

Solution

**CMR
INSTITUTE OF
TECHNOLOGY**



Sub:	Engineering Chemistry			Code:	18CHE22
Date: <u>23/06/2021</u>	Duration: <u>90</u> mins	Max Marks: <u>50</u>	Sem: <u>II</u>	Branch:	All

Internal Assessment Test I

1 (a) Explain the experimental determination of calorific value of solid/liquid fuel using Bomb calorimeter. (05 Marks) (CO3, L4)

Solution: Calorific values of solid or liquid fuels are determined by using **Bomb calorimeter**.

Principle: A known weight of the sample (solid or liq fuel) is burnt completely in excess of oxygen. The liberated heat is absorbed by the surrounding water and the calorimeter. Thus the heat generated during the combustion of fuel is equal to the heat absorbed by water and copper calorimeter. The GCV of fuel is calculated from the data.

Construction

The calorimeter consists of a stainless steel bomb. It has an airtight screw lid valve for introducing oxygen inside the bomb. It also has an electrical ignition coil for the initiation of combustion of fuel. The bomb is placed in a large well insulated Cu calorimeter. The calorimeter is equipped with a mechanical stirrer for dissipation of heat and a thermometer to read accurately the temperature rise.

Working

A known wt. of fuel (solid or liq) is placed in a small stainless steel crucible. The crucible is placed inside the bomb. The bomb is sealed airtight by the lid. The sealed bomb is placed in a large well insulated copper Calorimeter. The known mass of water is taken inside calorimeter. The water is continuously stirred by the mechanical stirrer. The initial temp of the water is carefully measured. The bomb is filled with oxygen and the combustion of fuel is initiated by passing electric current. As the sample burnt in the bomb, heat is liberated and it is absorbed by surrounding water and calorimeter. The temperature of water gradually rises and attains the maximum value. The maximum temp is carefully noted.

And, net

Where, F
kJ/kg) is

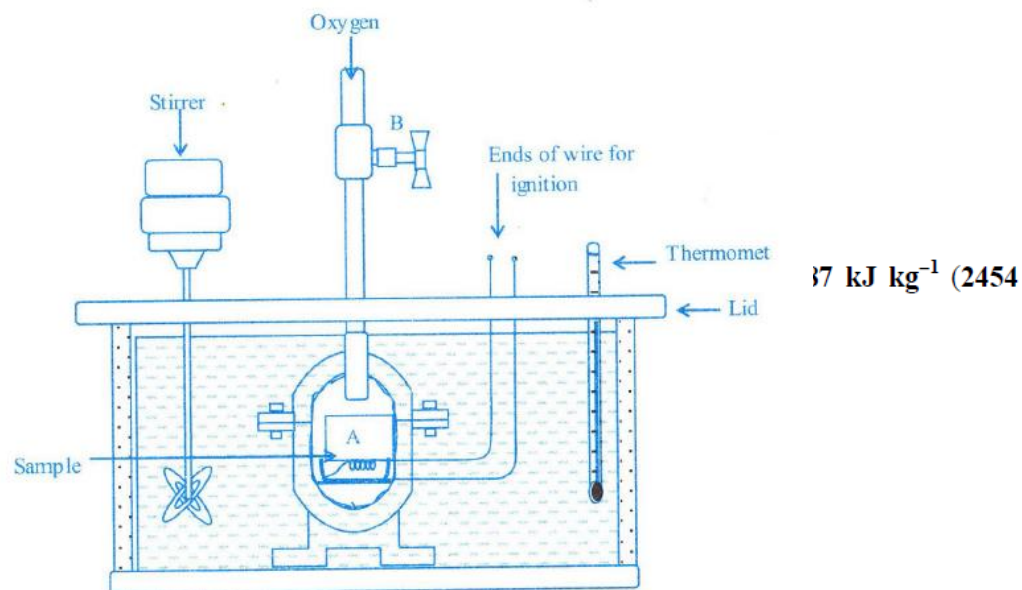


Fig. Bomb Calorimeter

Observation and calculation

Mass (wt) of the fuel = m (kg)

Mass of the water taken in calorimeter = W₁ (kg)

Water equivalent of calorimeter = W₂ (kg)

Initial temp. of water = T₁ °C

Final temp. of water = T₂ °C

Specific heat of water = s (4.18 KJ Kg⁻¹ °K)

Heat generated by burning 'm' kg of fuel = Heat gained by (surrounding water + calorimeter)

$$m \times \text{GCV} = (W_1 + W_2)(T_2 - T_1)(s)$$

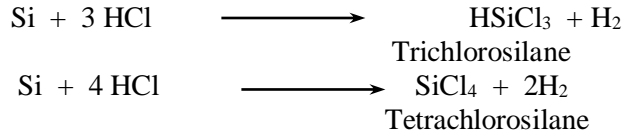
Where, 'GCV' is gross calorific value of the fuel.

