Welcome
Unit-2
Fuels and..

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L-11 Classification, Introduction, HCV & LCV

DEFINITION OF FUEL :-

Fuels can be defined as

- any combustible substance
- which during combustion gives
- large amount of heat
- which can be used economically for
- domestic and industrial purposes.

L-11 Classification, Introduction, HCV & LCV

- **During combustion of a fuel the atom of carbon, hydrogen etc.**
- **combine with oxygen and liberates large amount of heat and also**
- **forms new compounds like CO_2, H_2O etc.**
- **These new compounds have less energy.**

L-11 Classification, Introduction, HCV&LCV

- The heat released during combustion is the difference in reactants (C, H, O) and produces (CO_2, H2O) energy.

$$\text{Fuel} + O_2 \longrightarrow \text{Products} + \text{Heat}$$

(more heat) (less heat)

- Ex. – Combustion of carbon in oxygen; liberates 97 Kcal of heat

$$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g) + 97\ \text{Kcal}$$

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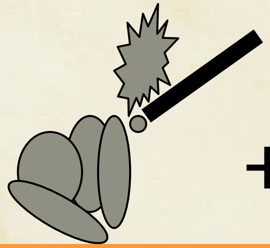

Fuel sample

+ oxygen ⟶ products+ heat

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CLASSIFICATION OF FUEL :-

- Fuels can be classified –

1. **On the basis of their Occurrence –**
   - **i) Natural or Primary fuel**
   - **ii) Artificial or Secondary fuel**
2. **On the basis of Physical State of aggregation –**

CLASSIFICATION OF FUEL

Fuels can be classified –

1. On the basis of their Occurrence -

(a) Natural or Primary fuel –

Fuels which are found in nature as such are called Natural fuels.

Ex. – Wood, Coal, Peat, Petroleum etc.

(b) Artificial or Secondary fuel –

Ex. – Coke, Petrol, Bio gas etc.

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A. **On the basis of their Occurrence –**

B. **Artificial or Secondary fuel –**

Fuels which are prepared form primary fuel are called secondary fuels.

- **Ex. – Coke, Petrol, Bio gas etc.**

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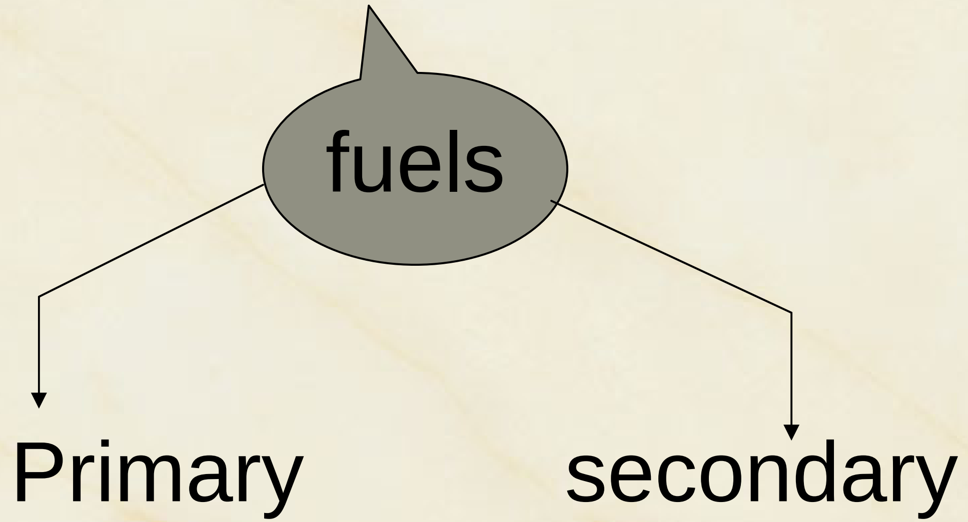
- On the basis of physical state



Primary fuels

- **Solid fuels**
  - Wood ,peat, Lignite, coal, dung
- **Liquid fuels**
  - Crude oil
- **Gaseous fuels**
  - Natural gas

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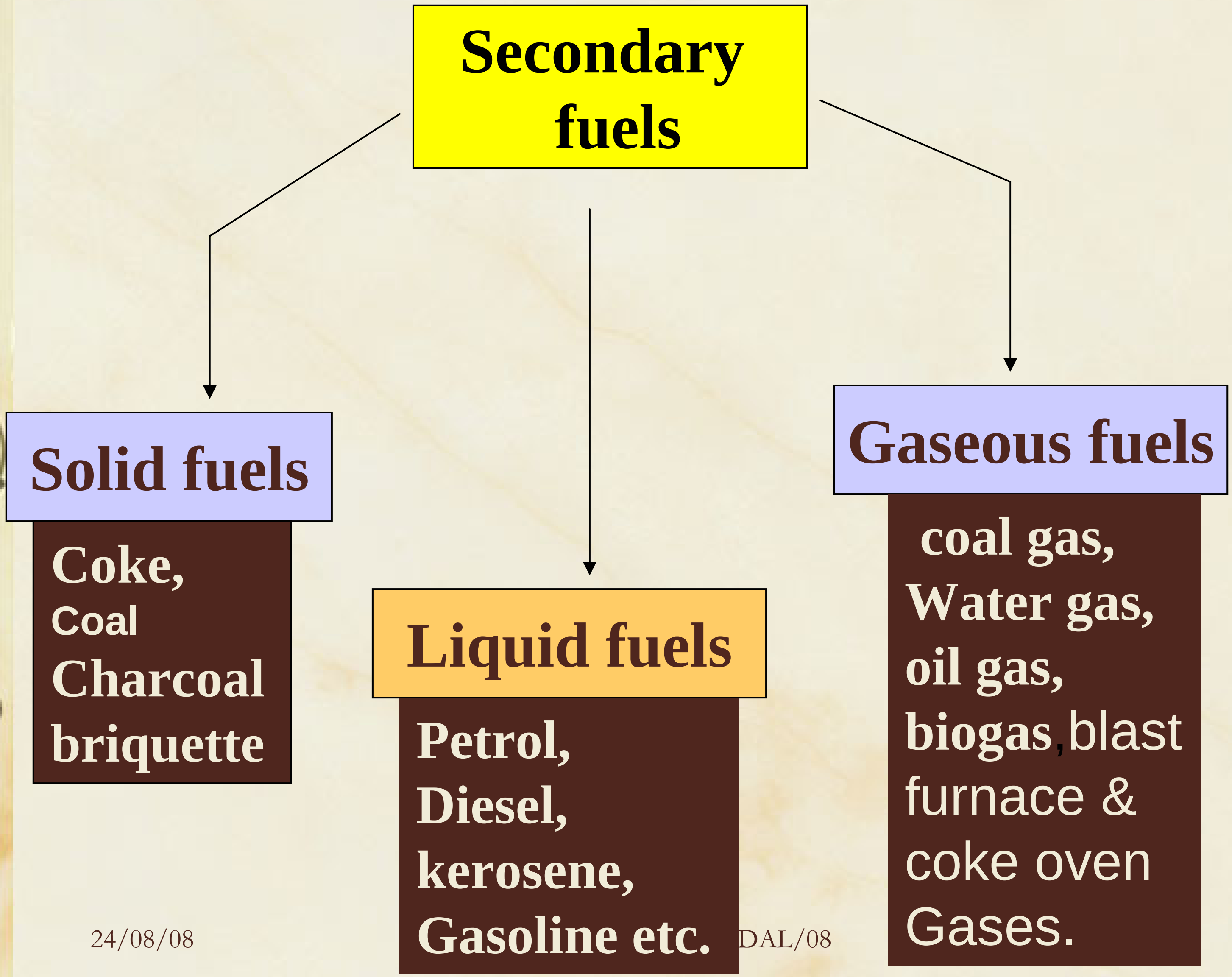
- **On the basis of Physical State of aggregation –**
- On this basis their are three types of solid, liquid and gas.

Fuels

- **Primary Fuels**
  - **Solid**: Wood, Peat, Lignite, Dung
  - **Liquid**: Crude Oil
  - **Gas**: Natural gas
- **Secondary Fuels**
  - **Liquid**: Petrol, Diesel, Kerosene, Coal Tar
  - **Gas**: Bio gas, Water gas, Oil gas, L.P.G. Gas
  - **Solid**: Coal, Coke, Charcoal


Secondary fuels
Solid fuels
Coke,
Coal
Charcoal
briquette
Liquid fuels
Petrol,
Diesel,
kerosene,
Gasoline etc.
Gaseous fuels
coal gas,
Water gas,
oil gas,
biogas,blast
furnace &
coke oven
Gases.

L-11 CALORIFIC VALUE

- Calorific value of a fuel is defined as:

- **"The amount of heat liberated when a unit mass or volume of fuel is burnt completely".**

- **Or**

CALORIFIC VALUE

- Calorific value of a fuel is defined as ***"the total quantity of heat liberated from the combustion of a unit mass of the fuel in air or oxygen."***

L-11 CALORIFIC VALUE

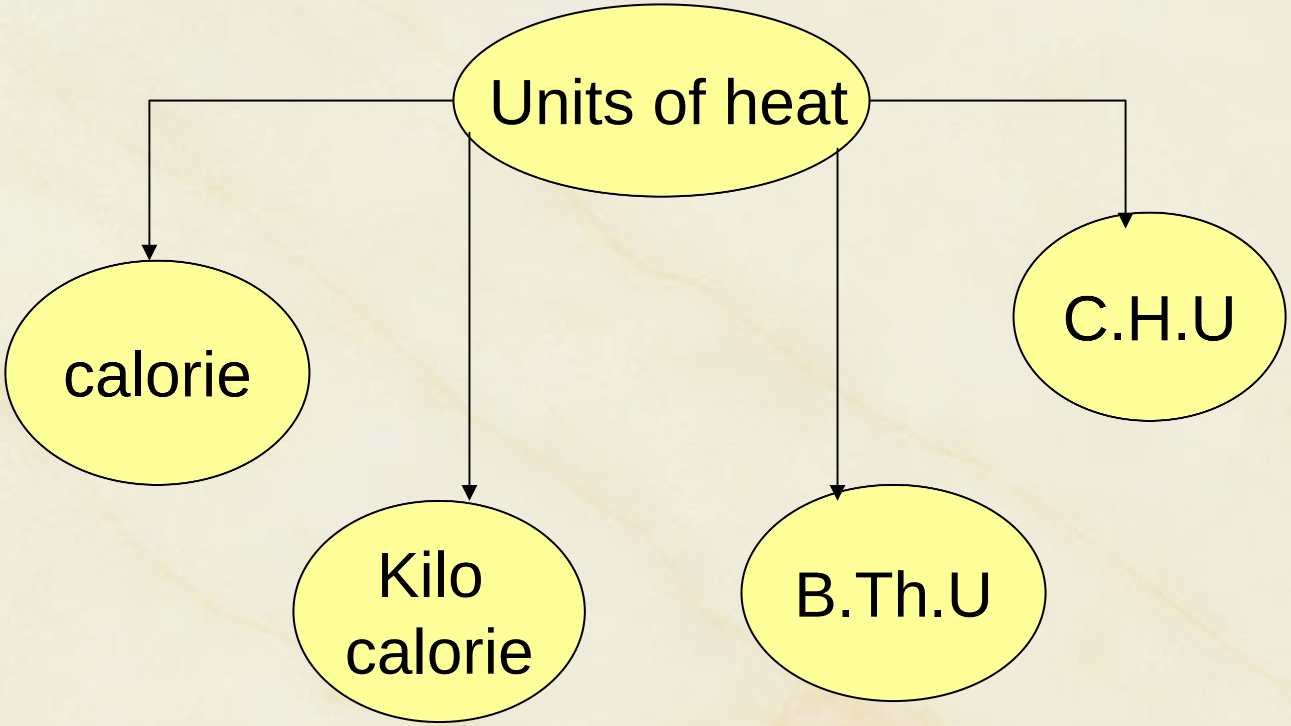
- Higher the calorific value,
- greater the quality of the fuel.
- Lower the calorific value
- lesser the quality of the fuel.

UNITS:

Calorie, Kilo Calorie,

B.Th.U.,C.H.U.

UNITS OF HEAT



L-11 CALORIFIC VALUE

- **1 Kcal = 1000 cal.**

1 Kcal = 3.968 B.Th.U.

1000 cal= 1 Kcal

1 Kcal = 3.968 B.Th.U. = 2.2 C. H. U.

- **Calorie : -**

- **Calorie is the amount of heat required to increase the temperature of 1 gm of water through one degree centigrade.**

- **Kilo Calorie** (Or Kilogram Centigrade Units)

- **It is equal to 1000 calorie,**

"The quantity of heat required to increase the temperature of one kilogram of water through one degree centigrade".

- **1 Kcal = 1000 cal.**

- **British Thermal Unit (B.Th.U.) : -**

"The quantity of heat required to increase the temperature of **one pound** of water through **one degree Fahrenheit.**"

- 1 Kcal = 3.968 B.Th.U.

