peroxy compound formation. By the use of these compounds knocking is reduced.

Unleaded petrol also allows the use of ***catalytic converter.*** It brings complete combustion of NO_x and CO. Unburnt hydrocarbons are also completely combusted.

Q7. Write a note on power alcohol (gasohol).

Power alcohol is gasoline blends containing ethanol which can be used as a fuel in internal combustion engines. Blend containing up to 25% of alcohol with petrol are used. The main objective of the power alcohol is to reduce oil imports and provide an alternative to non-renewable energy source i.e. gasoline.

The importance of power alcohol as fuel is:

- Octane number of alcohol is 90 where as the octane number of petrol is 60-70. Addition of alcohol to petrol increases the octane number of power alcohol. Hence, power alcohol possesses better anti-knocking properties.
- Because of the higher octane number, power alcohol can be used in engines with higher compression ratio without any change in engine design.
- No engine starting difficulties with power alcohol as fuel.

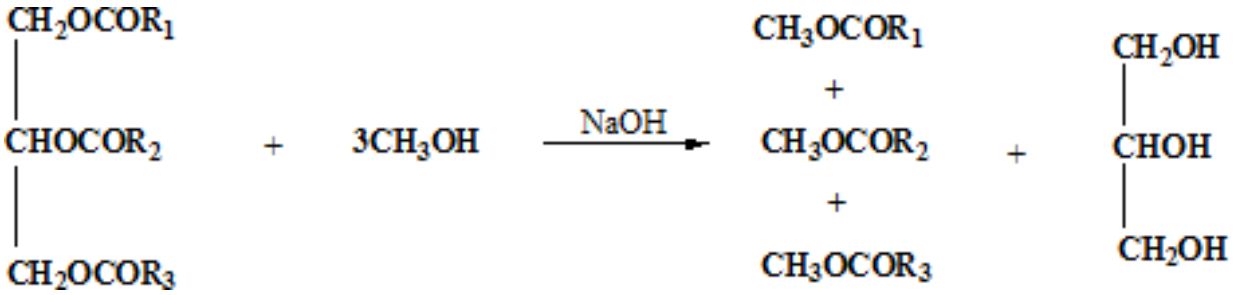
Disadvantages of power alcohol:

- The calorific value of alcohol is low. Hence, power alcohol has low calorific value.
- Due to oxidation of alcohols to acids, it is liable to cause corrosion in fuel storage tanks.
- At low temperature, there is a difficulty in starting the engine due to lower pressure of alcohol.

Q8. Write a note on Biodiesel.

Biodiesel is a renewable, oxygenated fuel obtained from a variety of vegetable oils and animal fats. Chemically biodiesel is a mixture of mono alkyl esters of long chain fatty acids. Biodiesel is produced from vegetable oils such as soya bean, jatropha, corn, sunflower, cotton seed, rubber seed etc., and animal fats like tallow, yellow grease, lard etc

Oils are triglycerides i.e. esters of fatty acids. These triglycerides are converted into biodiesel by a process called transesterification. Oils and fats are reacted with CH_3OH in the presence of base catalyst (NaOH) at 60-70 ^0C to produce fatty acid methyl esters (biodiesel) and the co-products such as glycerol.



Triglyceride (oil) Biodiesel (methyl ester) Glycerol

Advantages of biodiesel:

- It is made using renewable sources and readily undergoes biodegradation.
- Biodiesel has a higher cetane number (48-60) compared to diesel (40-55).
- Use of biodiesel reduces greenhouse gases (eco-friendly).
- Addition of 20% of biodiesel (B20) to diesel brings down the pollutants greatly without any engine modification.

Q9. What are fuel cells? Explain its working principle. Mention its advantages and limitations

Definition: Fuel cells are defined as galvanic cells in which chemical energy of a fuel is directly converted into electrical energy by means of redox reactions involving fuels and oxidants. Fuel cells give direct current as long as fuel and oxidant are supplied. A general fuel cell is represented as:

Fuel | electrode | electrolyte | electrode | oxidant

Working principle:

At anode: fuel undergoes oxidation as **Fuel → Oxidized product + ne^-**

At cathode: the oxidant gets reduced as **Oxidant + ne^- → Reduced product** The electrical output is a result of flow of electrons from anode to cathode through the external circuit.