$$\text{GCV} = \frac{(W_1 + W_2)(T_2 - T_1) 4.187}{m} \text{ KJ kg}^{-1} \dots\dots\dots(1)$$

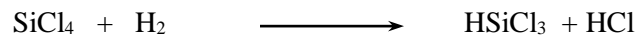
(b) Describe the production of solar grade silicon by Union Carbide process (05 Marks) (CO1, L2)

Solution: Preparation of Solar Grade Silicon by union carbide process:

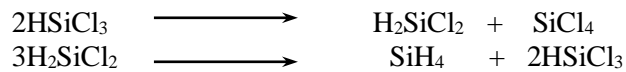
- Metallurgical grade silicon is heated to 300-350 °C and dry hydrogen chloride is passed. Trichlorosilane and a small amount of tetrachlorosilane are formed as given below



- Tetrachlorosilane is converted to trichlorosilane by treating with hydrogen at 1000°C.



- Trichlorosilane is passed through ion exchange resin containing quaternary ammonium salts to give dichlorosilane and tetrachlorosilane. Dichlorosilane subsequently forms trichlorosilane and silane (silicon tetra hydride).



- Tetrachlorosilane is hydrogenated again to trichlorosilane and trichlorosilane is again passed through ion exchange resin. The process is continued to get silane (silicon tetra hydride). Silicon hydride or silane obtained above is further purified by distillation. Silane is passed into a reactor containing heated silicon seed rods. Silane gets pyrolysed to form polysilicon (semiconductor grade silicon).



2 (a) Define Knocking? Explain mechanism of petrol Knocking in petrol engine and mention its ill effects. Which is the intermediate chemical functional group responsible for explosive combustion of petrol under knocking condition? (06 Marks) (CO3, L4)

Solution: Knocking: It is defined as the characteristic rattling, metallic sound produced due to thermal shock waves hitting the cylinder walls and piston during explosive combustion of fuel in an internal combustion (IC) engine. Following are the reasons for knocking to happen:

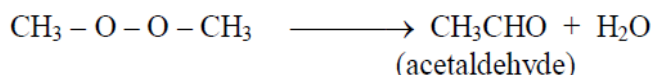
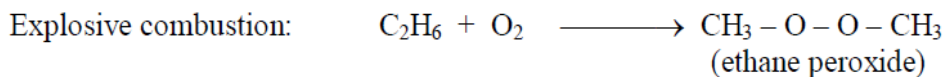
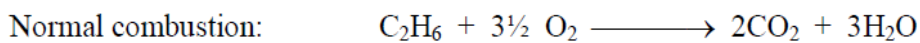
1. Higher compression ratio (CR) beyond the optimum level
2. Lower octane gasoline.
3. Formation of highly reactive intermediates (peroxides), which lead to explosive reactions.

Petrol Knocking: Petrol engine is spark ignited engine. Gasoline is burnt to produce energy.

During knocking, Petrol is vaporized and vapor is mixed with air. The petrol air mixture is drawn into combustion chamber (Suction stroke). The petrol air mixture is compressed (Compression stroke).

The mixture is ignited by a spark from spark plug and burnt. The gases produced by the combustion reaction expand. Expansion causes the piston to move i.e. kinetic energy is produced. When the flame front (after ignition) moves at optimum speed, fuel is burnt smoothly and completely. When the flame front moves slowly, products of initially burnt fuel, exert pressure on un-burnt fuel-air mixture. Due to build up of pressure, temperature will also increase. All the un-burnt fuel is ignited ahead of the flame front. This produces thermal shock waves (explosive combustion) which hit the cylinder walls and piston; resulting in a characteristic metallic sound called “knocking” or “pinking”.

The probable reactions during normal combustion and knocking are presented below taking ethane as the fuel component.



The unstable peroxides decompose readily to give a no. of gaseous compounds. This give rise to pressure waves which knocks.

Disadvantages of knocking:

- Produces undesirable rattling noise.
- Increased fuel consumption and lowered power output.
- Cause mechanical damage of engine parts because of overheating.
- Unpleasant driving.

(b) What is chemical fuel? Describe the classification of fuels. (04 Marks) (CO3, L1)

Solution: It is a chemical substance, which on combustion produces significant amount of heat that can be conveniently used for various purpose (domestic or industrial).



Fuels + oxygen \longrightarrow Combustion product + Heat
Classification: Fuels are classified based on (i) occurrence & (ii) physical state.

Primary fuels refer to fuels which occur naturally and require no processing before utilization. They are mainly fossil fuels.