- $\frac{C-5}{18} = \frac{F-32}{100} = \frac{K-273}{18}$

- **Centigrade Heat Unit (C.H.U.) : -**
- **“The quantity of heat required to raise the temperature of 1 pound of water through one degree centigrade.”**
- **1 Kcal = 3.968 B.Th.U. = 2.2 C. H. U.**

L-11 **CALORIFIC VALUE**

- **Definition of H. C. V./G.C.V.**

- **It is total amount of heat liberated when**
- **a unit mass or unit volume of fuel has been**
- **burnt completely and the products are cooled to**
- **room temperature.**

- **Higher Or Gross Calorific Value :-**

Hydrogen is present in almost all fuels when calorific value of such fuel is determined, hydrogen present is converted into steam.

- **If the products are brought to room temperature the latent heat of condensation of steam also gets included in the measurement of heat,**

then it is called Higher or Gross Calorific Value.

L-11 **CALORIFIC VALUE**

Definition of L. C. V./N.C.V.

- **"The net heat produced, when a unit mass or unit volume of the fuel is burnt completely and**
- **the combustion products are**
- **allowed to escape."**

Lower or Net Calorific Value [LCV/NCV]

In practice in any fuel when burnt, the water vapour and moisture etc.

- Escapes along with hot combustion gases.
- Since they are not condensed the lesser amount of heat is available…

- 1 part by weight of hydrogen gives 9 parts by weight of water as follows:-

H_2	+ O	$\longrightarrow$	H_2O
2g	16g		18g
1g	8g		9g

- Latent heat of steam is 587 Kcal/Kg.

L-11 **CALORIFIC VALUE**

NET CALORIFIC VALUE or

NCV = Gross calorific value – Latent heat of water vapour formed.

LOWER CALORIFIC VALUE or

Important

Dulong's formula for calculation of H. C. V.

Gross Calorific Value (GCV/HCV) =

$$1/100\ [8080 \times C + 34{,}500\ (H - O/8) + 2240 \times S]\ \text{Kcal/Kg.}$$

Net Calorific Value (NCV/LCV) =

$$= (GCV - 0.09\ H \times 587)\ \text{Kcal/Kg.}$$

L-11 Classification, Introduction, HCV&LCV

CHARACTERISTICS OF GOOD FUEL –

- **High Calorific Value**
- **Moderate Ignition Temperature**
- **Low Moisture Content**
- **Low Non-Combustible Matter**
- **Moderate Rate of Combustion**
- **…………**

L-11 Classification, Introduction, HCV&LCV

CHARACTERISTICS OF GOOD FUEL –

- ……..
- **Harmless Combustion Products**
- **Low Cost**
- **Easy to Transport**
- **Uniform Size**
- **Controllable Combustion**

L-11 Classification, Introduction, HCV&LCV

1. **High Calorific Value :- A fuel should have high calorific value, since**

- **the amount of heat liberated and temperature attained thereby depends upon the caloric value.**

L-11 Classification, Introduction, HCV&LCV

2. Moderate Ignition Temperature :-

because

- **A fuel having low ignition temperature can cause fire hazards**

- **during storage and transport, and….**

L-11 Classification, Introduction, HCV&LCV

(2.Moderate Ignition Temperature)

- **……..**
- **fuels having high ignition temperature is safe for storage and transport but**
- **there might be some difficulty during ignition.**

L-11 Classification, Introduction, HCV&LCV

3. Low Moisture Content :-

Moisture reduces its heating value.

4. Low Non-Combustible Matter : - After combustion the non – combustible matter remains,

- **generally in the form of ash or clinker.**

L-11 Classification, Introduction, HCV&LCV

(Low Non-Combustible Matter)

……..in the form of ash or clinker.

- **These reduce the heating value.**
- **Each % of non – combustible matter means a heat loss of about 1.5%.**
- **Hence, a fuel should have low non – combustible matter.**

L-11 Classification, Introduction, HCV&LCV

5. Moderate Rate of Combustion :- If the rate of combustion is low then

- **the required high temperature may not be available as well**
- **the fire might go out of control.**
- **So fuel must burn with a Moderate Rate.**

L-11 Classification, Introduction, HCV&LCV

6. Harmless Combustion Products :-

- **These should not pollute the atmosphere by**

- **emitting CO, SO_2, H_2S.**

L-11 Classification, Introduction, HCV&LCV

7. Low Cost :- **A good fuel should be**

- **readily available in bulk and at low cost.**

8. Easy to Transport :- **Fuel must be**

- **easily handle solid and liquid fuels**
- **can easily be transported from one place to another.**

L-11 Classification, Introduction, HCV&LCV

9. Uniform Size :- In case of solid fuel,

- the size should be uniform so that combustion is regular.

10.Controllable Combustion :- So that

- combustion can be started or stopped when required.

COMBUSTION :-

- **Combustion is an exothermic chemical reaction.**
- **It is followed by release of heat and light at a rapid rate,**
- **thus the temperature rises.**

L-11 Classification, Introduction, HCV&LCV

COMBUSTION :-

- ……..
- In combustion of fuel the atoms of carbon, hydrogen etc.
- combine with oxygen with the
- simultaneous liberation of heat at a rapid rate.

L-11 Classification, Introduction, HCV&LCV

- **Ignition Temperature :-**
- **It is the minimum temperature at which a**
- **substance ignites and burns**
- **without further addition of heat from outside.**
- **Calculation of Air Quantities**

- In combustion of fuel the atoms of carbon, hydrogen etc.

- combine with oxygen with the simultaneous liberation of heat at a rapid rate.

- **This energy is liberated due to the formation of new compounds having less energy in them.**

- **The energy (heat) released during combustion process**

is the difference in energy of reactants and that of products generated.

Fuel + O_2 ⟶ Products + Heat

(more heat) (less heat)

C (s) + O_2 (g) ⟶ CO_2 (g) + 97 Kcal

Ignition Temperature

- It is the **minimum temperature at which a substance ignites**

and

burns without further addition of heat from outside.

L-11 Classification, Introduction, HCV&LCV

- **Ignition Temperature :-.**

  Calculation of Air Quantities :-

  To find out the amount of air

- **required for the combustion of a unit quantity of a fuel,**

- **it is necessary to apply the following chemical principles –**

L-12 Numericals based on calorific values

Chemical principles –

- **Calculation of Air Quantities :-**
- Substance always **combine in definite proportion.** These proportions are determined by their molecular masses.
- **Mass Proportion**

$$C\ (s) \quad + \quad O_2\ (g) \longrightarrow CO_2\ (g)$$

12   32   44

Mass Proportion

1. **Substance always combine in definite proportion.**

These proportions are determined by their molecular masses.

L-12 Numericals based on calorific values

$$\underset{12}{C\ (s)} + \underset{32}{O_2\ (g)} \longrightarrow \underset{44}{CO_2\ (g)}$$

- This indicates that mass proportion of C and O_2 and CO_2 are (12:32:44).
- This means 12 gm of carbon requires 32 gm of oxygen and 44 gms of CO_2 formed.

L-12 Numericals based on calorific values

- 22.4 L of any gas at 0^0 C and 760 mm pressure has a mass equal to its 1 mol.
- Since the molar mass of O_2 is 32 gm
- thus 22.4 L of O_2 at S. T. P. will have a mass of 32 gm.

L-12 Numericals based on calorific values

- **Air contains *21%* of oxygen by volume and *23%* of oxygen by mass.**

- **Hence from the amount of oxygen required by the fuel, the amount of air can be calculated.**

L-12 Numericals based on calorific values

- 23 Kg of oxygen is supplied by 100 Kg of air

$\therefore$ 1 Kg of oxygen is supplied by

$$\frac{1 \times 100}{23} = 4.23$$ Kg.

= 4.23 Kg of air

- 21 m^3 of oxygen is supplied by 100 m^3 of air

$\therefore$ 1 m^3 of oxygen is supplied by 4.76 m^3 of air

$$\frac{1 \times 100}{21} = 4.76$$ m^3 of air

- **23 Kg of oxygen is supplied by 100 Kg of air**

then 1 Kg of oxygen is supplied by ----

air = 1x100/23 = 4.23 Kg of air

- 21 m^3 of oxygen is supplied by 100 m^3 of air

- 1 m^3 of oxygen is supplied by ----- of air = 1x100/21 = 4.76 m^3 of air

L-12 Numericals based on calorific values

4. 28.94 g mol^{-1} is taken as molar mass of air.

Minimum O_2 required for combustion = Theoretical O_2 required – O_2 present in fuel.

fuel.

- 2 16 18

5. Minimum O_2 required should be calculated on the basis of complete combustion.

6. **Minimum O_2 required should be calculated on the basis of complete combustion.**

- **If the combustion products contain CO and O_2,**
- **then excess O_2 is found by subtracting the amount of O_2 required to burn CO to CO_2.**

L-12 Numericals based on calorific values

7. **The mass of any gas can be converted to its volume by assuming that gas behaves ideally**

$$PV = nRT$$

P = Pressure (atm) **V = Volume (liters)**

n = No. of moles **T = Temp. (kelvin)**

L-12 Numericals based on calorific values

8. Total amount of hydrogen is either present in the combined form (H_2O) or free form.

Combined form is not combustible.

Rest of hydrogen is called available hydrogen, takes part in combustion.

L-12 Numericals based on calorific values

Rest of hydrogen is called available hydrogen, takes part in combustion.

$$2H_2 + O_2 \longrightarrow 2H_2O + \text{Heat}$$

Mass: 4 32

L-12 Numericals based on calorific values

- Now 1 part of hydrogen combines 8 parts by mass of oxygen,

so **available hydrogen** =

$$\left[\text{Mass of hydrogen} - \left\{\frac{\text{Mass of oxygen}}{8}\right\}\right]$$

L-12 Prncipals for….calorific values

10. Total amount of oxygen consumed by the fuel will thus be given by

the sum of the amount of oxygen

required by the individual combustible constituents present in the fuel.

- **Nitrogen, ash and CO_2 present in fuel are non- combustible matters. Hence they do not take oxygen during combustion process.**

- **Since air has *23% by wt. of oxygen* or *21% by volume* of oxygen.**

L-12 Numericals based on calorific values

10. Total amount of oxygen…….

- Since air has 23% by wt. of oxygen or 21% by volume of oxygen.

- For complete combustion.

(i) $$\text{wt.} = \text{Net } O_2 \times \frac{100}{23} \text{ gm.}$$

(ii) $$\text{Vol.} = \text{Net } O_2 \times \frac{100}{21} \text{ m}^3$$

L-12 Numericals based on calorific values

- Conversion of volume into weight
- $1\ m^3 = 1000L$

and for air 1L $\times \left(\frac{mol}{22.42}\right) \times \left(\frac{28.95g}{mol}\right)$

Thus 1L = $\frac{28.94}{22.4}$ gm

Most commonly combustion reactions are

L-12 Numericals based on calorific values

- Most commonly combustion reactions are –

(i) $H_2 + O_2 \longrightarrow H_2O$

(ii) $S + O_2 \longrightarrow SO_2$

(iii) $CO + ½\ O_2 \longrightarrow CO_2$

(iv) $CH_4 + 2\ O_2 \longrightarrow CO_2 + 2H_2O$

(v) $C_2H_4 + 3\ O_2 \longrightarrow 2CO_2 + 2H_2O$

L-13 Bomb Calorimeter

Principle

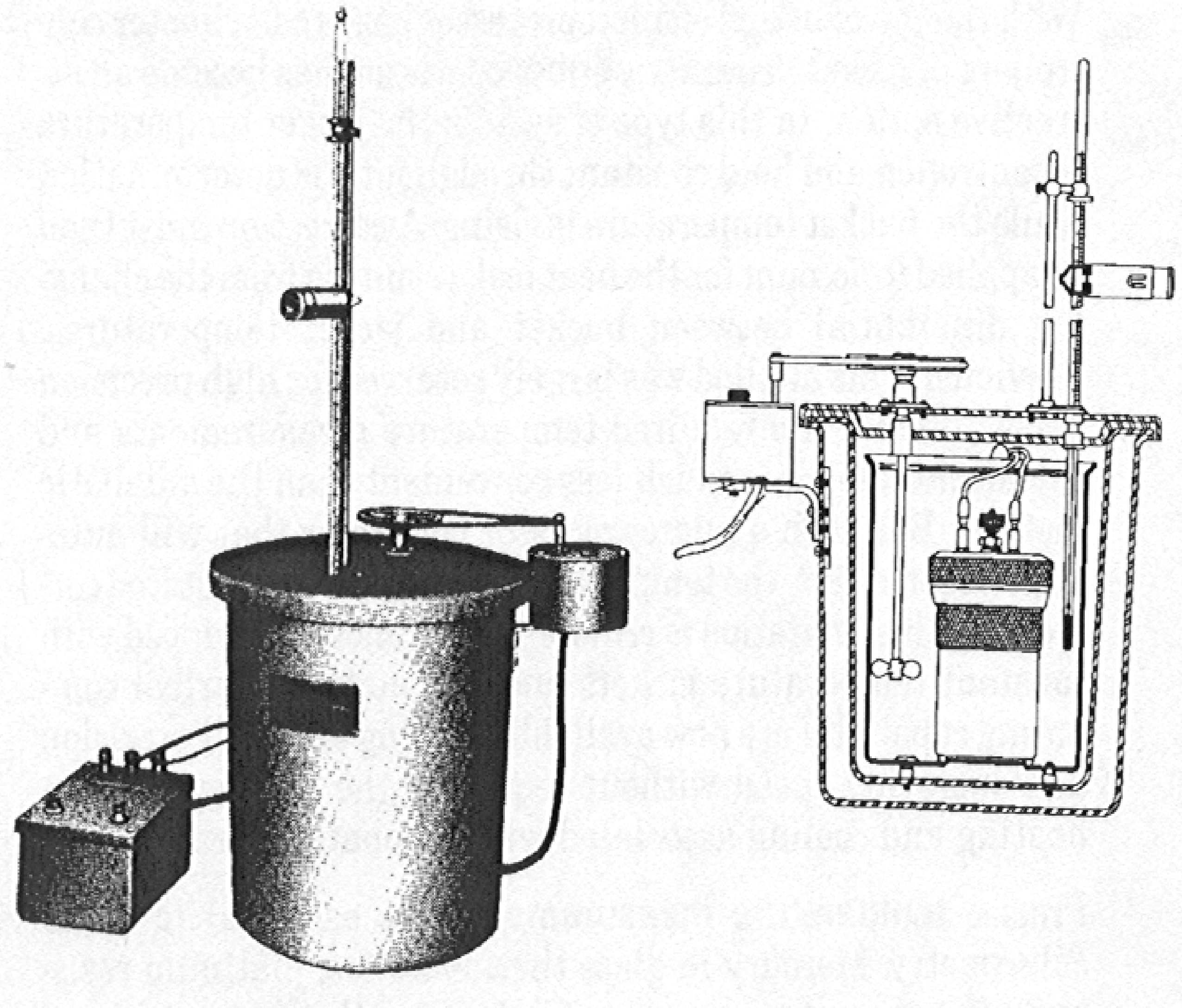
- A known mass of the fuel is burnt and the quantity of heat produced is absorbed in water and measured, then the quantity of heat produced by burning a unit mass of the fuel is calculated.

