

Solutions

**CMR
INSTITUTE OF
TECHNOLOGY**



Sub:	Engineering Chemistry	Code:	18CHE12
Date: <u>25/10/2019</u>	Duration: <u>90</u> mins	Marks: <u>50</u>	Sem: <u>I</u>
			Branch: <u>All</u>

Internal Assessment Test II

1. (a) Explain the experimental determination of calorific value of solid/liquid fuel using Bomb calorimeter. (05 Marks) (CO3, L3)

Solution:

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

Principle: A known weight of the sample (solid or liquid 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.

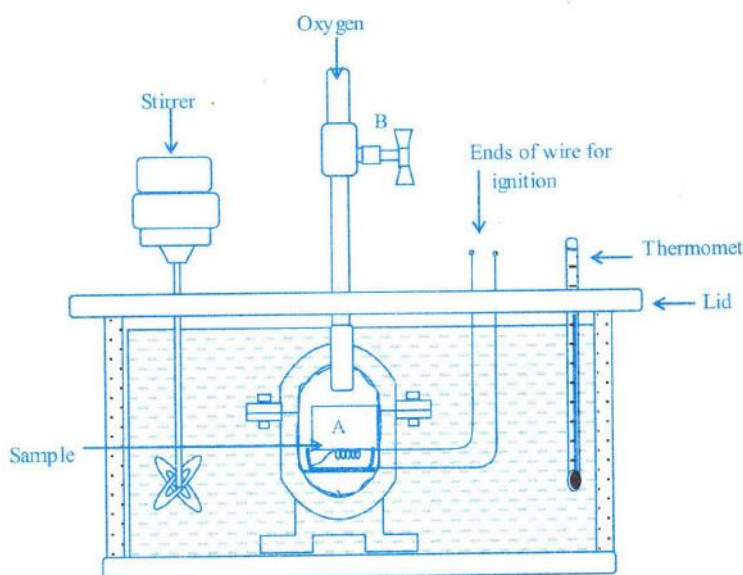


Fig. Bomb Calorimeter

Observation and calculation

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

Mass of the water taken in calorimeter = W_1 (kg)

Water equivalent of calorimeter = W_2 (kg)

Initial temp. of water = T_1 °C

Final temp. of water = T_2 °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.

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

And, net calorific value,

$$\text{NCV} = \text{GCV} - 0.09 \times H \times L_v \text{ KJ kg}^{-1} \quad \dots\dots\dots(2)$$

Where, H is the percentage amount of hydrogen in the fuel and $L_v = 587 \times 4.187 \text{ kJ kg}^{-1}$ (2454 kJ/kg) is the latent heat of condensation of steam.

(b) What are PV cells? Explain construction and working of PV cell. (05 Marks) (CO3, L3)

Solution:

Photovoltaic cells or solar cells are semi conductor 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

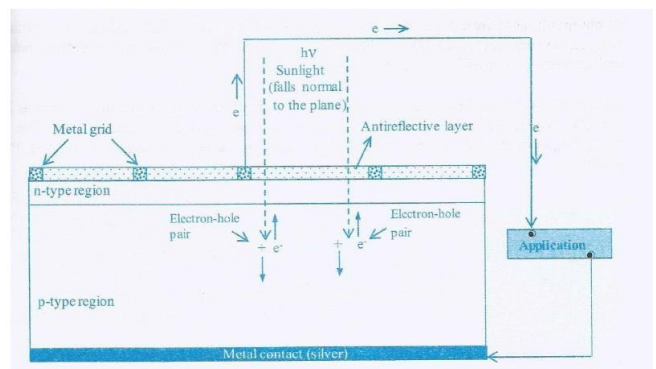


Fig. Photovoltaic cells

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.

2 (a) 0.95 g of coal sample (carbon 90%, H₂ 5% and ash 5%) was subjected to combustion in Bomb calorimeter mass of water taken in calorimeter was 2.6 kg and the water equivalent of calorimeter is 0.55 kg. The rise in temperature was found to be 3.2 °C. Calculate higher and lower calorific values of the sample. Latent heat of steam=2457 kJ/kg and specific heat of water = 4.187 kJ/kg/ °C. (05 Marks) (CO3, L3)