Secondary fuels refer to energy sources derived from primary sources by subjecting them to treatments. Secondary fuels are made to meet the demands of better quality fuels.

Based on Physical state	Based on Occurrence	
	Primary (natural)	Secondary (derived from primary)
Solid	Wood, coal, peat, etc.	Charcoal, coke, etc.
Liquid	Petroleum (crude oil)	Gasoline, diesel, kerosene, etc.
Gaseous	Natural gas	Producer gas, water gas, coal gas, biogas, etc.

3(a) On burning 0.81 g of a solid fuel in bomb calorimeter, the temperature of 1.5 kg of water is raised from 24°C to 27.6°C. Water equivalent of calorimeter, specific heat of water and latent heat of steam are 200 grams, 4.187 kJ/kg and 587 cal/gram respectively. If the fuel contains 5% hydrogen, calculate gross and net calorific values. (05 Marks) (CO3, L4)

Solution: Given, $m = 0.81\text{g} = 0.81 \times 10^{-3}\text{ kg}$

$$W_1 = 1.5\text{ kg}$$

$$W_2 = 200\text{g} = 0.2\text{ kg}$$

$$(T_2 - T_1) = (27.6 - 24)^\circ\text{C} = 3.6^\circ\text{C}$$

$$\%H = 5\%$$

$$S = 4.187\text{ kJ kg}^{-1}\text{ }^\circ\text{C}^{-1}$$

$$L_q = 2454\text{ kJ/kg}$$

$$\begin{aligned} \text{GCV} &= \frac{(W_1 + W_2)(T_2 - T_1)s}{m} \\ &= (1.5 + 0.2) \times 3.6 \times 4.187 / 0.81 \times 10^{-3} \\ &= 31635.11\text{ kJ/kg} \end{aligned}$$

$$\begin{aligned} \text{NCV} &= \text{GCV} - 0.09 \times \%H \times L_v \\ &= 31635.11 - 0.09 \times 5 \times 2454 \\ &= 30529.46\text{ kJ/kg} \end{aligned}$$

(b) What are PV cells? Explain construction and working of PV cell. (05 Marks) (CO1, L3)

Solution: Photovoltaic cells or solar cells are semiconductor device that converts sunlight into direct current (DC) electricity. As long as light is shining on the solar cell, it generates electrical power. When light stops, electricity stops.

Construction & Working of PhotoVoltaic Cells-

PhotoVoltaic Cells consist of a semiconductor diode (p-n junction) made of a silicon. It has two electrical contact, on one of its sides, a mettalic grid is used and on the other side a layer of noble metal (such as Ag) is used. The metal grids permits the light to fall on the diode between the grid lines. Electromagnetic radiation consists of particle called photon ($h\nu$). They carry a certain amount of energy given by the Plank quantum equation. $E = hc/\lambda$ where, h = Planck's constant, c = velocity of light, λ = wavelength of the radiation. The electromagnetic radiation (sunlight) falls normal to the plane of the solar cell, the photons which possess energy sufficient to overcome the barrier potential are absorbed, electrons are ejected and electron-hole pairs are formed. The electrons move towards the n-region (as it is positively charged). The electrons are driven into the external circuit and used for various applications or appliances.

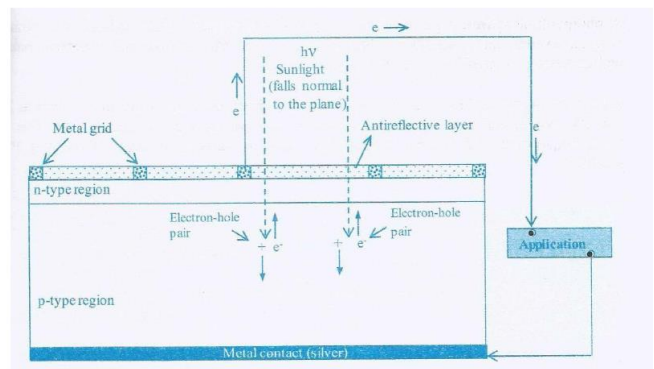


Fig. Photovoltaic cells

The electrons move towards the n-region (as it is positively charged). The electrons are driven into the external circuit and used for various applications or appliances.

4 (a) Explain the theory, instrumentation and application of Colorimetry. (06 Marks) (CO5, L3)

Solution: It is an analytical technique used for determination of conc. of compound in a solution. It is used for those solution which are coloured or which gives a colour when mixed with a suitable reagents.

A measure of the variation of the color of a solution with change in concentration of the solute forms the basis of colorimetry.