Advantages of fuel cells:

- High efficiency of energy conversion process (75%).
- They are eco-friendly as the products of the overall reactions are not toxic and hence pose no pollution problems.
- They can produce direct currents for long periods at a low cost.
- Recharging of fuel cells is not needed
- No moving parts and so elimination of wear and tear

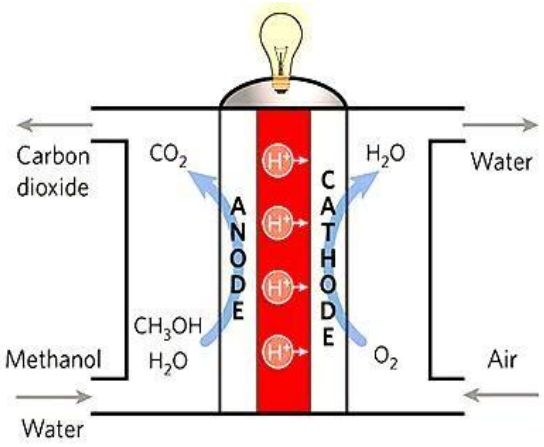
Limitations of fuel cells:

- The electrode used is Pt, Ag or alloys of noble metals, which are costly.
- The power generated is moderate.

Q10. Give the construction, working and applications of Methanol-Oxygen fuel cell.

Construction:

Anode : Porous Ni electrode impregnated with Pt/Pd catalyst
Cathode : Porous Ni electrode coated with Ag catalyst
Fuel : Methanol
Oxidant : O_2/Air
Electrolyte : H_2SO_4



Working: Methanol mixed with sulphuric acid (3.7M) is circulated through the anode chamber. Pure oxygen is passed through the cathode chamber and sulphuric acid (electrolyte) is placed in the central compartment. A membrane is inserted adjacent to the cathode on the inner side to minimize diffusion of methanol into the cathode thereby reducing the concentration of methanol near the cathode. In the absence of a membrane, methanol diffuses through the electrolyte into the cathode and undergoes oxidation. The EMF the cell is 1.20V at 25°C.

The electrode reactions are:

At anode: $CH_3OH\ (l) + H_2O\ (l) \rightarrow CO_2\ (g) + 6H^+(aq) + 6e^-$

At cathode: $3/2\ O_2\ (g) + 6H^+\ (aq) + 6e^- \rightarrow 3H_2O\ (l).$

Overall reaction: $CH_3OH\ (l) + 3/2\ O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l).$

Note: An advantage of the use of an acid electrolyte is that the CO_2, a product of the reaction can be removed easily. In case of alkaline electrolyte (KOH), it combines with CO_2 and gets converted into carbonate. This decreases the efficiency because of the increasing concentration polarization at the electrode surface and decreasing the conductivity if the electrolyte.

Applications:

- Military applications
- Large scale power production

Q11. Give the construction, working and applications of Solid-oxide fuel cell (SOFC's).

Construction:

Anode: Electronically conducting porous Ni/ Yttria-Stabilized Zirconica (Ni/YSZ)

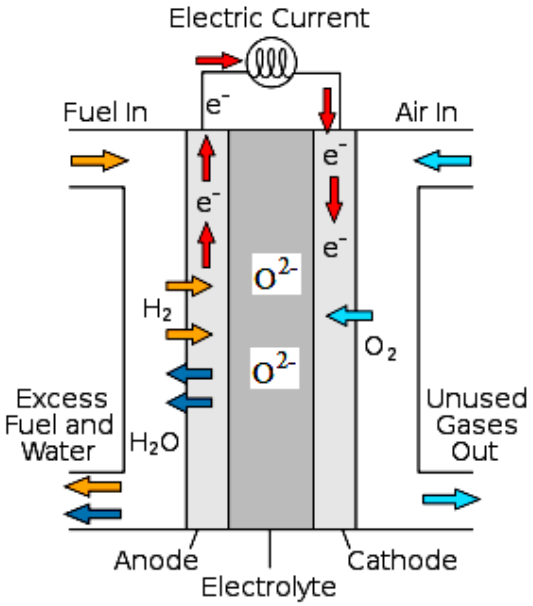
Cathode : Electronically conducting porous Lanthanum Manganate ($LaMnO_3$)

Fuel : H_2/ CO

Oxidant : Air/ O_2

Electrolyte : Yttria-Stabilized Zirconica (an oxygen ion conducting electrolyte)

Working: Solid oxide fuel cell consists of two porous ceramic electrodes separated by oxide ion conducting electrolyte. The oxygen is supplied at the cathode undergoes reduction to form oxide ions, which migrate to the anode though the oxide ion conducting electrolyte. At the anode, oxide ions combine with H_2 or CO in the fuel to form H_2O and CO_2, liberating electrons. Electrons flow from the anode through the external circuit.



The electrode reactions are:

At anode: $H_2 + O^{2-} \rightarrow H_2O$

At cathode: $1/2\ O_2 + 2e^- \rightarrow O^{2-}$

Overall reaction: $H_2 + 1/2\ O_2 \rightarrow H_2O$

Advantages:

- High efficiency
- long-term stability
- fuel flexibility
- low emissions and low cost.