Solution: Given, m = 0.95g = 0.95 × 10⁻³ kg

$$W_1 = 2.6 \text{ kg}$$

$$W_2 = 0.55 \text{ kg}$$

$$(T_2 - T_1) = 3.2^\circ\text{C}$$

$$\%H = 5\%$$

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

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

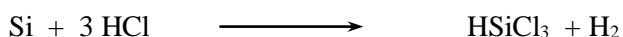
$$\begin{aligned} \text{GCV} &= \frac{(W_1 + W_2)(T_2 - T_1) s}{m} \\ &= \{(2.6 + 0.55) (3.2) 4.187\} / 0.95 \times 10^{-3} \\ &= 44426.27 \text{ kJ/kg} \end{aligned}$$

$$\begin{aligned} \text{NCV} &= \text{GCV} - 0.09 \times \%H \times L_v \\ &= 44426.27 - 0.09 \times 5 \times 2454 \\ &= 43320.27 \text{ kJ/kg} \end{aligned}$$

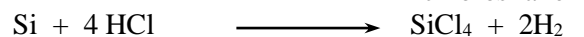
(b) Describe the production of solar grade silicon by Union Carbide process (05 Marks) (CO3, L3)

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



Trichlorosilane



Tetrachlorosilane

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

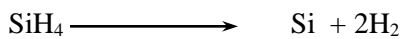


- Trichlorosilane is passed through ion exchange resin containing quaternary ammonium salts to give dichlorosilane and tetrachlorosilane. Dichlorosilane subsequently forms trichlorosilane and silane (silicon tetra hydride).



- 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).



3 (a) Explain the theory, instrumentation and applications of Colorimetry. (06 Marks) (CO5, L4)

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.

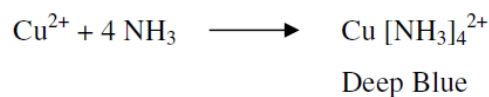
If the path length of the cell is kept constant, then, absorbance A is proportional to the concentration c .

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).

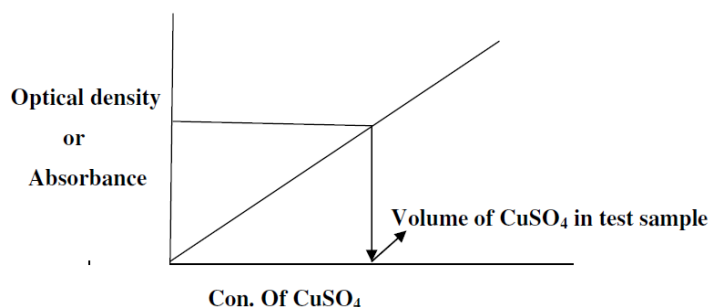
- ϵ is a constant for a given substance at a given wavelength. Since all the solutions are copper sulphate solutions, and the wavelength is kept constant at 620nm, ϵ is constant.
- Since same cuvette is used for all the solutions, t is constant.

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.

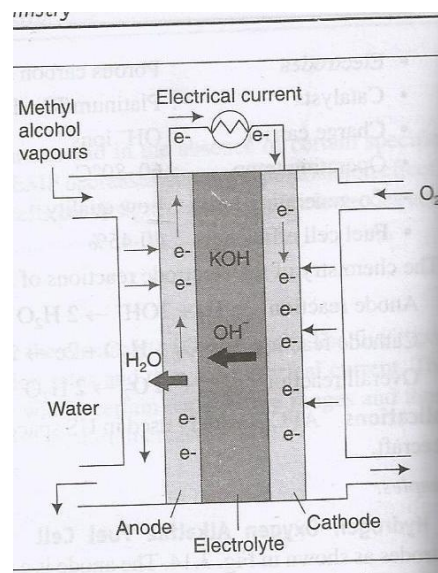


Colorimetric estimations can be applied to estimate copper in brass, manganese in steel, glucose in fluids, Fe in haematite etc.

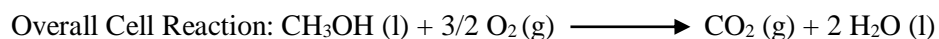
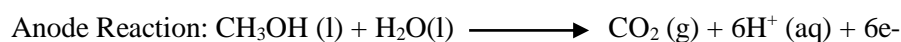
(b) Describe construction and working of CH₃OH-O₂ fuel cell. (04 Marks) (CO3, L3)

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.