Theory: When a monochromatic radiation of intensity I is passed through a solution of a sample under investigation taken in a cell, a portion of the radiation is absorbed (I_a), a portion is reflected (I_r) and the remainder is transmitted (I_t), then,

$$I = I_a + I_r + I_t$$

For a glass cell, I_r is negligible and therefore the above equation reduces to

$$I = I_a + I_t$$

Colorimetric estimation is based on the Beer-Lambert law.

Beer Lambert's Law: According to this the amount of light absorbed is directly proportional to the conc. and path length of solution. Combining equations for Beer's law and Lambert's law, equation for Beer-Lambert's law can be written obtained;

$$I_t = I_o e^{-kct}$$

Or
$$I_t = I_o 10^{-\epsilon ct}$$

where ϵ called *molar absorptivity* or *molar absorption coefficient*, is a constant for a given substance at a given wavelength. If c is expressed in mol. dm^{-3} and t in centimeters, ϵ has the unit $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$.

The above equation can be written as

$$\log \frac{I_o}{I_t} = \epsilon ct \quad \text{Or} \quad A = \epsilon ct$$

This equation is referred to as Beer-Lambert's law.

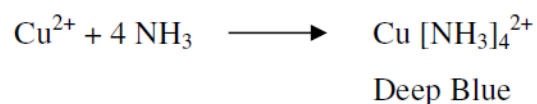
If the path length of the cell is kept constant, then, absorbance A is proportional to the concentration c .

Where A is absorbance, ϵ is molar absorptivity or molar extinction coefficient, and t is the path length (the length of the solution through which the light passes).

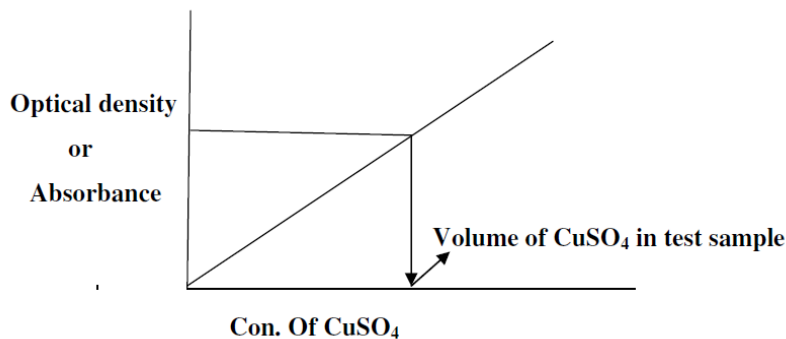
- ϵ is a constant for a given substance at a given wavelength. Since all the solutions are copper sulphate solutions, and the wavelength is kept constant at 620nm, ϵ is constant.
- Since same cuvette is used for all the solutions, t is constant.

Colorimetric Estimation of Copper:

- A series of solutions of copper sulphate of different concentrations is prepared.
- Each of these solutions is treated with ammonia solution.
- Deep blue colored cupraammonium complex is formed.



- This complex shows maximum absorbance at **620** nm.
- Hence, the absorbance of each of the above solutions is measured against blank at 620 nm.
- A graph of absorbance against concentration is plotted to get a calibration curve.
- The calibration curve is a straight line passing through the origin.
- The absorbance of the test solution against blank at 620nm is measured.
- From the calibration curve, the concentration of the analyte is determined.



(b) What is unleaded petrol? Give examples of 3 additives which can be used in unleaded petrol. Mention its advantages. (04 Marks) (CO3, L2)

Solution: An alternative to increase the octane rating of gasoline and employ higher CR or power output is to blend gasoline with compounds of higher octane rating. Gasoline or petrol with better anti-knock properties, however, without the presence of leaded compounds but with the presence of higher octane blending reagents is called unleaded petrol.

Following are three blending reagents:

- Methyl tertiary butyl ether (MTBE)
- Ethyl tertiary butyl ether (ETBE)
- Ethanol

Advantages:

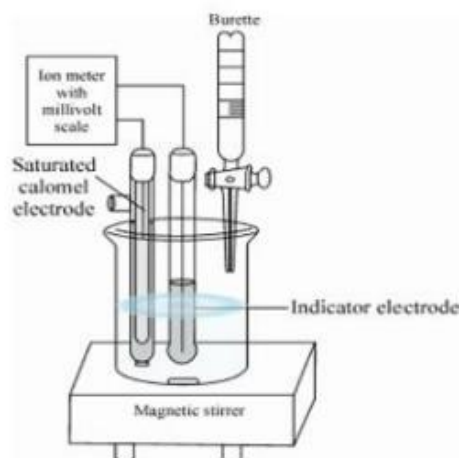
1. Higher octane number, higher CR and higher power output with better anti-knock characteristics.
2. Better combustion efficiencies because blending agents are also oxygenates and lower the emissions of volatile organic contents.
3. Emission of leaded compounds is avoided safeguarding the health of living beings.
4. Catalytic converters are employable with vehicle exhaust lines and relatively safer combustion products are ensured.