L-13 Bomb Calorimeter

Determination of Calorific Value (By Bomb Calorimeter)

- This apparatus is used to find the calorific value of

  solid and liquid fuels.



1341 Plain Jacket Calorimeter

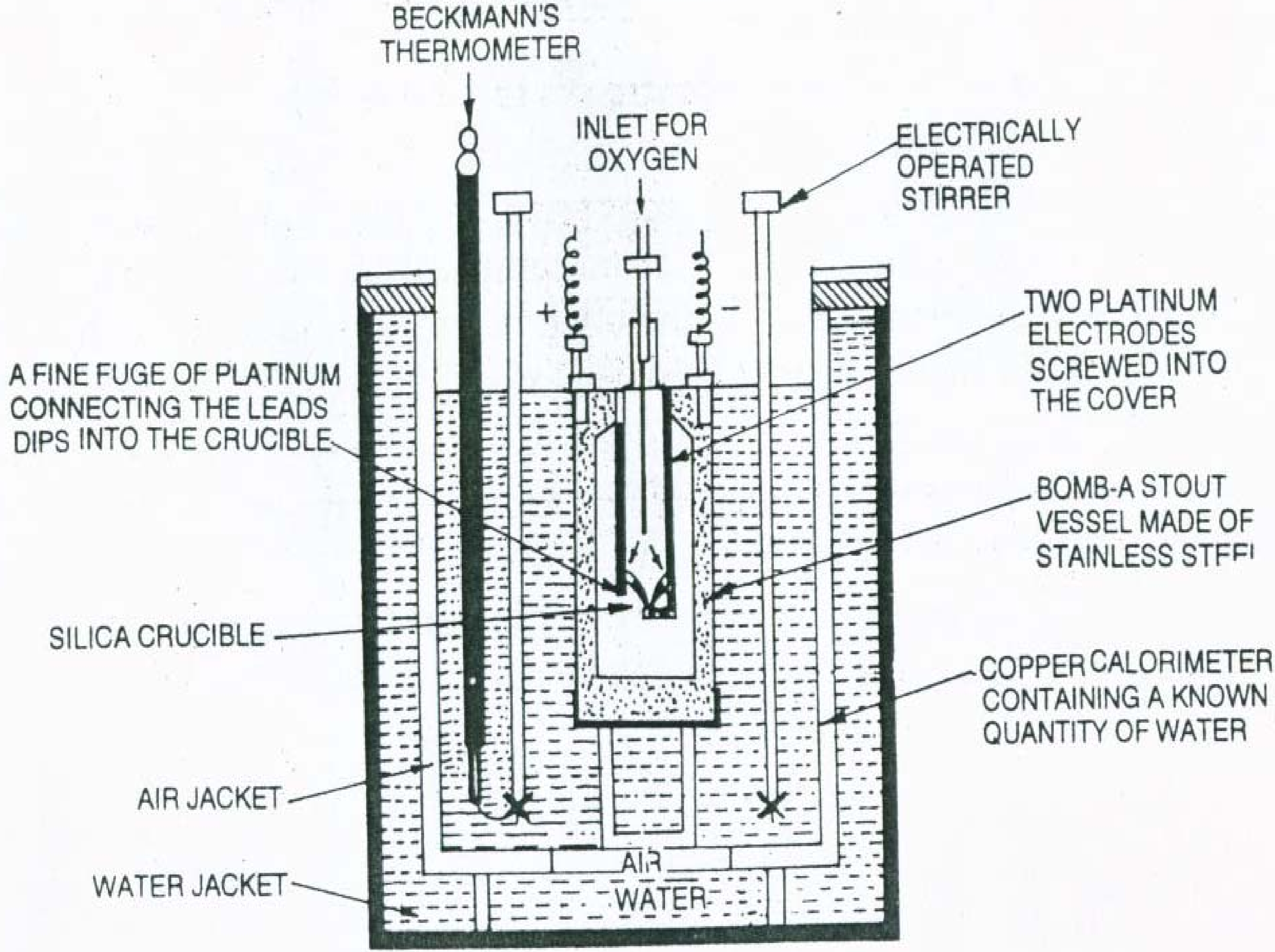
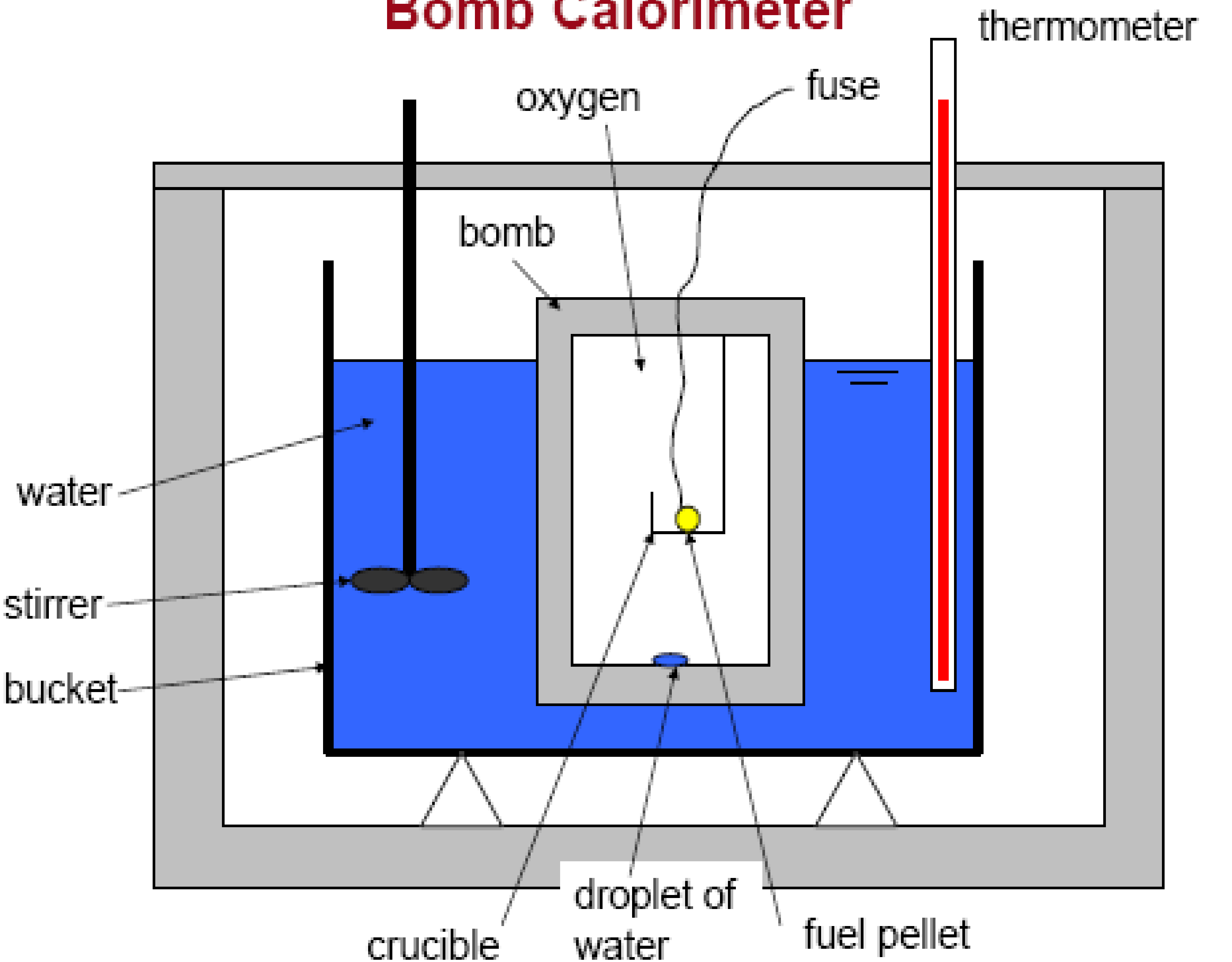


Fig. *Bomb Calorimeter*

Bomb Calorimeter



How Does it Work?

1. Detonate the bomb

2. Measure the resulting temperature rise of water, bomb, and bucket (all of these are assumed to be at the same temperature)

3. You know the heat capacity of the water (you measure how much you put in) and the bomb and bucket (from the mfg.)

4. The product of the temperature rise and heat capacity is related to the energy given off by the fuel

L-14 Bomb Calorimeter

Construction

- It consist of a **strong cylindrical stainless steel Bomb.**
- In which **combustion of fuel** is made to takes place.

L-14 Bomb Calorimeter

- The Bomb is provided with two electrical leads made up of platinum which are fixed.

- A silica crucible is kept inside the apparatus, in which weighed quantity of fuel is taken.

L-14 Bomb Calorimeter

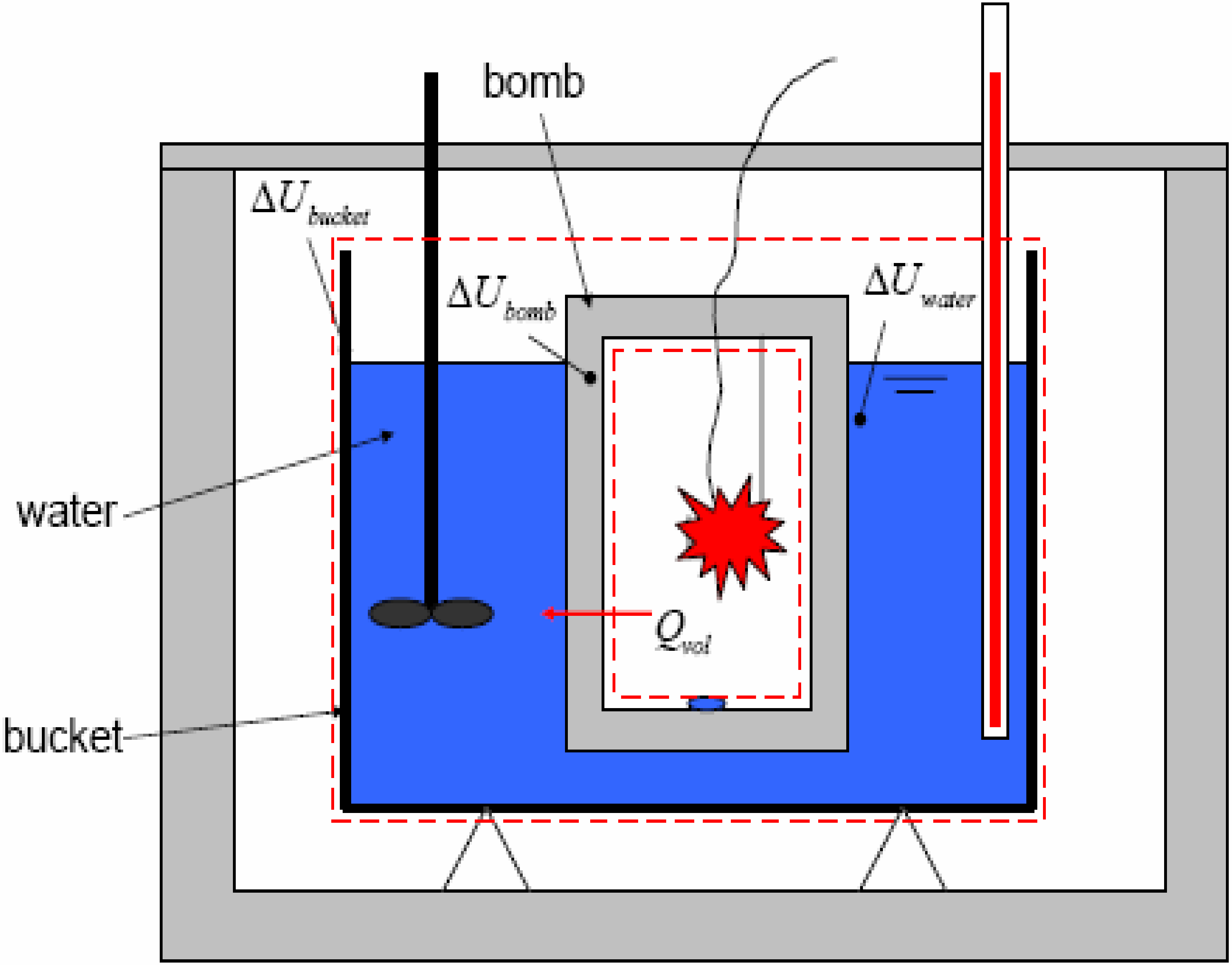
- A fuse wire of platinum is dipped in the fuel taken in the crucible.
- Its ends are connected to the battery.
- The Bomb is placed in the copper calorimeter, containing known quantity of water.