Disadvantages:

High operating temperature which results in longer start-up times and mechanical and chemical compatibility issues.

Q12. Differentiate between fuel cell and a conventional battery.

	Fuel cell	**Battery (conventional cell)**
1	In Fuel cells, reactants are fed from outside and the products are removed constantly.	Batteries are not being supplied with reactants constantly. Reactants are the integral part of the battery
2	They do not store chemical energy. Fuel cells are energy conversion devices	They store chemical energy. Batteries are energy storage devices
3	They offer high energy conversions i.e, are more efficient	Efficiency of a battery is low.
4	They operate as long as the reactants are supplied to the electrodes from outside and do not need recharging	They operate until reactants stored in it are completely used up and secondary batteries need recharging
5	No toxic species are formed in a fuel cell and are more eco-friendly	Less eco-friendly

SOLAR ENERGY

Solar energy is the radiant energy due to illumination of the sun. It can be converted into various forms of energy such as thermal and electrical energies. The main advantage of using solar energy as a source of energy are that, it is readily available, free of cost and eco friendly. Solar energy alone can supply much more energy than the earth demands, but the only disadvantage that the sun does not shine all the time and not everywhere equally. Most of the other power sources like wind energy, wave energy and hydroelectricity have a common origin in sun.

Applications of solar energy: Solar energy is most commonly used in calculators, watches and other portable electronic devices as power supply source. In remote village places solar energy is the only way to meet energy requirements for lighting, domestic water supply and irrigation by using solar pumps. Solar energy is directly used for cooking in solar cooker, for heating rooms to maintain warmth and for heating water.

Solar energy utilization and conversion:

Utilization of solar energy: The solar energy utilization can be of two types.

a. Direct solar power. 2. Indirect solar power.

Direct solar power: It involves only one step transformation into a usable form.

- Photo voltaic cell is used to generate electricity.

- Sun light hits the dark absorber surface of a solar thermal collector and the surface warms. The heat energy may be carried away by fluid circuit.
- Sun light strikes a solar sail on a space craft and is directly converted into a force on the sail which causes the motion of the craft.

Indirect solar power: It involves more than one transformation to reach a usable form.

- Vegetation uses photosynthesis to convert solar energy to chemical energy which can be later burnt as fuel to generate electricity (bio mass).
- Hydroelectric dams and wind turbines are powered by solar energy through its interaction with the earth's atmosphere and resulting weather phenomena.
- The ocean thermal energy production uses thermal gradients that are present across ocean depths to generate power. The temperature differences are ultimately due to energy from the sun.

Conversion of solar energy: Solar energy may be converted to two useful forms of energy**.**

- **Thermal conversion:** In this method heat from the direct rays of sun is absorbed in the form of infrared radiation by the surfaces, water or air and put to many uses. The solar radiations are absorbed by flat plate collectors and the heat energy so produced is used for desalination process, warming water for domestic purpose, to keep the buildings warmth, metallurgical operations etc.

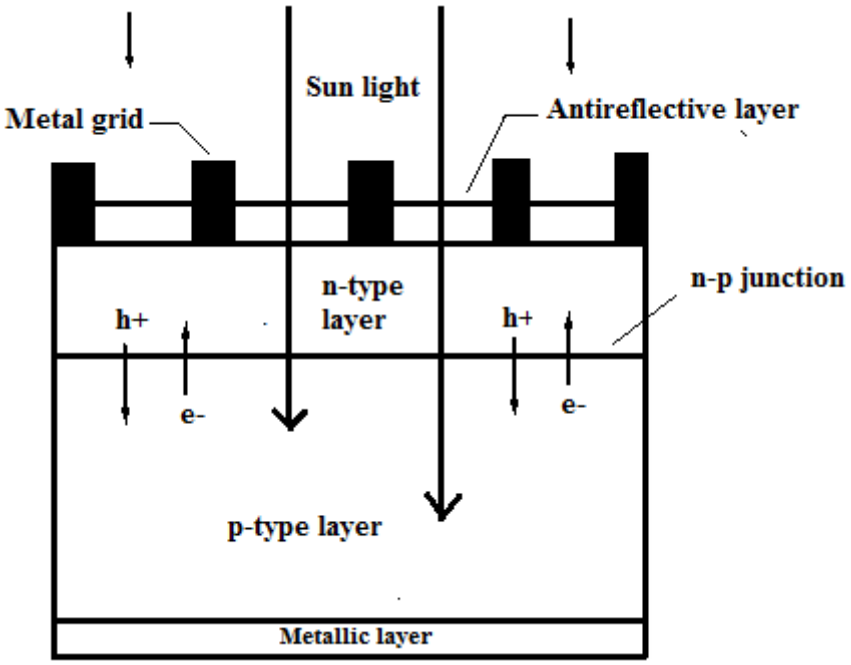
- **Photo conversion:** In photo conversion sun light is used to generate electricity by photo electric effect. When solar energy falls on the metal surface, it is absorbed. The electrons are excited and ejected from the metal surface. The electrons flow through the external circuit against the current and produce electrical energy. Photo voltaic cells or solar cells are designed based on this principle.