5(a) Explain the theory, instrumentation and application of Potentiometry. (06 Marks) (CO5, L3)

Solution: Potentiometry is the determination of concentration of a solution by measuring the e.m.f.

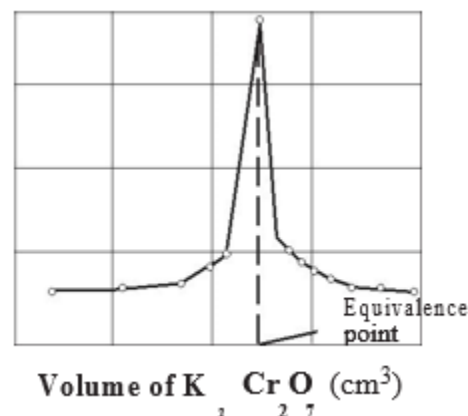
Theory : The estimation of concentration of substances in solution by the measurement of emf is known as potentiometric titration. When a metal M is immersed in a solution containing its own ions M^{n+} , the electrode potential is given by Nernst equation. Thus, the concentration can be calculated, provided E° of the electrode is known. If an electrode of the metal reversible with respect to the corresponding ions is placed in the solution, the potential will vary throughout the titration. Initially the change in potential will be small. At the equivalence point, there will be a steep rise in the potential. The equivalence point can be determined by plotting the change in potential against volume of titrant added.

Instrumentation: A potentiometer consists of: (i) Calomel electrode as a reference electrode, (ii) Platinum electrode as an indicator electrode, (iii) a device for measuring the potential and (iv) magnetic stirrer.



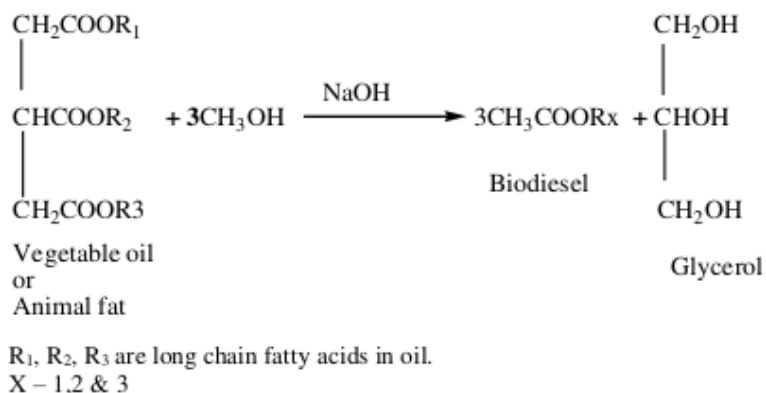
Application : Potentiometric estimation of FAS using standard $K_2Cr_2O_7$ solution

Pipette out 25ml of FAS into a beaker. Add 1 t.t dil H_2SO_4 , immerse calomel electrode + platinum electrode into it. Connect the assembly to a potentiometer and measure the potential by adding $K_2Cr_2O_7$ in the increments of 0.5ml. Plot a graph of $\frac{\Delta E}{\Delta V}$ against volume of $K_2Cr_2O_7$, and determine the equivalence point. From the normality and volume $K_2Cr_2O_7$, solutions calculate the normality and the weight of FAS in the given solution.



(b) Write a short note on biodiesel. (04 Marks) (CO3, L2)

Solution: Biodiesel refers to a vegetable oil or animal fat based diesel fuel consisting of long chain alkyl esters. It is a mixture of mono alkyl ester of long chain fatty acid. Biodiesel is produced by ‘Trans – esterification’ of vegetable oil or animal fat. It involves reaction of vegetable or animal oil (triglycerides) with an excess of alcohol in presence of a catalyst to give monoalkyl ester of long chain fatty acid and glycerol. Commonly methanol is used to produce methyl esters (Fatty acid methyl ester – FAME). Ethanol is used to produce ethyl ester (Fatty acid ethyl ester – FAEE) biodiesel.



The mixture is allowed to settle down at the bottom of tank, after that byproduct glycerol is simply drawn off from the bottom of the vessel. Excess methanol is removed through distillation. The upper layer is purified further and used. It has characteristics of diesel fuel.

Advantages –

1. It is obtained from renewable energy sources
2. It lacks unpleasant odour of petroleum diesel.
3. It is non – toxic.
4. It is biodegradable.
5. It is simple to produce.
6. It is non – hazardous and is safe to store.