- The copper calorimeter is surrounded by an air jacket, which is further enclosed in a vessel containing water.

- The calorimeter is provided with an electrically operated stirrer and Beckmann's thermometer.

- **Which can read accurately temperature difference upto 1/100th of a degree.**

Bomb Calorimeter



WORKING

- **A known mass of fuel is taken in crucible.**
- **A fine mg wire touching the fuel sample.**
- **Bomb filled with oxygen to 25 atmospheric pressure.**

- **The Bomb is then lowered into copper calorimeter,**

  having a known mass of water.

- **The stirrer is worked and initial temperature of water is noted.**

- The electrodes are then connected to 6-volt battery.
- The sample burns and heat is liberated.
- The maximum temperature is recorded.

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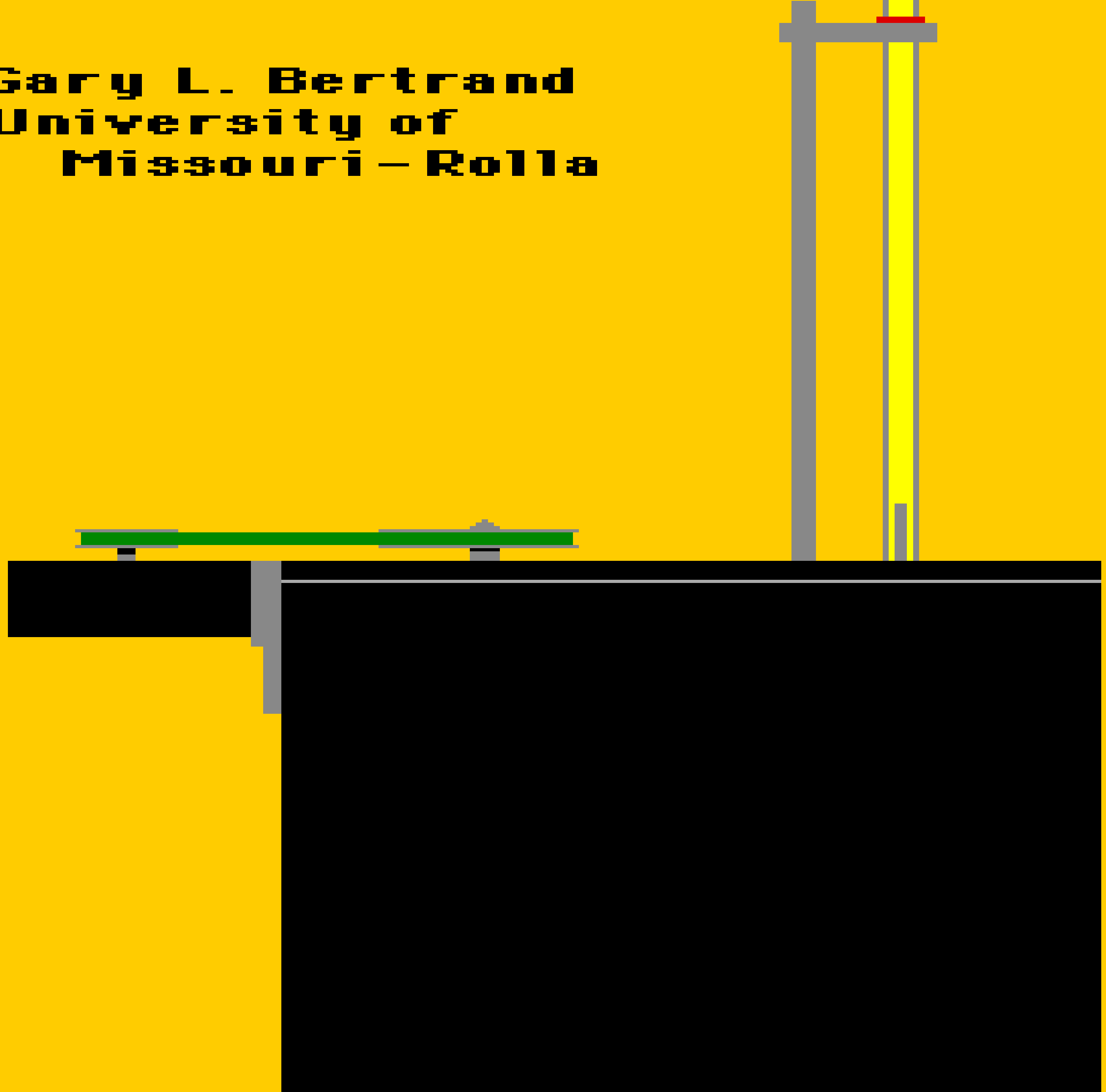


Calculation :-

Let - x = Mass of fuel (In gm.)

W = Mass of water in calorimeter.

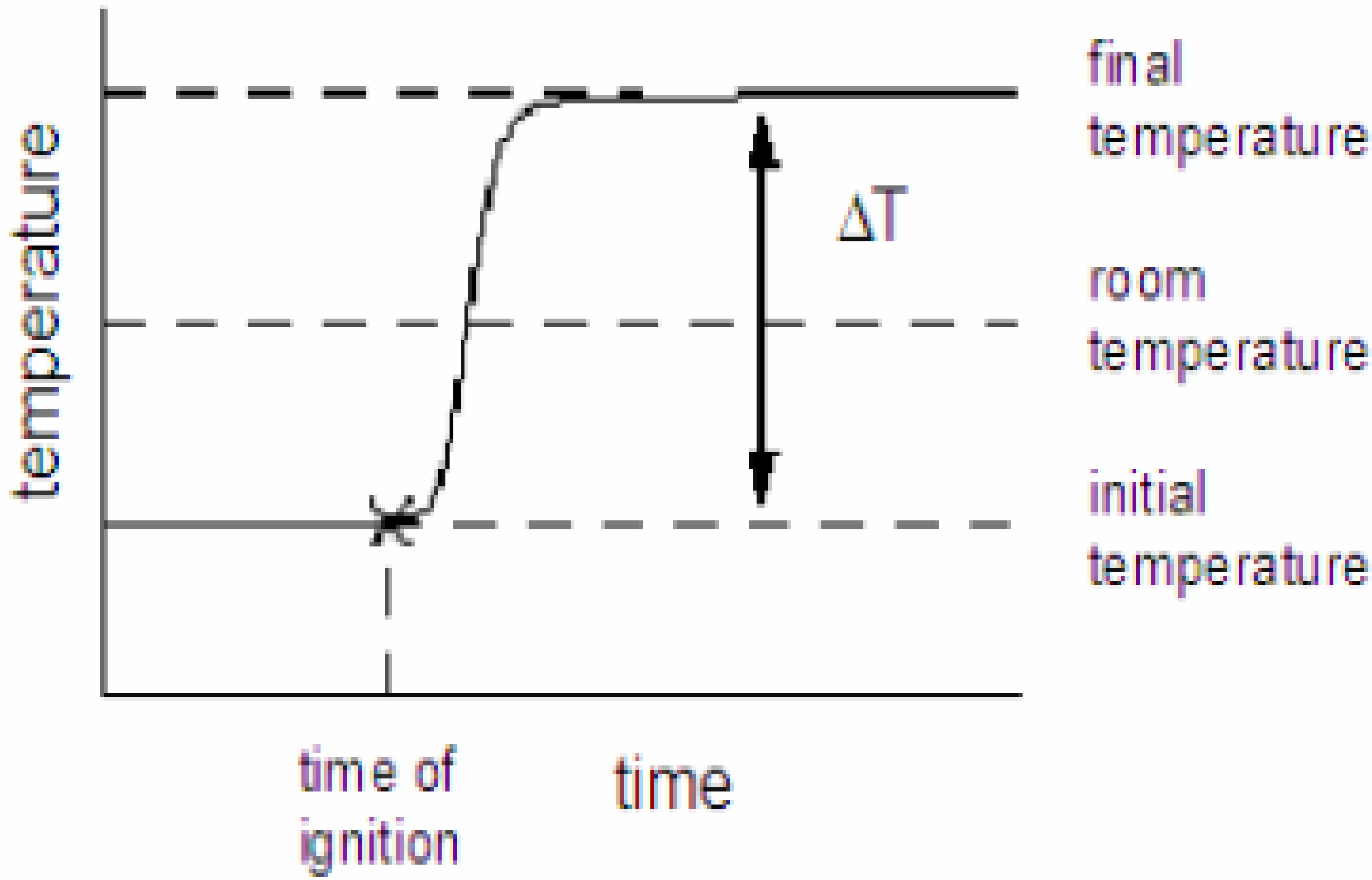
w = Water equivalent in g of calorimeter, stirrer, thermometer etc.

t_1 = Initial temperature of water in calorimeter.

t_2 = Final temperature of water in calorimeter.

L = Higher calorific value of fuel (in cal/gm).

Measurement



- Heat liberated by burning of fuel = xL

  and heat absorbed by water and apparatus, etc. $= (W+w)(t_2 - t_1)$.

But

- Heat liberated by fuel = Heat absorbed by water and apparatus.

$$xL = (W + w)(t_2 - t_1)$$

L-13 Bomb Calorimeter

- **Heat liberated by fuel= Heat absorbed by water & apparatus**

$xL = (W+w)(T_2 - T_1)$

- Initial temp.of water in calorimeter = T_1
- Final temp. of water in calorimeter = T_2
- Mass of fuel = x (in gm)
- Heat liberated by burning of fuel = xL
- Heat absorbed by water = $W(T_2 - T1)$
- Heat absorbed by apparatus = $w(T_2 - T_1)$
- **H.C.V of fuel (L) = $(W + w)(T_2 - T_1) / x$ cal/gm**
- **L.C.V = (H.C.V – 9 × H/100 × 587) cal/gm**

L-13 Bomb Calorimeter

Heat liberated by fuel= Heat absorbed by water & apparatus

$$xL = (W+w)\ (T_2-T_1)$$

$$\text{H.C.V of fuel (L)} = (W + w)(T_2 - T_1)/x \ \text{cal/gm}$$

$$\text{L.C.V} = (\text{H.C.V} - 9 \times H/100 \times 587) \ \text{cal/gm}$$

CORRECTIONS

- **To get more accurate results, the following corrections are applied**

- **Fuse wire correction**
- **Acid correction**
- **Cooling correction**

Fuse Wire Correction

- The heat liberated as measured above, includes the heat given out by ignition of fuse wire used,

- hence it must be subtracted from the total value.

Acid Correction

- Fuels having S and N are oxidized into H_2SO_4 and HNO_3.
- Exothermic reaction

$$S + 2H + 2O_2 \longrightarrow H_2SO_4 + Heat$$

$$2N + 2H + 3O_2 \longrightarrow 2HNO_3 + Heat$$

- Formation of acid is an **"exothermic reaction".**
- So the **measured heat also includes the heat given out** during the acid formation.
- Hence it has to be **subtracted** from the total value.

L-13 Bomb Calorimeter

Correction

To get more accurate results, the following corrections are applied : -

- **Fuse Wire Correction:**
- **Acid Correction:**

$$S + 2H + 2O_2 \longrightarrow H_2SO_4 + Heat$$

Exothermic reactions

$$2N + 2H + 3O_2 \longrightarrow 2HNO_3 + Heat$$

- **(iii)Cooling Correction:**

$$L = \frac{(W-w)\ (t_2-t_1+\text{cooling correction}) - (\text{Acid}+\text{fuse corrrection})}{\text{Mass of fuel (x)}}$$

L-13 Bomb Calorimeter

Numerical-1(ex. 3)

0.72 gm of a fuel containing 80% carbon, when burn in a bomb, increased the temp. of water from 27.3^0 to29.1^0 C.

- If the calorimeter contains 250 gm of water and its water equivalent is 150 gm. Calculate the HCV in kJ/kg.

L-13 Bomb Calorimeter

Solution : -

Given values are:

x = 0.72 gm,

W = 250 g,

w = 150 g,

$t_1 = 27.3^0C$,

$t_2 = 29.1^0 C$

L-13 Bomb Calorimeter

$$\therefore \text{HCV (L)} = \frac{(W+w)\ (t_2 - t_1)}{x} \ \text{Kcal/kg}$$

$$\text{or} \quad L = \frac{(250+150)(29.1-27.3)}{0.72}$$

$$\text{or} \quad L = 1{,}000 \ \text{kcal/kg.}$$

$$= 1{,}000 \times 4.2 \ \text{kJ/kg.}$$

Bomb Calor..Numerialsc

NUMERICAL NO. – 2(ex.4)

- On burning 0.83 g of a solid fuel in a bomb the temperature of 3,500 g of water increased from 26.5^0C to 29.2^0C.
- Water equivalent of calorimeter and latent heat of steam are 385.0 g and 587.0 cal/g.
- If the fuel contains 0.7% H, calculate its gross and net calorific value.