Q13. Define Photovoltaic cells or solar cells. Explain the construction and working of a Photovoltaic cell.

Definition: Photovoltaic cells are the semiconductor devices that generate direct current from sunlight. When semiconductors such as silicon are illuminated by photons (eg. from sun light), electricity is generated.

Construction & working of a photovoltaic cell: The solar cell is a semiconductor diode. A typical photovoltaic cell is composed of a thin wafer consisting of a ultra thin layer of phosphorous doped (n-type) silicon on top of boron doped (p-type) silicon. Hence a p-n junction is formed between the two. A metallic grid forms one of the electrical contacts of the diode and allows light to fall on the semiconductor between the grid lines. An anti reflective layer between the grid lines increases the amount of light transmitted to the semiconductor. The cell's other electrical contact is formed by the metallic layer on the back of the solar cell. A conventional solar cell is shown in Fig.

When light radiation falls on the p-n junction diode, electron-hole pairs are generated by the absorption of the radiation. The electrons are drifted to and collected at the n-type end and the holes are drifted to and collected at the p-type end. When these two ends are electrically connected through a conductor, there is a flow of current between the two ends through the external circuit. Thus photoelectric current is produced and available for use such as lighting spinning of fans, working of motors.



Solar cell structure

Q14. Explain the production of solar grade silicon by Union carbide process. The usual source of silicon is Quartz (silica or sand). Quartz is melted in the presence of coke and reduced to silicon in an electric furnace at over 1900^{0}C.

$$SiO_2 + 2\ C \rightarrow Si + 2CO$$

This molten silicon is drawn from the bottom of the furnace. The molten crude silicon is refined by treating with oxygen and slag forming additives like sand, limestone. The metallic elements in the silicon are oxidized and the oxides form slag with silica and limestone.

$$SiO_2 + 2\ Ca \rightarrow Si + 2CaO$$

$$SiO_2 + 2\ Mg \rightarrow Si + 2MgO$$

$$4Al + 3SiO_2 \rightarrow 3Si + 2Al_2O_3$$

The silicon obtained here is called metallurgical silicon which is 98% pure.

Solar grade silicon can be obtained in the following steps:

1. The metallurgical grade silicon is treated with hydrogen chloride gas at 300^{0}C to form trichlorosilane ($SiHCl_3$) and a small amount of tetrachlorosilane.

$$Si + 3HCl \rightarrow SiHCl_3 + H_2$$

$$Si + 4HCl \rightarrow SiCl_4 + 2H_2$$

2. Silicon tetra chloride is reduced with hydrogen at 1000^0 C in a reactor.

$$SiCl_4 + H_2 \rightarrow HSiCl_3 + HCl$$

3. The purified trichlorosilane is then passed through a fixed bed column filled with quaternary ammonium ion exchange resins acting as catalysts.

$$2HSiCl_3 \rightarrow H_2SiCl_2 + SiCl_4$$

$SiCl_4$ is recycled to the hydrogenation reactor. Dichloro silane is passed through a second fixed bed column filled with quaternary ammonium ion exchange resin, when H_2SiCl_2 is converted to silane .

$$3\ H_2SiCl_2 \rightarrow SiH_4 + 2HSiCl_3$$

Silane is separated by fractional distillation and trichlorosilane is recycled to the ion Exchange resin column.

4. Silane is further purified by distillation and then passed into a heated chemical vapour deposition reactor containing mounted silicon seed rods. On the surface of these seed rods silane decomposes and silicon deposits on them in pure form.

$$SiH_4 \rightarrow Si + 2H_2$$

Q16. List the advantages and disadvantages of photovoltaic (PV) cells.

a) Advantages of PV cells::

- Energy source is vast and essentially infinite.
- Solar cells need no recharging like batteries and produce electrical energy as long as sunlight is available.
- Solar cells have no movable parts and hence do not suffer from wear and tear.
- The materials used in PV cells do not corrode and serve for long duration.
- They operate at ambient temperature.
- PV cells involve no emissions, no combustion or radioactive residues for disposal.
- PV cells are environment friendly, do not contribute to global climate change or pollution
- low operating costs and quick installation.
- High reliability in modules.
- High public acceptance and safety record.

b) Disadvantages of PV cells:

- Poor reliability of auxiliary elements including storage
- The installation cost is high.
- PV cells generate only DC current and must be converted into AC power when used in distribution grids.
- Sun light is diffuse source, i.e , it is relatively low density energy.