Working:



4 (a) Explain the theory, instrumentation and applications of Conductometry. (06 Marks) (CO5, L4)

Solution:

Ohm's law 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.

$$i = \frac{E}{R}$$

The reciprocal of the resistance is called the conductance. The resistance of a homogeneous material of uniform cross section with an area of a sq. cm. And length l cm is given by

$$R = \frac{\rho \times l}{a}; \quad k = C [l/a]$$

where r is the specific resistance. The reciprocal of the specific resistance is termed the specific conductance, ρ . It is the conductance of a cube of material 1 cm in length and 1cm in cross section.

Instrumentation

- Conductometer consists of two platinum electrodes and a conductance measuring device.
- The two electrodes have unit area of cross section and are placed unit distance apart. They are dipped in the electrolyte solution taken in the beaker.
- The assembly responds rapidly to the changes in the concentration of the analyte under test.
- A simple arrangement of conductometric titration is depicted in figure. The solution to be titrated is taken in the beaker, titrant is added from a burette and the solution is stirred. The conductance is measured after the addition of the titrant at intervals of 1 mL

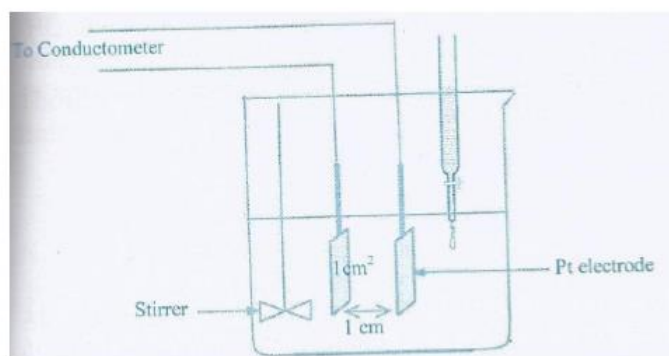


Fig: Conductometric Titration Unit

Application of Conductometric Titrations:

1. Titration of acid mixture with strong base
2. Titration of strong acid with strong base
3. Titration of weak acid with strong base.

(b) What is knocking? Discuss mechanism of knocking in petrol engine. (04 Marks) (CO3, L3)

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:

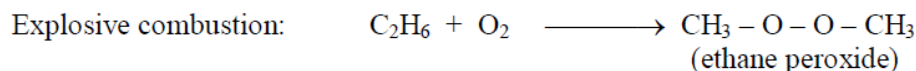
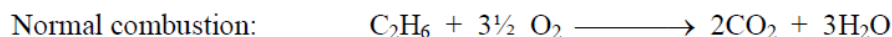
- Higher compression ratio (CR) beyond the optimum level
- Lower octane gasoline.
- Formation of highly reactive intermediates (peroxides), which lead to explosive reactions.

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

During knocking,

- Petrol is vaporised and vapour 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.



5 (a) Explain the theory, instrumentation and applications of Potentiometry. (06 marks) (CO5, L4)

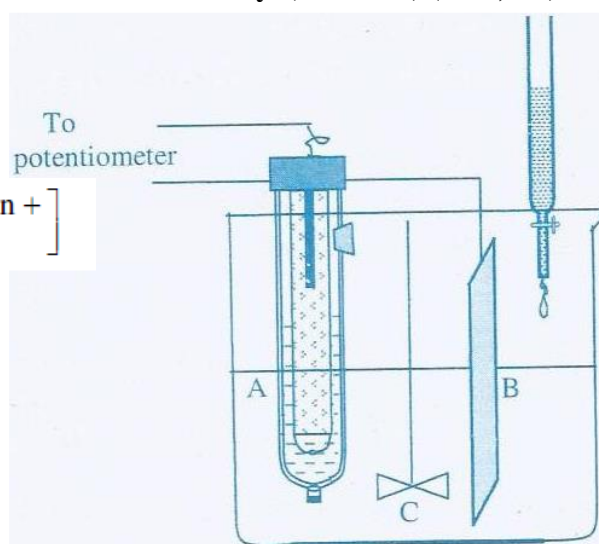
Solution: Potentiometry is the determination of concentration of a solution by measuring the e.m.f.

Theory:

When a metal M is immersed in a solution containing its own ions M^{n+} , the electrode potential is given by Nernst equation.