Disadvantages-

1. Lower fuel economy and power
2. More expensive

Applications-

1. Used in conventional power generation.
2. Used as a heating fuel in boilers.
3. It can be used in most diesel engines.
4. It can be used to remove paints, adhesive etc.

6(a) Explain the theory, instrumentation and method of determination of concentration of an alkali and alkaline earth metal using flame photometry. (06 Marks) (CO5, L3)

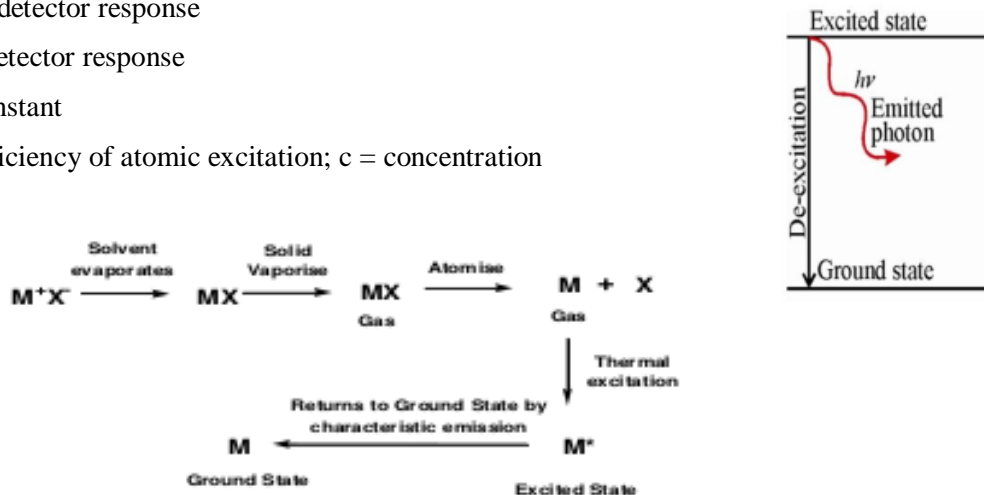
Solution: Theory: Flame photometry is an atomic emission technique used for detection of metals. The technique involves the following sequence:(i) Liquid sample containing metal salt solution is introduced into a flame, (ii) Solvent is first vaporized, leaving particles of solid salt which is then vaporized into gaseous state (iii) Gaseous molecule dissociate to give neutral atoms which can be excited (made unstable) by thermal energy of flame (iv) The unstable excited atoms return back to ground state by emitting characteristic radiation. (v) The intensity of emitted light is proportional to the concentration of the element and given as $E = k$

$\alpha cE =$ detector response

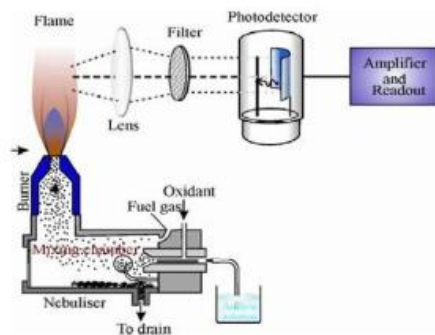
$cE =$ detector response

$k =$ constant

$\alpha =$ efficiency of atomic excitation; $c =$ concentration



Instrumentation: A simple flame photometer consists of the following basic components: a) The burner; b) Nebuliser and mixing chamber; c) Simple color filters; d) Photocell-detector. The sample containing the analyte is aspirated into the flame. Radiation from resulting flame is collected by the lens and allowed to pass through an optical filter, which permits only the radiation characteristic of the element under investigation into the detector. The output from detector is read out on a display device.



Application: 1) Flame photometer can be applied both for quantitative and qualitative analysis of elements. 2) The presence of various alkali and alkaline earth metals in soil sample can be determined. (3) Soft drinks, fruit juices and alcoholic beverages can also be analyzed by using flame photometry to determine the concentrations of various metals and elements. 4) The Na + and K + ion concentrations can be determined in blood serum sample. Process: Quantitative analysis by flame photometry is done by calibration curve method. For this, a series of standard solution of analyte is prepared, aspirated into flame and emission of each solution is measured in flame photometer. Then calibration curve is obtained by plotting emission intensity against concentration of standard solutions. Sample solution is also properly diluted and then its emission is measured. From calibration curve, concentration of sample solution can be determined.

(b) Define fuel cell. Mention any three differences between conventional cell and fuel cell. (04 Marks) (CO3, L2)

Solution: A fuel cell is a device that converts the chemical energy of a fuel (hydrogen, natural gas, methanol, gasoline, etc.) and an oxidant (air or oxygen) into electricity.