Bomb Calorimeter-Numericals

Given values:

x = 0.83 gm,

W = 3,500 g,

w = 385.0 g,

$t_1 = 26.5^0C$,

$t_2 = 29.2^0$

% H = 0.7%

Latent Heat = 587 cal/g.

Bomb Calorimeter-numericals

$$\therefore HCV/GCV/(L) = \frac{(W+w)(t_2-t_1)}{x} \text{ Kcal/kg}$$

$$L = \frac{(3500+385)(29.2-26.5)}{0.83} = 12,638$$

L = 12,638 cal/g =12.638 kcal/kg

Bomb Calorimeter-problem

$$NCV/LCV = GCV - 0.09H \times 587$$

$$= 12638 - 0.09 \times 0.7 \times 587$$

$$= 12638 - 37 \text{ cal/g}$$

$$= 12601 \text{ cal/g}$$

L-14 Proximate & Ultimate Analysis of coal

Analysis of coal

- Proximate analysis

- Ultimate analysis

L-14 Proximate & Ultimate Analysis of coal

Proximate analysis

- Proximate analysis, which includes the determination of **moisture, volatile matter, ash and fixed carbon.**

- Proximate analysis give valuable information about the **practical utility of coal.**

L-14 Proximate & ……. Analysis of coal

- It involves determination of the following
- **Moisture Content**
- **Volatile Matter**
- **Ash**
- **Fixed carbon**

L-14 Proximate & …….
Analysis of coal

Moisture content

- High % of moisture is not good because
- It increase the cost of coal as well as transportation charges.
- Hence lesser the moisture content better will be the quality of coal.

L-14 Proximate & ……..
Analysis of coal

It quenches the fire in the furnace,

but presence of moisture upto 10%

produces a more uniform fuel bed and less of fly ash.

Moisture in coal evaporates during the burning.

The moisture losses the calorific value of fuel.

L-14 Proximate & ……..
Analysis of coal

Determination of moisture content

- By heating a small amount of coal powder in a crucible at ***105 – 110^0 C***

for one hour **in an electric hot air oven**

and

- then cool, weighing till the weight becomes constant.

L-14 Proximate &……. Analysis of coal

% of moisture =

$$\frac{\text{loss in wt of the fuel sample} \times 100}{\text{wt of coal sample taken}}$$

L-14 Proximate & ……..
Analysis of coal

Volatile Matter

The volatile matter will combustible or non combustible gases.

The presence of non combustible gases are always undesirable.

L-14 Proximate & ……..
Analysis of coal

When coal has high volatile matter then high proportion of fuel distill over as gas.

So higher volatile matter in coal is undesirable.

L-14 Proximate & ……..
Analysis of coal

Coal having higher volatile matter burns with long flame, high smoke and low calorific value

When by product recovery is the main object, volatile matter has special significance.

L-14 Proximate & ……..
Analysis of coal

In coal gas plant and carbonization plants.

Medium volatile matter containing coal give hard and strong coke on carbonization.

L-14 Proximate & ……..
Analysis of coal

Determination

- By heating moisture free coal in silica **crucible with lid** in a **muffle furnace** at

- **925^0C ± 20^0C for 7 minutes**

and

cooled in desiccators and weighed again.

L-14 Proximate & ……..
Analysis of coal

- % of volatile matter =

$$\frac{\text{loss in wt of the fuel sample* x 100}}{\text{wt of coal taken}}$$

*due to the removal of volatile matter

L-14 Proximate & ……..
Analysis of coal

Ash Content

- When all combustible substances have been burnt only ash is left in coal.
- It is not needed because.
- It causes hindrance to the flow of air and heat.

L-14 Proximate & ……..
Analysis of coal

It increases cost of storage.

It reduces calorific value of fuel.

Burning of coal becomes irregular due to formation of clinkers.

(fused lumps of ash).

L-14 Proximate & ……..
Analysis of coal

Determination

- Weighed amount of dry coal is burnt in a muffle furnace for ½ hour at **750^0C.**
- So the matter left is ash only.

$$\% \text{ of ash} = \frac{\text{wt of the ash left } \times 100}{\text{wt of coal taken}}$$

L-14 Proximate & ……..
Analysis of coal

Fixed carbon

After determination of moisture,

- volatile matter,

and

- ash, the remaining part is fixed carbon

Higher the % of fixed carbon greater the calorific value.

L-14 Proximate & ……..
Analysis of coal

Determination

- **By deducting** the sum total of moisture, volatile matter and ash from 100%

% of fixed carbon = 100 - % (Moisture + Volatile matter + Ash)

Ultimate analysis

L-14 ……… & Ultimate Analysis of coal

- It is useful for combustion calculation.

- It includes the **H, N, S, ash and oxygen.**

L-14……….. & Ultimate Analysis of coal

Significance

- **Greater the % of C and H, better is the coal** and give high calorific value.

- Carbon % is the basis of classification of coal.

L-14……….. & Ultimate Analysis of coal

- Hydrogen is mostly associated with volatile matter

  and

  hence it affects the calorific value of coal .Higher % is undesirable.

L-14……….. & Ultimate Analysis of coal

- Determination
- About 1 – 2 gm of coal sample is burnt.

- **C and H are converted in to CO_2 and H_2O.**

L-14……….. & Ultimate Analysis of coal

- They passed in two bulbs.
- One bulb contain weighted amount of anhydrous $CaCl_2$ which absorb water.

$$CaCl_2 + 7H_2O \longrightarrow CaCl_2 . 7H_2O$$

L-14……….. & Ultimate Analysis of coal

- Second bulb contain weighted amount of KOH which absorb CO_2.

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

L-14……….. & Ultimate Analysis of coal

- wt. of $CaCl_2$ and KOH bulbs are measured.

- Increase in weight of $CaCl_2$ bulb shows weight of H_2O

  and

- Increase in weight of KOH bulb is weight of CO_2.

L-14……….. & Ultimate Analysis of coal

$$C \quad + \quad O2 \longrightarrow CO2$$

12 44

$$\frac{\text{wt. of C}}{\text{wt. of } CO_2} = \frac{\text{At.wt.} = 12}{\text{mol.wt} = 44}$$

$$\% \text{ of C} = \frac{\text{wt. of carbon}}{\text{coal taken}} \times 100$$

x/12g(mol)of C found in y/44g(mol)CO_2

$$\therefore \% \text{ of C} = \frac{\text{Increase in wt. of KOH} \times 12}{\text{wt. of coal taken} \times 44} \times 100$$

L-14……….. & Ultimate Analysis of coal

$$H_2 + \tfrac{1}{2} O_2 \longrightarrow H_2O$$

$$2 \qquad\qquad\qquad 18$$

$$\frac{\text{wt.of } H_2}{\text{wt.of } H_2O} = \frac{\text{At.wt.}= 02}{\text{mol.wt}=18}$$

$$\%\text{ of H} = \frac{\text{wt.of hydrogen}}{\text{wt.of coal}} \times 100$$

x/2g(mol)of H_2 is found in y/18g(mol)of H_2O

$$\%\text{ of H} = \frac{\text{Increase in wt. of } CaCl_2 \times 2}{\text{wt. of coal taken} \times 18} \times 100$$

L-14……….. & Ultimate Analysis of coal

Nitrogen

- N_2 in non combustible,
- Has no CalorificValue
- Hence a good quality coal have little amount of N.

L-14……….. & Ultimate Analysis of coal

Determination

- Nitrogen estimation is carried out by **Kjeldahal's method.**
- About 1 gm of coal is heated with conc. H_2SO_4.
- Clear solution obtained which is of ammonium sulphate ($(NH_4)_2 SO_4$).

L-14……….. & Ultimate Analysis of coal

- It is treated with NaOH to liberate ammonia.

- This ammonia is absorbed in known volume of standard H_2SO_4.

L-14……….. & Ultimate Analysis of coal

- And unused H_2SO_4 is then determined from the volume of acid used by ammonia liberated,

- the % of N in coal is calculated as follows

L-14……….. & Ultimate Analysis of coal

$$N_2 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 + NaOH \longrightarrow$$

$$2Na_2SO_4 + 2NH_3 + 2H_2O$$

- $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

L-14……….. & Ultimate Analysis of coal

$$\% \text{ of N} = \frac{\text{wt. of nitrogen}}{\text{wt. of coal taken (1gtm)}} \times 100$$

$$\% \text{ of N} = \frac{(V_1 - V_2) \text{ x N(mol)/L x 14 x100}}{X}$$

N gives the value of mol/L

$$\% \text{ of N} = \frac{(v_1 - v_2)\text{ml x N(mol) x 14 x 100}}{X \text{ x } 1000\text{ml}}$$

$$\% \text{ of N} = \frac{(v_1 - v_2) \text{ x N x 1.4}}{X}$$

L-14……….. & Ultimate Analysis of coal

SULPHUR

Significance

- It contributes to the heating value of coal but on combustion gives acids SO_2 and SO_3, which have harmful effect of corroding the equipments. And cause air pollution.

L-14……….. & Ultimate Analysis of coal

Determination

- Known amount of coal is burnt in bomb calorimeter **sulphur is converted into sulphates**

- they are treated with Barium chloride to precipitate as $BaSO_4$.

L-14……….. & Ultimate Analysis of coal

The ppt. of $BaSO4$ is filtered, washed dried and heated to constant weight.

$$S \longrightarrow SO4^{--} \longrightarrow BaSO4$$

$$\frac{\text{wt. of sulphur}}{\text{wt. of } BaSO_4} = \frac{\text{At. wt s} = 32}{\text{mole wt. } BaSO_4 (233)}$$

Ash : - Same as Proximate Analysis

L-14 Proximate & Ultimate Analysis of coal

Let wt. of $BaSO_4$ precipitate is W_2 gm.

Hence, wt. of S = $\frac{32}{233} \times W_2$ gm

x/32(mol) of S is found in y/233(mol) of $BaSO_4$

∴ % of S = $\frac{\text{wt. of } BaSO_4 \text{ obtained} \times 32}{\text{wt. of coal taken} \times 233} \times 100$

∴ % S = $\frac{W_1}{W_2} \times \frac{32}{233} \times \frac{100}{1}$

L-14 Proximate & Ultimate Analysis of coal

L-14……….. & Ultimate Analysis of coal

Oxygen

- High oxygen content in coals have high inherent moisture and low calorific value.
- An **increase in 1% oxygen** content decreases the calorific value **about 1.7%.**

L-14……….. & Ultimate Analysis of coal

Determination

- It is determined indirectly by deducting the combined % of (C, H, N, S and Ash) from 100.

% of oxygen =

100 - % (C + H + N + S + ash).

L-15 Numerical based on Analysis of Coal

NUMERICAL NO. – 1

- 0.5 g of a sample of coal was used in a bomb for the determination of C.V., Calorific value of coal has to be 8,600 cal/g. The ash formed in the bomb calorimeter was extracted with acid and acid was treated with barium nitrate solution and a precipitate of $BaSO_4$ was obtained.

L-15 Numerical based on Analysis of Coal

- Precipitate was filtered, dried and weighed. The weight of precipitate was found to be **0.05g.** calculate the **% of sulphur** in the coal sample.

L-15 Numerical based on Analysis of Coal

- **Solution :-**

$$\% \text{ of sulphur } = \frac{\text{wt. of BaSO}_4 \text{ ppt} \times 32}{\text{wt. of coal taken} \times 233} \times 100$$

$$\% \text{ of S} = \frac{0.05 \times 32 \times 100}{0.5 \times 233}$$

% of S = 1.373%

L-15 Numerical based on Analysis of Coal

NUMERICAL-2

A sample of Gondwana coal of Jharia was analysed as follows; Exactly 2.500 gm was weighed into silica crucible. After heating for 1 hour at 110^0C,

The residue weighed 2.415 gm.

The crucible was then covered with a Vented lid and strongly heated for exactly 7 minutes at 950^0C $\pm$ 20^0C.

The residue weighed 1.528 gm.

L-15 Numerical based on Analysis of Coal

The crucible was then heated without the cover until constant weight was obtained.

The last residue was found to weigh 0.245 gm.

(i) Calculate the % of result of above analysis

(ii) To which type does the above description belong ?

L-15 Numerical based on Analysis of Coal

NUMERICAL-2

A sample of Gondwana coal of Jharia was analysed as follows; Exactly 2.500 gm was weighed into silica crucible. After heating for 1 hour at 110^{0}C,

The residue weighed 2.415 gm.

The crucible was then covered with a Vented lid and strongly heated for exactly 7 minutes at 950^{0}C ± 20^{0}C.

The residue weighed 1.528 gm.

L-15 Numerical based on Analysis of Coal

Solution:

Mass of coal sample = 2.5 gm.

Mass of moisture in coal sample =

2.5 – 2.415 = 0.085 gm.

Mass of volatile matter =

2.415 – 1.528 = 0.887 gm.

Mass of ash = 0.245 gm.