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$$

Thus, the potential of an electrode E depends upon the concentration of the ion M^{n+} to which it is reversible. In potentiometric titration the potential is measured. The potential developed is a function of the concentration of the ions of the analyte. Assume the concentration of the analyte to be x mol dm⁻³. Let y mol dm⁻³ is the volume of titrant added at given instant and z mol of the product is formed under above conditions. The value of z will change throughout the course of titration because y is being changed continuously. If an



indicator electrode 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. Beyond the equivalence point, there will be no significant change in the potential. The equivalent point can be determined by plotting change in potential against volume of titrant added.

Instrumentation: A potentiometer consists of a reference electrode, an indicator electrode and a device for measuring the potential. The emf of indicator electrode depends upon the concentration of ions of analyte.

A is a ref. electrode (Saturated calomel electrode), B is the indicator electrode and C is a mechanical stirrer. A known volume of the analyte is taken in a beaker and its potential is determined by connecting the assembly to a potentiometer. The titrant is added in increments of 1 mL and the potential is measured each time. Close to the equivalence point the potential tends to increase rapidly. A few readings are taken beyond the equivalence point. The equivalence point is determined by plotting change in potential against the volume of the titrant.

Application of Potentiometric Titrations:

(i) Acid – Base titrations (ii) Redox Titrations (Oxidation reduction titration) (iii) Precipitation Titration

(b) Write a short note on i) Unleaded petrol and ii) Power alcohol (04Marks) (CO3, L2)

Solution: (i) **Unleaded Petrol:** 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 some blending reagents:

- Methyl tertiary butyl ether (MTBE)
- Ethyl tertiary butyl ether (ETBE)
- Methyl tertiary amyl ether
- Ethyl tertiary amyl ether
- Methanol
- Ethanol
- Isopropanol, etc.

All the above blending reagents have higher octane rating of nearly 100 or more. When blended with gasoline in proportions of more than 10% (unlike 0.1% of ethyl fluid) overall octane rating of the blend is increased and so is the anti-knock property of the blend.

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.

(i) **Power Alcohol:** A blend containing **10 to 85% of ethanol and 15-90% of gasoline**, used as fuel is known as power alcohol. The addition of alcohol to petrol increases its octane number. Power alcohol is used as a fuel by blending with petrol in IC engine. It is also blended with diesel to form E-diesel. Power alcohol has calorific value of about 7000 cal/g and its octane no. is 90.

Advantages:

- Addition of alcohol to petrol increases octane number (octane number of ethanol is 112) and reduces knocking.
- Because of increased O.N., it can be used in engine with high CR, thus better power output is achieved.
- Because, alcohol contains oxygen, it is referred as oxygenate which assist better combustion efficiency. Also, VOC (volatile organic content) emissions are reduced or pollution is lessened.

- Alcohol can be synthesized from plants. Thus, especially, with higher proportion of alcohol, one has a sustainable fuel [an alternative to fast depleting fossil fuels].
- When synthesised, helps in improved economy of a country because imports are avoided.

Disadvantages:

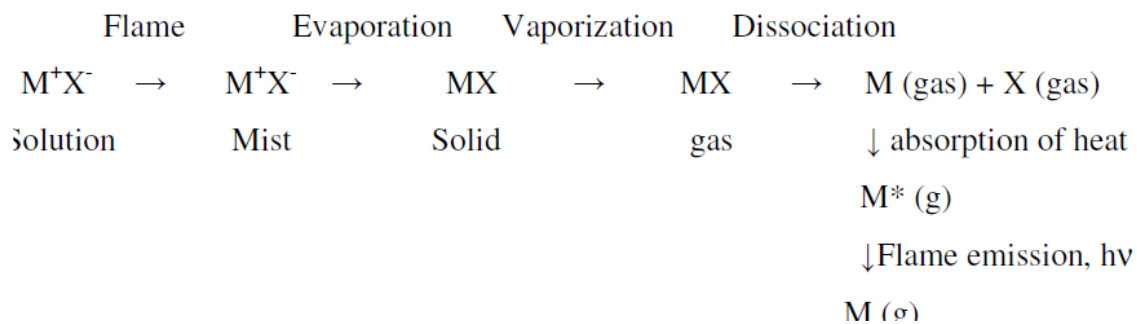
- Lowers the calorific value of the fuel (two third that of gasoline).
- Atomization is difficult because of high surface tension of alcohol.
- Alcohol gets oxidised to acids and may corrode concerned engine equipment.
- Modification of CR of the engine is required otherwise, power out put is reduced. (Gasoline engines generally have a CR of around 8 which need be increased to around 12).
- Alcohol as such has good affinity for water and as a result separation of alcohol and petrol layers takes place especially at low temperature. To avoid this blending agent such as benzene or toluene are used.