	Conventional Cell		Fuel Cell
1.	Anodic and cathodic compartments are preloaded and reaction products are retained in the battery.	1.	Permit continuous movement of fuel, oxidant and reaction products in and out of battery.
2.	They have definite amount of stored energy.	2.	They are only energy conversion devices, do not store any energy.
3.	As long as active components exist, battery continues delivering energy.	3.	As long as fuel and oxidant are supplied at respective electrodes, energy is available.

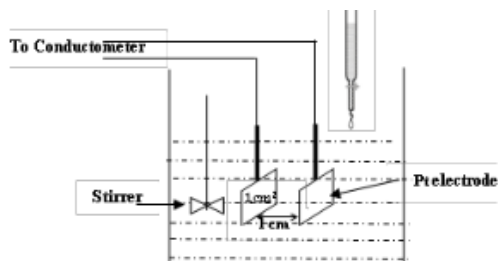
7(a) Explain the theory, instrumentation and application of Conductometry. (06 Marks) (CO5, L3)

Solution: Theory: Conductometry is based on Ohm's law which states that the current i (amperes) flowing in a conductor is directly proportional to the applied electromotive force, E (volts), and inversely proportional to the resistance R (ohms) of the conductor. $i = E/R$

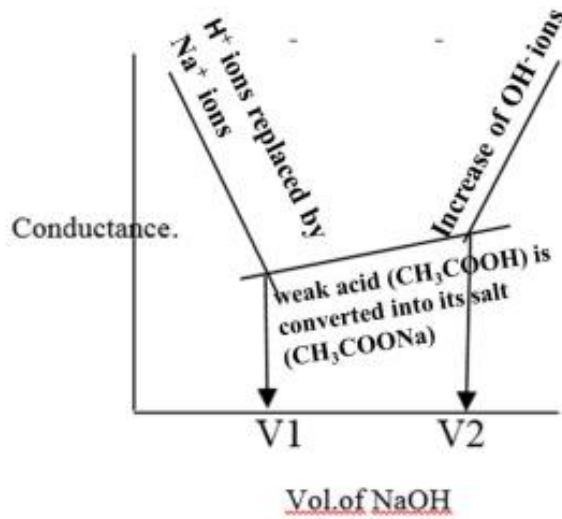
The reciprocal of the resistance is called the conductance. Specific conductance of a solution is defined as the conductance of a solution present between two parallel electrodes which have 1cm^2 area of cross section and which have kept 1cm apart.

The principle underlying conductometric titrations is the substitution of ions with a specific mobility by ions of another specific mobility. Therefore, the conductance of solution depends on the number of mobility of ions. The equivalence point is determined graphically by plotting conductance against titer values.

Instrumentation: Conductometer consists of conductivity cell having two platinum electrodes and a conductance measuring device. The two electrodes have unit area of cross section and are placed unit distance apart. A simple arrangement of conductometric titration is depicted in figure. The solution to be titrated is taken in the beaker.



Application: Conductometric titrations of acids and base: Pipette out 50ml of sample (Acid mixture) into a beaker. Immerse the conductivity cell into it. Connect the conductivity cell to a conductivity meter and measure the conductance by adding NaOH from the burette by increment of 1ml . Plot a graph of conductance against volume of NaOH . Determine the neutralization point from the graph. $[(\text{HCl} + \text{CH}_3\text{COOH}) \text{ Vs } \text{NaOH}]$: The conductance decreases upon adding NaOH to acid mixture due to substitution of highly mobile H^+ ions by the less mobile Na^+ ions. This trend continues till all the H^+ ions of HCl replaced i.e, the strong acid is neutralized. Continued addition of NaOH raises the conductance moderately, as the weak acid (CH_3COOH) is converted into its salt (CH_3COONa). Further addition of NaOH raises the conductance steeply due to the presence of OH^- ions. The titration curve in the graph given determines the location of the equivalence points.



(b) Describe the construction and working of solid-oxide fuel cell. (04 Marks) (CO1, L2)

Solution: Introduction: A solid oxide fuel cell (or SOFC) is an electrochemical conversion device that produces electricity directly from oxidizing a fuel. Fuel cells are characterized by their electrolyte material, the SOFC has a solid oxide or ceramic electrolyte.