L-15 Numerical based on Analysis of Coal

Analysis of coal

% of moisture = $\frac{0.085\times100}{2.5}$ = 3.4% Ans.

% of volatile matter = $\frac{0.887\times100}{2.5}$ = 35.48% Ans.

% of ash = $\frac{0.245\times100}{2.5}$ = 9.8% Ans.

% of fixed carbon = 100 – (3.4 + 35.48 + 9.8)

= 51.32 Ans.

L-15 Numerical based on Analysis of Coal

Solution:

Mass of coal sample = 2.5 gm.

Mass of moisture in coal sample =

2.5 – 2.415 = 0.085 gm.

Mass of volatile matter =

2.415 – 1.528 = 0.887 gm.

Mass of ash = 0.245 gm.

L-15 Numerical based on Analysis of Coal

L-14 Proximate & Ultimate Analysis of coal

L-16 High & Low Temperature Carbonization

Carbonization:-

- The process of converting coal into coke is called carbonization.

- When a coking coal is heated in the absence of air, the porous, hard and strong residue left is called Coke.

L-16 High & Low Temperature Carbonization

CARBONIZATION

conversion

- **Coal** ⟶ **coke**

In absence of air

L-16 High & Low Temperature Carbonization

Coal can be classified in to two types –

1. **Non Coking Coals: - Which has no fusing effect. They are known as 'free burning coals'.**

2. **Coking Coals: - Such coals give porous, hard and strong residue after heating in absence of air. They are used in 'Metallurgical Purposes' because they are quite strong.**

L-16 High & Low Temperature Carbonization

Coal

- **Coking Coal**
- **Non Coking Coal**

L-16 High & Low Temperature Carbonization

Types of Carbonization:-

Depending upon the temperature, carbonization is of two types –

1) Low temp. carbonization

2) High temp. carbonization

L-16 High & Low Temperature Carbonization

Carbonization:-

1. **Low Temperature Carbonization (L.T.C.) (500 – 750^0 C): -**

- **In this process, the heating of coal is carried at 500 – 750^0 C.**
- **The yield of coke is about 75 – 80% and**
- **it contain about 5 – 15% volatile matter.**

L-16 High & Low Temperature Carbonization

- **It is not very strong so can't be used as a metallurgical coke. Since it is easily ignited, it is a valuable, smokeless fuel for domestic use.**
- **The by – product gas produced by this process is richer in heating value.**
- **Hence it is more useful fuel. This process is carried out both with coking and non coking coals.**

L-16 High & Low Temperature Carbonization

2. **High Temperature Carbonization (H.T.C.) (> 900^0C): -**

- In this process, the heating of coal is carried out at **900^0 C – 1200^0 C.**
- The yield of coke is about **65 to 75%** volatile matter is **1 – 3%.**
- It is very **hard, strong, pure, porous so it is used in Metallurgical coke.**
- The by product gas produced by this process is high in volume but has low calorific value.

L-16 High & Low Temperature Carbonization

	Low Temperature Carbonization	High Temperature Carbonization
1. Heating temp;	About 500 – 750^0 C	About 900 – 1200^{0}C
2. Yield of coke;	75-80%	65 to 75%
3. Volatile matter;	5-15%	1 – 3%
4. Mechanical strength;	Not strong	Strong
5. Calorific value;	High about 6500- 9500	Low about 5400-6000 Kcal/m^3

L-16 High & Low Temperature Carbonization

	Low Temperature Carbonization	High Temperature Carbonization
6. Quantity of; by product	About 130-150	About 300-390 m^3/tonne
7. Coke produced;	is soft	Is hard
8. Use of coke;	Domestic	Metallurgical purpose
9. % of aromatic hydrocarbon;	Lower	Higher
10. Smoke produced;	Smokeless	Smoky

L-16 High & Low Temperature Carbonization

1. **Low** temperature **carbonization**

Temp. 500 – 600 ^{0}C

- **Manufacturing of domestic coke**
- **Poor mechanical strength**
- **Calorific value – 6500 to 9500 Kcals/m^3**

L-16 High & Low Temperature Carbonization

2. High temperature carbonization

- Temp. 900 – 1200 ^{0}C
- Manufacturing of metallurgical coke
- Good mechanical strength
- Calorific value of gas – 5400 to 6000 Kcals/m^3

L-16 High & Low Temperature Carbonization

L-17 Manufacture of coke Otto-Hoffman Method

- **Manufacture of Metallurgical Coke; By Otto Hoffmann's By – Product Oven Method.**
- **"Regenerative Principle of Heat Economy"**

L-17 Manufacture of coke Otto-Hoffman Method

- Introduction: -

Otto Hoffmann developed modern method for manufacturing metallurgical coke. In order to

1. Increase the thermal efficiency of carbonization process,
2. Recovery of by products.

L-17 Manufacture of coke Otto-Hoffman Method

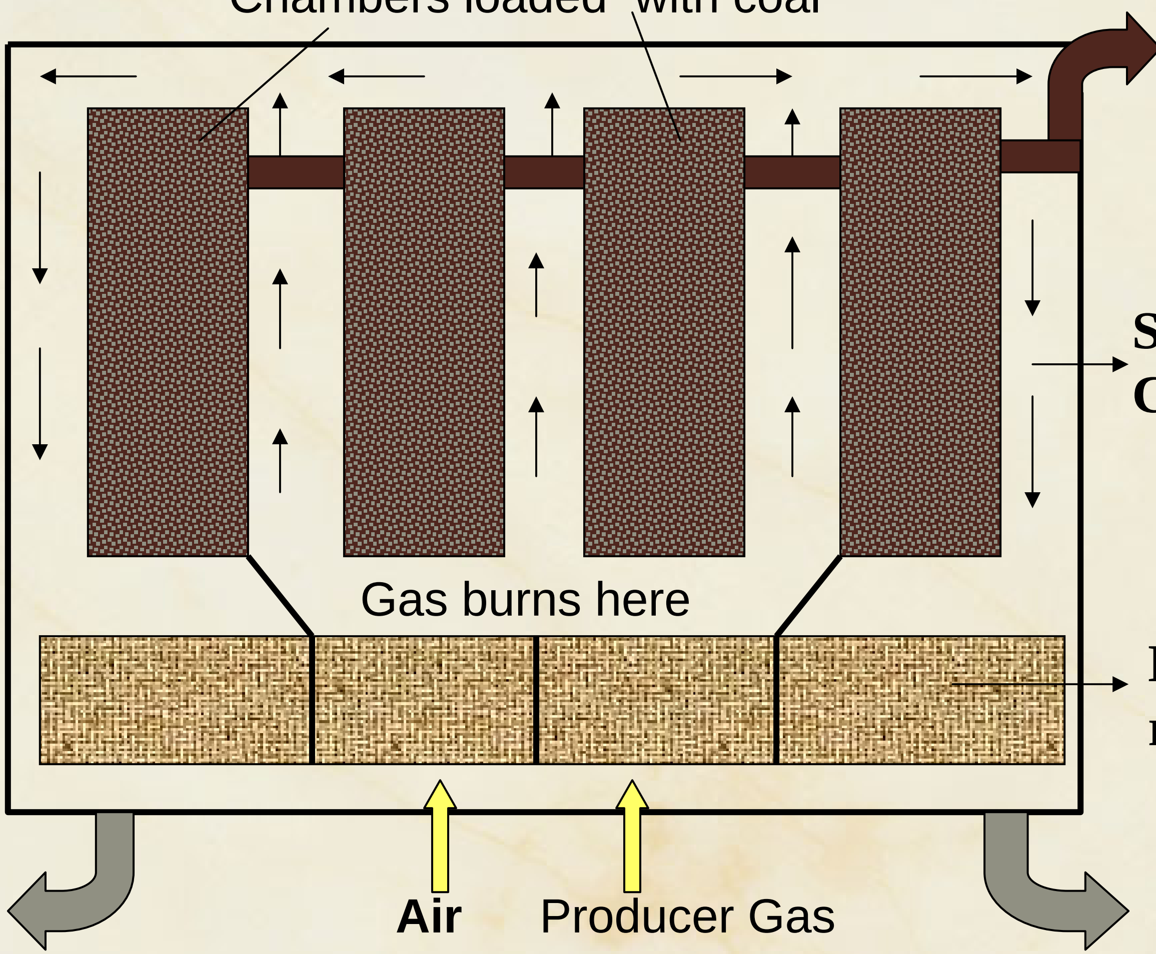
Construction :-

- The by product coke oven consists of a number of **narrow silica chambers**
- each chambers is about **10 -12** meter long, **3 – 4m** wide and **0.40 – 0.45** m thickness.
- These chambers are **erected side by side** with Vertical Flues in between them to form a sort a battery.

L-17 Manufacture of coke Otto-Hoffman Method

- Each chamber has Charging Hole at the top for charging the coal and removal of volatile matter (gas) takes off .
- More over heating is done on the basis of ‘Regenerative System of heat economy’,
- so utilizing the waste flue gases for heating the checker work of bricks.

Otto Hoffman's process



L-17 Manufacture of coke Otto-Hoffman Method

- Theory: - Coking process is done in narrow ovens, which are heated from both sides because coal is poor conductor of heat. The coals adjacent to oven walls get heated first and the plastic zone formed in the case of caking coals moves away from the walls towards the central zone.

L-17 Manufacture of coke Otto-Hoffman Method

- The plastic zone though mobile is such a bad conductor of heat that while the inner zones are getting heated, the semi – coal at the outer zones would have been converted into coke.

L-17 Manufacture of coke Otto-Hoffman Method

- **Working: -** Finely crushed coal is introduced in the charging holes at the top of chamber. And cut the supply of air. The ovens are heated to 1200^0C by burning gas (producer gas). Each oven is separated from another oven by a vertical flue in which the fuel gas burns.

L-17 Manufacture of coke Otto-Hoffman Method

- These ovens work on the Regenerative principle of heat economy. The flue gases produced during combustion, before escaping to chimney, pass on their heat to one or two sets of checker brick, until this brick has been raised to temp. about 1000^0C.

L-17 Manufacture of coke
Otto-Hoffman Method

- The inlet gas are passed through the heated checker brick, which get preheated, while the flue gases leave their acquired heat to one generator the other generator is used for preheating the incoming air. Heating is continued, until all the volatile matter has escaped. It takes about 11 – 18 hrs for carbonization of a charge of coal.

L-17 Manufacture of coke Otto-Hoffman Method

- **Quenching: -** After the completion of carbonization, the discharging doors are lifted by a crane and the red hot coke is pushed out into a coke car. The car carries it to quenching station where the coke comes into contact with a spray of cooling water.

L-17 Manufacture of coke Otto-Hoffman Method

- Then it is supplied for different purposes. In place of wet quenching, ‘dry quenching’ can also be done. It has many advantages, because the coke produced is more strong, dense, non reactive. Coke is cheaper also and contains lesser dust than ‘wet quenching’.

L-17 Manufacture of coke Otto-Hoffman Method

Recovery of By Products: -

The gas coming out from the oven is known as **'Coke Oven Gas'.**

- It is mainly consist of NH_3, H_2S, C_6H_6, **Tar, Naphthalene** etc.

L-17 Manufacture of coke Otto-Hoffman Method

- Recovery of by products
- Recovery of Tar
- Recovery of Ammonia
- Recovery of Naphthalene
- Recovery of Benzene
- H_2S

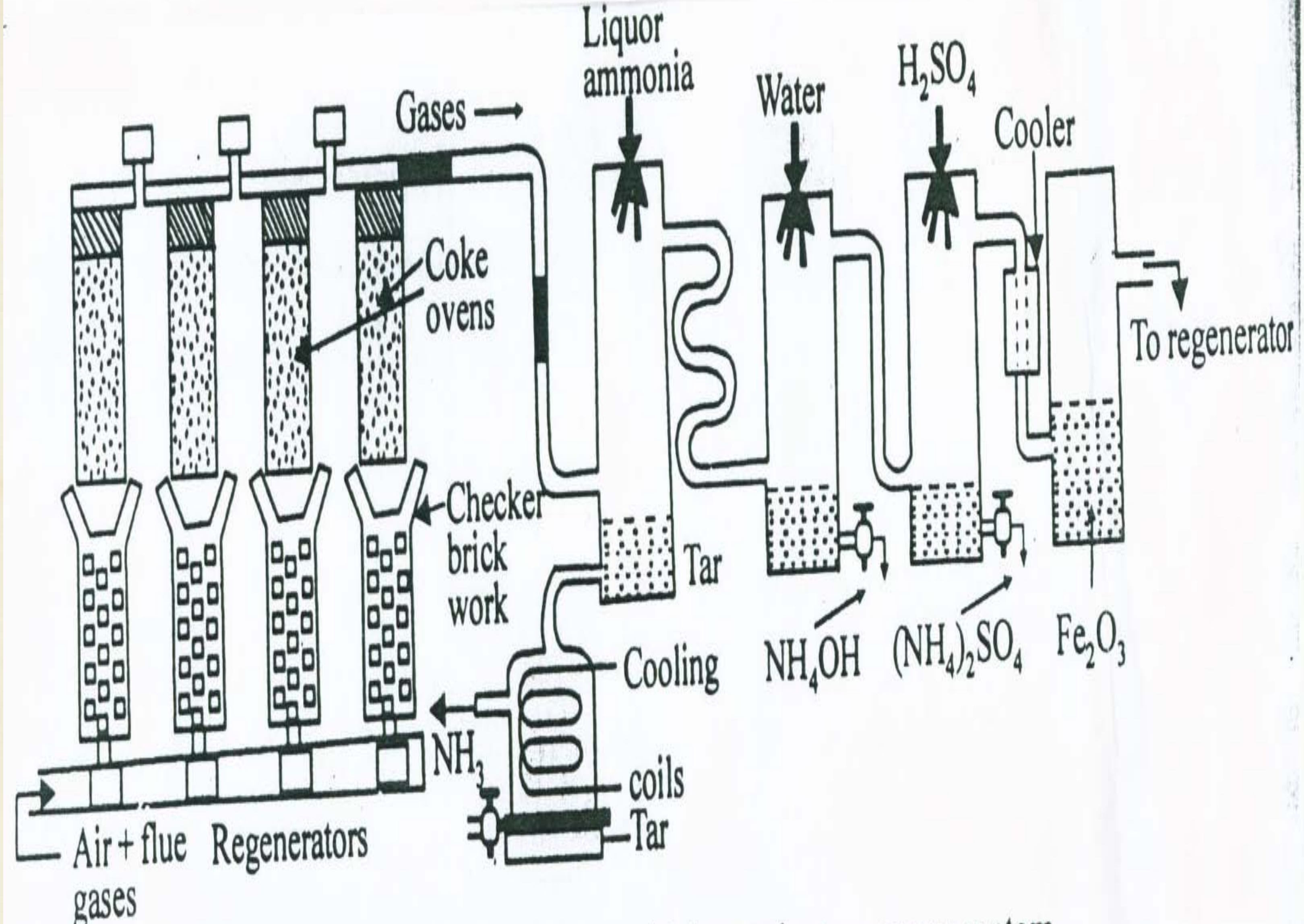


Fig. 2.6. Chamber ovens with byproduct recovery system.