6 (a) Explain the theory, instrumentation and applications of flame photometry. (06 Marks) (CO5, L4)

Solution: Solution: The principle of flame photometry is atomic spectra arising due to the emission of different wavelength when atoms are excited in a flame. Emission of characteristic radiation by an element and the correlation of the emission intensity with concentration of the element form the basis of flame photometry. This instrument is used to measure the concentration of only alkali metals and alkaline earth metals. When a solution containing sample element or ion is aspirated into the flame, following changes takes place,

- Firstly, solvent gets evaporated leaving behind salt (solid residue) in the flame.
- Then, salt gets evaporated into salt vapours, which further undergo dissociation into its constituent atoms.
- Some of the metal atoms formed may absorb heat energy from flame and get electronically excited to their higher energy level. Being unstable in the excited state, atoms fall back to their ground state, by emitting the energy in form of light radiation.
- Intensity of emitted light is proportional to number of atoms in the excited state, which in turn is proportional to the concentration of solution fed into the flame.
- Different metals emit their characteristic radiations at different wavelengths, they do not interfere with each other, even when they are present together.

Series of changes taking place at the flame are summarized as follows:



Intensity of emitted radiation, measured as detector response is related to the concentration by an expression similar to Beer's relation,

$$E = k \alpha c$$

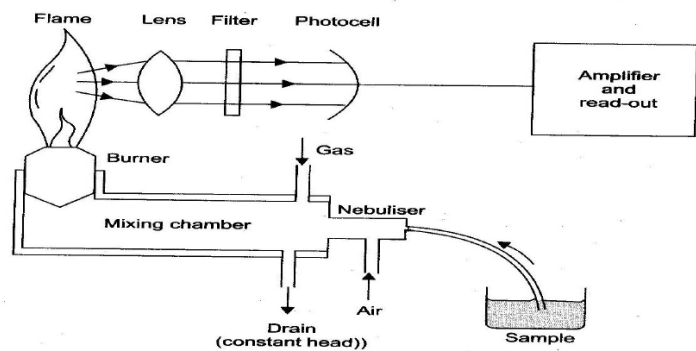
E = detector response

k = constant

α = efficiency of atomic excitation

c = concentration

INSTRUMENT:



Schematic Layout of Flame Photometer

Flame photometer consists of an **atomizer**, **mixing chamber**, **burner**, **filter**, **detector** and a **display device**. Pressurized air is passed into atomizer and due to suction sample solution is drawn into the atomizer. Inside atomizer it mixes with air stream as a fine mist and passes into the mixing chamber. In mixing chamber it mixes with gas and then passes into burner where mixture is burnt. The emitted radiation from flame passes through lens and then through a filter which allows only radiation characteristic of element under study to pass through detector. The output from detector is read out on a display device.

Procedure:

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) Differentiate between conventional cell and fuel cell. (04 Marks) (CO3, L3)

Solution:

	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.
4.	Generally function at ambient temperatures without an active catalyst being employed.	4.	Generally work at higher temperature or in presence of an electrocatalyst.

7. (a) Explain the theory and instrumentation of atomic absorption spectroscopy. (06 Marks) (CO5, L4)

Solution: **Atomic absorption spectroscopy** is a technique which studies absorption of electromagnetic radiations in relationship to molecular structure. It is a technique for measuring the concentration of various elements in the sample through their absorption of light. It is a relatively simple and reliable technique which uses absorption of optical radiation by free atoms for determining the contents of different elements.

Atomic absorption spectroscopy is based on the principle that when a beam of electromagnetic radiation is passed through a substance, the radiation may either be absorbed or transmitted depending upon the wavelength of the radiation.

The absorption of radiation would bring about an increase in the energy of the molecule. The energy gained by the molecule is directly proportional to the wavelength of radiation. The increase in the energy of the molecule leads to the electronic excitations where electrons jump to higher energy levels. A particular wavelength that a given molecule can absorb depends upon the changes in vibrational, or rotational or electronic states.

When a monochromatic radiation of frequency ν is incident on a molecule, the molecule in the gaseous state E_1 absorbs a photon of energy $h\nu$, it undergoes a transition from lower energy level to higher energy level.