Construction: Anode : Porous electrode made up of Ni:
ZrO₂

Cathode : Strontium doped lanthanum magnetite

Electrolyte : Solid Ytria stabilized Zirconia

Fuel : H₂

Oxidant : O₂

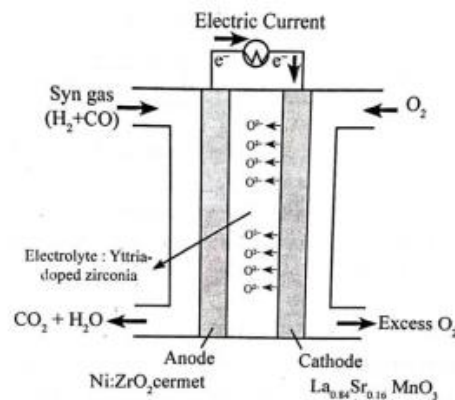
Charge carriers : O²⁻ ions

Operating temperature : 1000°C

Fuel cell efficiency : 50-60 %

Working :

Solid oxide fuel cells are a class of fuel cells characterized by the use of a solid oxide material as the electrolyte. SOFCs use a solid oxide electrolyte to conduct negative oxygen ions from the cathode to the anode. The electrochemical oxidation of the oxygen ions with hydrogen liberates H₂O and two electrons on the anode side. Electrons flow from the anode through the external circuit to the cathode.



Reactions :



8(a) 0.65g of coal sample (carbon 90%, H 2.5% and ash 5%) was subjected to combustion in a bomb calorimeter. Mass of water taken in the calorimeter was 2.4 L and the water equivalent of the calorimeter was 750 g . The rise in temperature was found to be 2.9 °C. Calculate the gross and net calorific values of the sample. Latent heat of steam = 2.457 KJg⁻¹ and specific heat of water = 4.187 KJ Kg⁻¹ K⁻¹. (05 Marks) (CO3, L4)

Solution: Given, m = 0.65g = 0.65 × 10⁻³ kg

$$W_1 = 2.4\text{L} = 2.4 \text{ kg}$$

$$W_2 = 750\text{g} = 0.75 \text{ kg}$$

$$(T_2 - T_1) = 2.9^\circ\text{C}$$

$$\%H = 2.5\%$$

$$S = 4.187 \text{ kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$$

$$L_q = 2454 \text{ kJ/kg}$$

$$\begin{aligned} \text{GCV} &= \frac{(W_1 + W_2)(T_2 - T_1) s}{m} \\ &= (2.4 + 0.75) * 2.9 * 4.187 / 0.65 * 10^{-3} \\ &= 58843.45 \text{ kJ/kg} \end{aligned}$$

$$\begin{aligned} \text{NCV} &= \text{GCV} - 0.09 \times \%H \times L_v \\ &= 58843.45 - 0.09 \times 2.5 \times 2454 \\ &= 58290.62 \text{ kJ/kg} \end{aligned}$$

(b) Describe the construction and working of CH₃OH-O₂ fuel cell. Mention its applications. (05 Marks) (CO1, L2)

Solution: Construction: Methanol – oxygen fuel cell consist of

1. Anode – It is a porous platinum (Pt) electrode.
2. Cathode - It is a porous platinum (Pt) electrode.
3. Electrolyte – Aqueous sulphuric acid (H₂SO₄)
4. Active components: (a) Fuel – Methanol mixed with sulphuric acid supplied at anode.
(b) Oxidant – Pure oxygen is supplied at cathode.

5. Adjacent to cathode towards electrolyte side, a semi permeable membrane is inserted to allow the diffusion of H^+ ions, but disallow the diffusion of methanol and its direct oxidation at cathode.

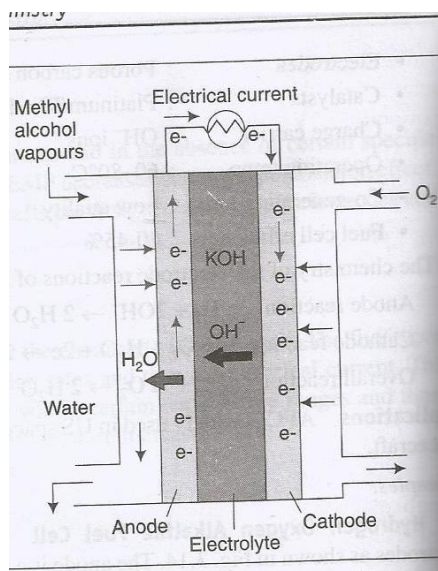
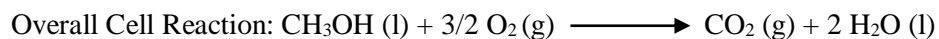
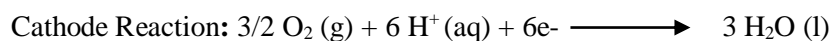
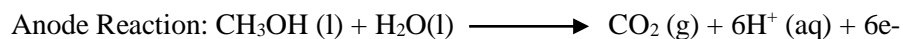


Fig: Methanol – oxygen fuel cell

Working:



Applications:

1. used in automobiles, military applications.
2. Power backup and portable instruments.
3. in large scale power production.