L-17 Manufacture of coke
Otto-Hoffman Method

Recovery of Tar: -

The gas passed through a tower in which liquid ammonia is sprayed.

- Here dust **and tar get collected in a tank below,** which is heated by steam coils to recover back ammonia.
- **The ammonia is used again.**

L-17 Manufacture of coke Otto-Hoffman Method

Recovery of Ammonia: -

The gas from the chamber is then passed a tower in which water is sprayed.

Here ammonia goes into solution as NH_4OH.

L-17 Manufacture of coke Otto-Hoffman Method

- **Recovery of Naphthalene: -**

The gas then passed a tower in which very cold/chilled water is sprayed. When naphthalene gets condensed.

L-17 Manufacture of coke Otto-Hoffman Method

- **Recovery of Benzene: -**

  The gas is then **sprayed with petroleum** when benzene and its homologous can be recovered.

- **Recovery of H_2S :-** The gas is then passed to a purifier, packed with moist Fe_2O_3.

L-17 Manufacture of coke Otto-Hoffman Method

- After some time, when all Fe_2O_3 is changed into Fe_2S_3

$$Fe_2O_3 + 3H_2S \longrightarrow Fe_2S_3 + 3H_2O.$$

$$Fe_2S_3 + 4O_2 \longrightarrow 2FeO + 3SO_2 \uparrow$$

$$4FeO + O_2 \longrightarrow Fe_2O_3 + 3H_2O.$$

L-17 Manufacture of coke Otto-Hoffman Method

Significance of Recovery of By Product

Coke oven gas contains large no. of valuable impurities.

1. **Tar: -** Tar is used for road making; it gives on fractional distillation benzene, toluene, naphthalene etc.

L-17 Manufacture of coke Otto-Hoffman Method

2. **Ammonia: -** The removal of ammonia from the gas is necessary to avoid the blockage of gas pipes by ammonium carbonate.

3. **Naphthalene: -** Naphthalene and other higher aromatics present in vapours, may cause blocking of the gas pipes.

L-17 Manufacture of coke Otto-Hoffman Method

4. **Benzene: -** Is an important solvents and raw materials for plastic.

5. **H_2S :-** Sulphur compounds may get oxidized to SO_2 and finally to H_2SO_4 obtained.

$$Fe_2O_3 + 3H_2S \longrightarrow Fe_2S_3 + 3H_2O$$

L-17 Manufacture of coke Otto-Hoffman Method

- After time, when all Fe_2O_3 is changed into Fe_2S_3

$$Fe_2S_3 + 4O_2 \longrightarrow 2FeO + 3SO_2 \uparrow$$

$$4FeO + O_2 \longrightarrow Fe_2O_3 + 3H_2O.$$

L-17 Manufacture of coke
Otto-Hoffman Method

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- Petroleum
- Petra = Rock
- Oleum = Oil
- Dark greenish brown viscous oil found in deep earth crust .

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Liquid Fuel; Petroleum (Its Chemical Composition)

- Petroleum or crude oil is dark greenish – brown viscous oil found deep in earth's crust.

Petra = Rock and Oleum = Oil

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Petroleum is also called mineral oil because it occurs beneath the earth.

The composition (Average) of petroleum is –

C = 80 to 87 %

H = 11.1 to 15 %

S = 0.1 to 3.5 %

O = 0.1 to 0.9 %

N = 0.4 to 0.9 %

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- Refining of crude oil
- **Step 1. Separation of water**
- **Step 2. Removal of harmful sulphur compound**
- **Step 3. Fractional distillation**

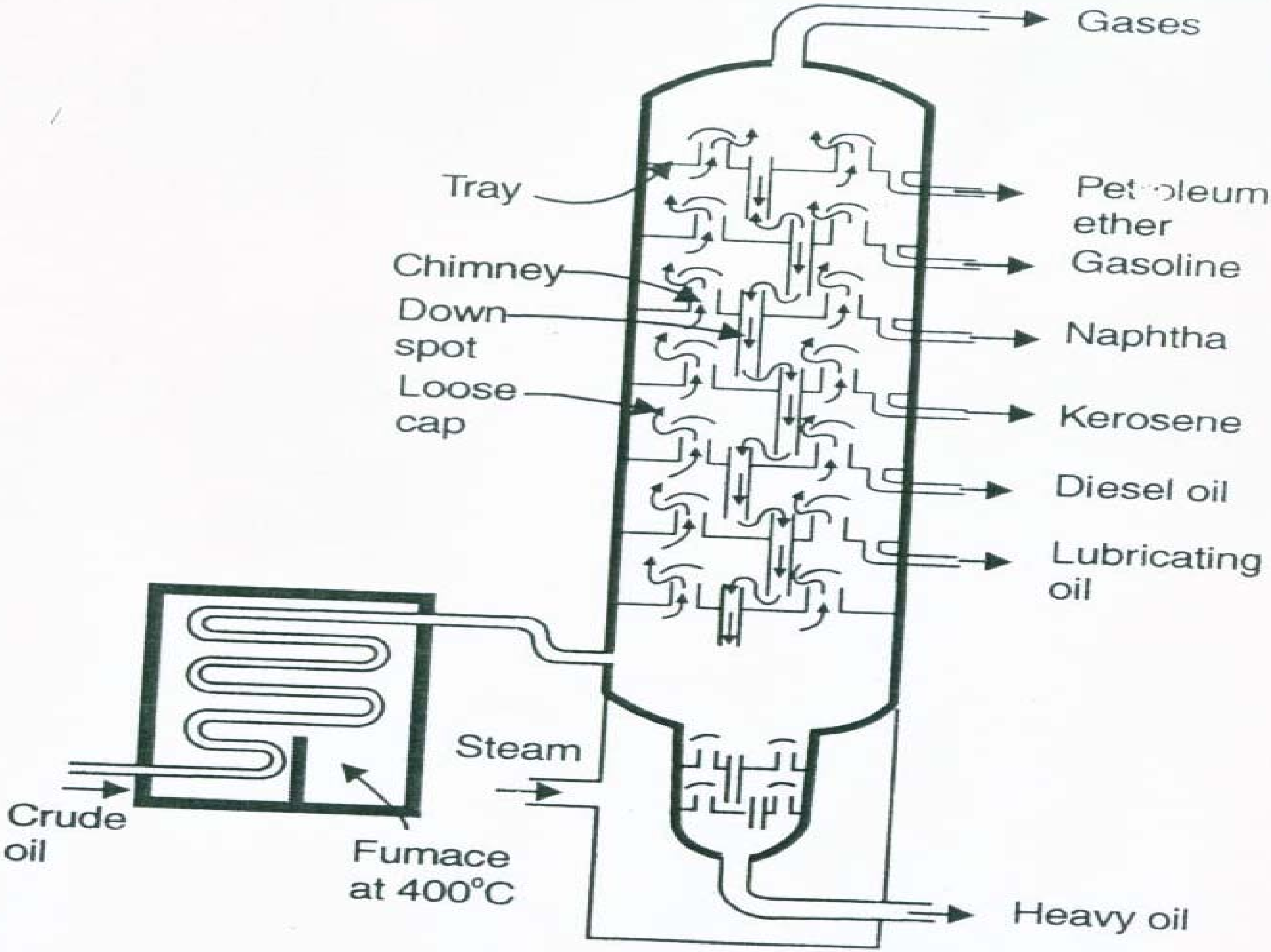


Fig. Fractional distillation of crude petroleum.

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Composition	Remarks
Hydrocarbons -	Present about 70% Normal branched, cycloalkanes present.
Sulphur containing compounds -	Sulphur is present in either free form or compound form like H_2S, Thiols, Thiophene, and Thioalkanes.
Oxygen containing compounds -	$(C_4 – C_9)$ carboxylic acids occur in low boiling fractions while Naphthenic acid occur in high boiling fraction.

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Composition	Remarks
Nitrogen containing compound-	Mainly in form of pyrrole, indole pyridine, quinoline etc.
Inorganic compounds -	These are organo metallic compounds of Cu, Fe, Ni and V.

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Fractional Distillation

Introduction: -

- The crude oil is separated into various fractions (having different boiling points) with the help of fractional distillation.
- These fractions are finally converted into desired specific products by removing impurities. The process is called **'refining of crude oil'**.

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- **Process: -** The crude oil is heated to about 400^0C in a pipe, where all volatile matter are evaporated.
- The hot vapors are then passed through a tall cylindrical tower, known as **'Fractionating Column'** containing a number of horizontal stainless steel trays at short distances.
- …………

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- These trays are provided with individual Chimney which are covered with a loose cap.
- As the vapors go up, they become gradually cooler and fractional condensation takes place at different heights of column.
- Higher boiling fraction condenses first while the lower boiling fractions turn-by-turn.

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- Various Fractions by Distillation of Crude Oil

Name of fraction	Boiling Temp.	Approximate Composition interms of HC	Uses
Uncondensed gas	< 30^0C	C_1 to C_4 ethane, propane	Used as L.P.G.
Petroleum ether	30 – 70^0C	C_5 to C_7	Used as solvent
Gasoline or petrol	40 to 120^0C	C_5 to C_8	Used as fuel for IC engines solvent

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- Various Fractions by Distillation of Crude Oil

Name of fraction	Boiling Temp.	Approximate Composition interms of HC	Uses
Naphtha	120 to 180^{0}C	C_8 to C_{10}	Solvent, in dry cleaning
Kerosene Oil	180 to 250^{0}C	C_{10} to C_{16}	Fuel, in preparing laboratory gas
Diesel Oil	250 to 320^{0}C	C_{10} to C_{18}	Used as diesel engine fuel
Heavy Oil	320 to 400^{0}C	C_{17} to C_{30}	For getting gasoline by cracking

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

A brief description of 3 major important liquids.

1. **Gasoline or Petrol Fraction: -**

- It is a mixture of hydrocarbon from **pentane to Octane.** This fraction is obtained between 40 to 120^0C.

- This fraction is highly volatile and inflammable and used as **fuel for internal combustion (IC) engines**. It's C. V. = 11,250 cal/gm.

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

2. **Diesel Oil: -** It is mixture of hydrocarbon from C_{10} to C_{18}. This fraction is obtained between 250 to 320^0C. It is used as a fuel for diesel engine. It's C. V. = 11,000 cal/gm.

3. **Kerosene Oil: -** It is mixture of hydrocarbons from C_{10} to C_{16}. It does not vaporize easily. It is used as a domestic fuel, jet engine fuel. It's C. V. 11,100 cal/gm.

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- Knocking
- Ignition temperature
- Compression ratio
- Knocking and compression ratio

i

Knocking

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Knocking and Chemical Structure

Two main terminology used in knocking is -

1. **Ignition Temperature: -** It is the minimum temperature at which the combustion is self start.