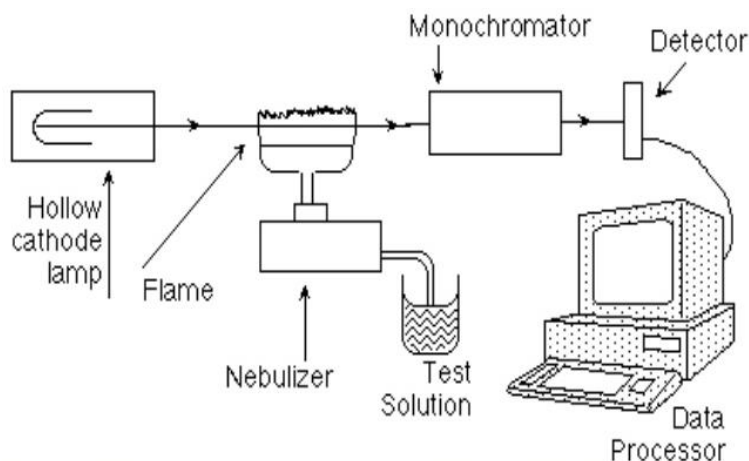
A detector is placed to collect the radiation after interaction with the molecule which shows that intensity has reduced. With wide range of frequencies, the detector shows the energy has been absorbed only from the frequency.

$$\nu = (\Delta E)/h$$

Therefore we obtain an absorption spectrum which is defined as a record of the radiation absorbed by the given sample as a function of wavelength of radiation.

The energy difference between the levels is given as,

$$\Delta E = E_2 - E_1 = h\nu = hc/\lambda.$$



The instrument used for recording a spectrum is known as spectrometer or spectrophotometer.

In the atomic absorption spectrometer, the source of radiation in the spectrometer is the tungsten filament emitting white light or hydrogen discharge lamp. The radiation from the source is directed by some device (for example in this case a mirror) on the sample. The radiation then passes through an analyser (the grating in this case), which selects the frequency reaching the detector at any given time. The signal from the detector passes then to a recorder which is attached to the analyser so as to produce a trace of the absorbance of varying frequencies.

Atomic absorption spectroscopy has various applications in various fields.

- One of the major applications of atomic absorption spectroscopy is for the determination of structural elucidation of various substances. This technique is more beneficial as a very small quantity of substance is required for analyzing.
- Atomic absorption spectroscopy can be used to analyze water for its metal quantity if present.
- Atomic absorption spectroscopy is used in many pharmaceutical manufacturing processes where small quantities of catalyst remain in the final product.
- Atomic absorption spectroscopy can also be used in biological tissues such as blood, liver, brain tissue, muscle tissue and fluids for analyzing metals.

(b) Describe the construction and working of solid-oxide fuel cell. (04 Marks) (CO3, L3)

Solution: 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.

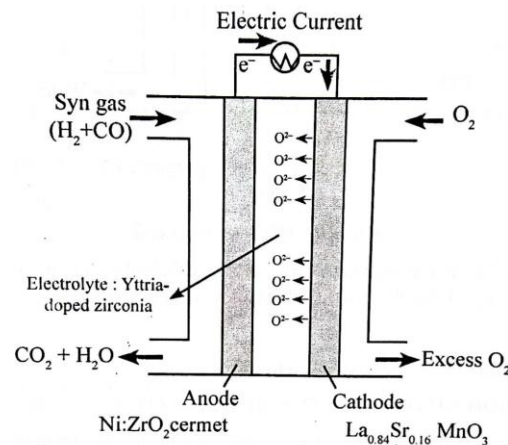


Fig : Solid Oxide fuel cell

Construction:

Anode : Porous electrode made up of Ni: ZrO₂

Cathode :

Fuel : H₂ solid

Electrolyte : Solid Yttria stabilized Zirconia

Electrodes : Carbon or metal based

Catalyst : Ceramic

Charge carriers : O²⁻ ions

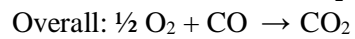
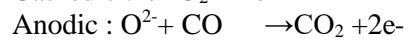
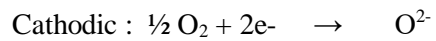
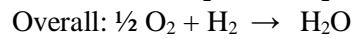
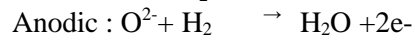
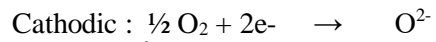
Operating temperature : 1000°C

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 :



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