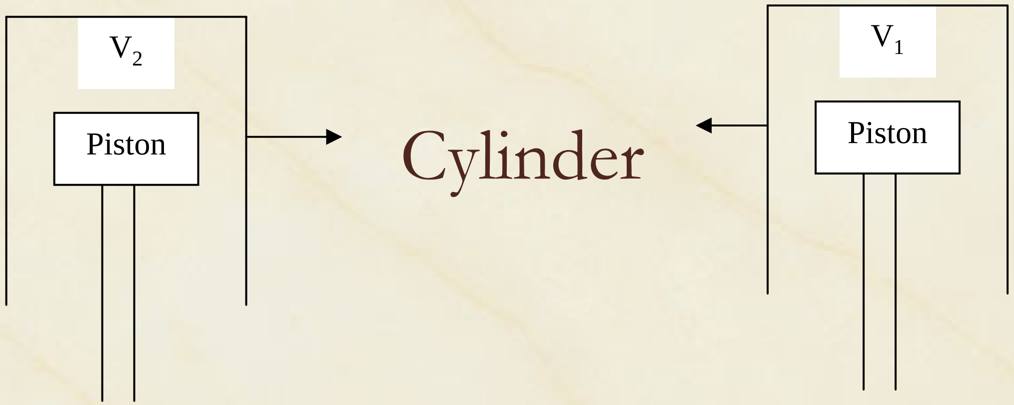
L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

2. Compression Ratio: - The power and efficiency of IC engine depends upon compression ratio (C.R.).

- The ratio of gaseous volume (V_1) in cylinder at the end of suction stroke to the volume (V_2) at the end of compression stroke of the piston.
- **As $V_1 > V_2$ ⟶ $CR = \frac{V_1}{V_2} = > 1$**

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

'CR indicates the extent of compression of fuel air mixture by piston'.



$$C.\ R. = \frac{V_1}{V_2}$$

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

What is Knocking ?

- The fuel air mixture gets heated to a temperature **greater than its ignition temperature** due to compression ratio.

- This leads to **spontaneous combustion** even before sparking.

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- It is also possible that the last portion of the fuel – air – mixture undergoes **self – ignition after sparking and give detonating shock wave (explosion).**

- The resulting shock wave dissipates its energy by **hitting the cylinder walls and piston, and emitted sound is Knocking.**

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- IC engine = Internal Combustion Engine.

"The uneven burning of fuel is knocking".

Knocking depends on: -

1. fuel taken, **2.engine design,**

3. shape of head, **4.location of plug,**

5. chemical structure of fuel,

6. running conditions.

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Consequence of Knocking -

1. Decreased power output.
2. **Mechanical damage** by over heating of the cylinder parts.

With increase in C.R., efficiency of IC engine also increases but

after critical C.R., tendency to knock also increases.

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Chemical Structures and Knocking

- Knocking tendency decreases with increase in the compactness of the molecules.
-
- Double bonds and cyclic compound.

Knocking tendency decreases

- **n - alkanes > mono substituted alkane > cycloalkane > alkene > aromatics**

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Branched chain paraffin's have higher anti knocking properties.

Ex. Thus **2 – Methyl hexane** has an octane no. **of 55** while

2:2 dimethyl pentane has an octane no. **of 80.**

- **Aromatic hydrocarbon such as benzene and toluene** has high octane number.
- **Olefins have** higher anti – knock properties.

i

OCTANE NUMBER

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

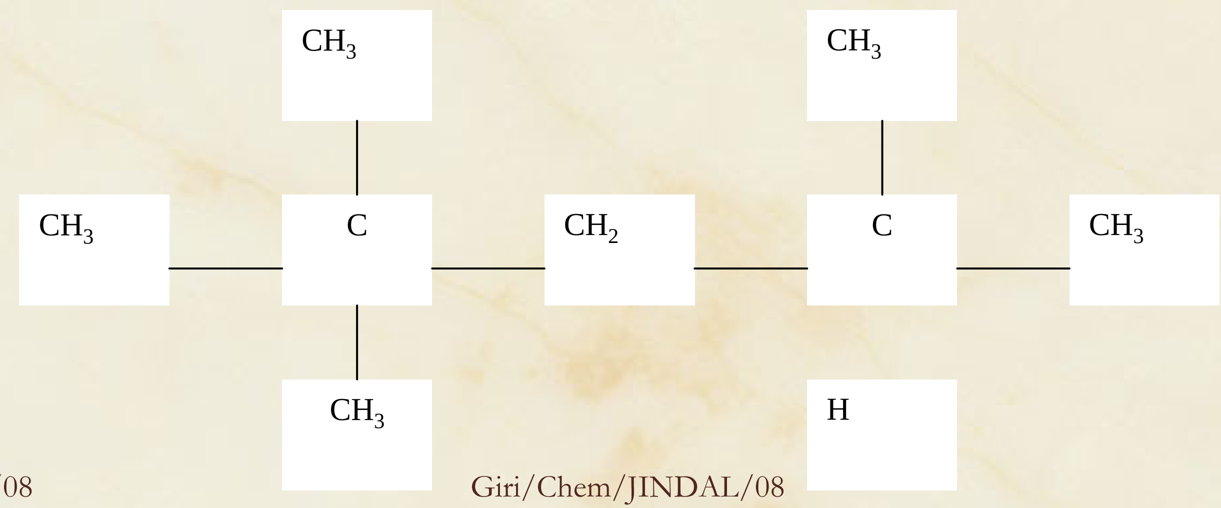
OCTANE NUMBER

Octane number or rating of a gasoline(or any other IC engine fuel) is **the percentage of isooctane in a mixture of isooctane and n-heptane,** which matches the fuel under test in knocking characteristics.

e.g. **“80-octane” means 80:20 mixture of iso-octane and n-heptane**

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- **Octane Number**
- The knocking tendencies of a fuel are expressed by ‘Octane Number’. It is found that the hydrocarbon iso- octane (C_8H_{18}) having formula –



L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- This shows very little tendency to detonate (explosion) when mixed with air. Hence **Octane number is 100.**
- On the other hand the straight chain hydrocarbon, n – heptane (C_7H_{16}) having formula –

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

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

H H H H H H H
| | | | | | |
H- C-C-C-C-C-C-C-H
| | | | | | |
H H H H H H H

n-Heptane

(Octane No.=0)

H CH_3 H CH_3 H
| | | | |
H- C--C--C-C—C-H
| | | | |
H CH_3 H H H

Iso-octane

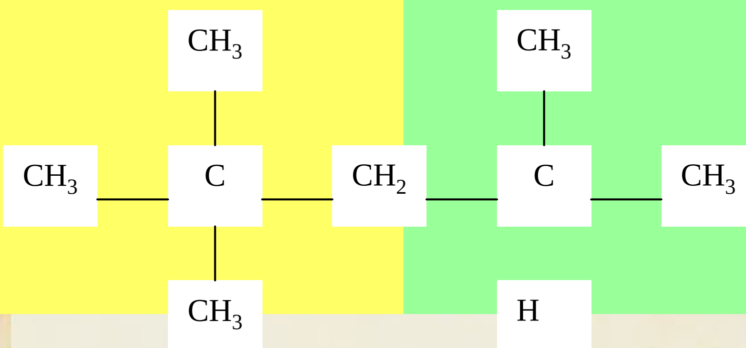
(2;2;4-trimethyl pentane)

(Octane No.=100)

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- **Octane rating is given by Graham Edgar in 1926.**

Fuel	Octane Number	Characteristics
N- heptane	**0**	**Knocks severely**
Iso-Octane	**100**	**High Resistance to knocking**



L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Hydrocarbon	Octane Number
Benzene	100+
Isopentane	90
Cyclohexane	77
2 – methyl pentane	71
n – pentane	62
n – hexane	26

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- **Anti – Knocking Agents: -** Tetra ethyl lead (TEL) and diethyl telluride [$(C_2H_5)_2$ Te] are anti knocking agents.
- TEL gives Pb and PbO_2 during combustion. Pb and PbO_2 decrease engine life, hence they must be removed by adding ethylene dibromide.

$$Pb, PbO_2 + C_2H_4Br_2 \longrightarrow PbBr_2 + CH_2{=}CH_2$$

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

$$Pb, PbO_2 + C_2H_4Br_2 \longrightarrow PbBr_2 + CH_2{=}CH_2$$

- $PbBr_2$ is volatile and escapes in atmosphere but creates pollution problem.
- **The adding of TEL in fuel is called 'Doping'.**

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- Unleaded petrol.
- Benzene
- Addition of TEL is called as “Doping”

i

Cetane Number

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- **Cetane Number – Diesel Engine Fuel: - The** knocking tendency of **diesel oil** are expressed in terms of **cetane number.**
- Diesel engine fuels have a **long chain hydrocarbon,** which has a very short ignition lag.
- This means that it is essential that the hydrocarbon molecules in a diesel fuel should be '**Straight Chain'.**

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- In the diesel engine, air is first drawn into cylinder, and then compressed.
- At the end of compression stroke, **diesel is injected.**
- The Oil (Diesel) absorbs the heat from the air and it **ignites spontaneously** as it attains ignition temperature (500^0C)

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- The combustion of fuel in a diesel engine is not instantaneous,
- the **"interval between the start of fuel injection and its ignition is called the 'ignition delay' "**

Ignition delay is due to

(a) Engine Design

(b) Mixing of spray (fuel) and air

(c) Chemical nature of fuel.

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- If ignition delay is long, it will lead to fuel accumulation in the engine even before the ignition.
- When ignites creates explosion.
- This is diesel knock. It is shown in '**Cetane number**'.

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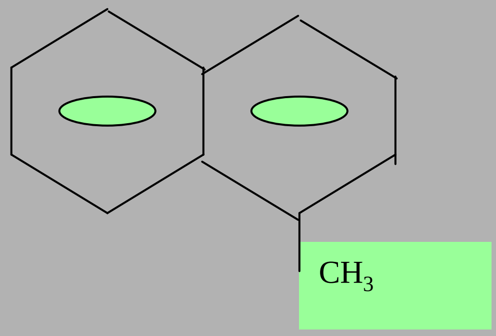
Cetane number: -

- Saturated hydrocarbon has a short ignition lag so its cetane no. is 100 and
- aromatic hydrocarbon has very long ignition lag so its cetane no. is zero (0).

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Compound	Cetane Num.	Ignition lag
Cetane ($C_{16}H_{34}$)	100	Very short
Methyl Napthelene ($C_{11}H_{10}$)	0	Long



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- **"The % of cetane and α - methyl naphthalene is give by cetane number"**

Consider the following series –

- **n alkanes > naphthalenes > alkanes > branched-alkanes >aromatics**

- Ignition delay increases from left to right.

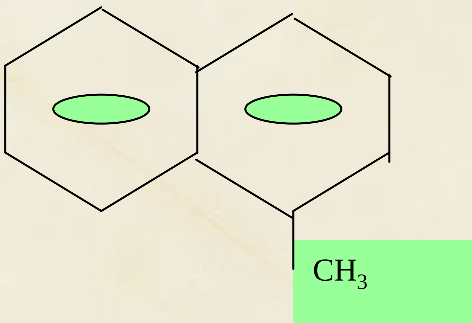
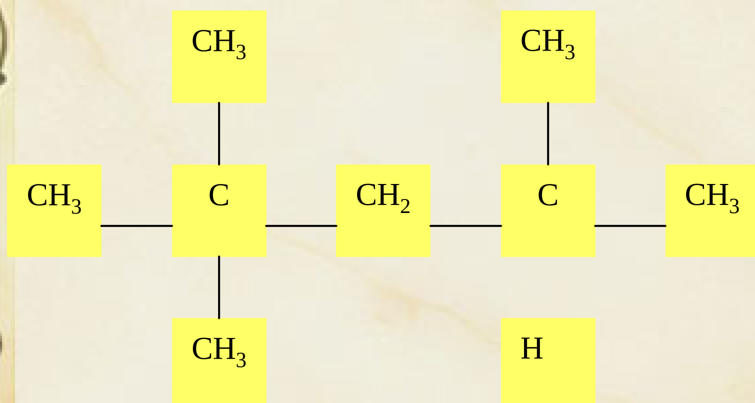
L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

n alkanes > naphthalenes > alkanes > branched-alkanes >aromatics

- **Ignition delay increases** from left to right.
- **Ignition quality increases** from right to left.
- **Cetane no. increase** from right to left.

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Difference between Octane no. and Cetane no.

Octane No.	**Cetane No.**
Is the % of iso-octane in a mixture of isooctane and n-heptane.	Is the % of cetane in a mixture of cetane and α-methyl naphthalene.
CH3 – (CH2)5 – CH3 n – heptane Knocks badly (Octane no. – 0)	α - methyl naphthalene (Cetane No. = 0) 
 **Iso – Octane (Octane no = 100)** • Give little knocking.	**CH3 — (CH2)14 — CH3** (Cetane No. = 100)

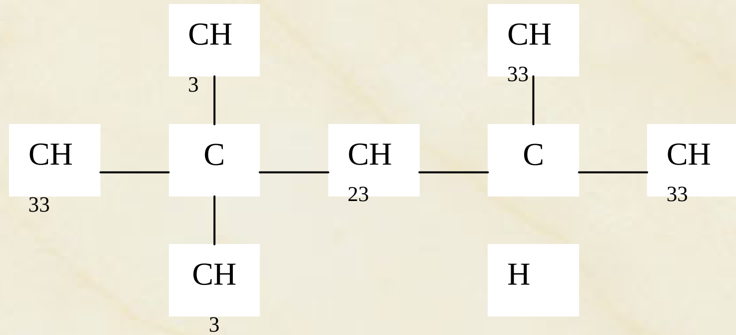
contd. Next slide

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Difference between Octane no. and Cetane no.

Octane No.	Cetane No.
• It is used for internal combustion engine	It is used for diesel fuel.
Octane no. can be raised by **adding TEL or (C2H5) Te.**	Cetane no. can be raised **by addition of dopes like ethyl nitrite.**
HC which are poor diesel fuel are good gasoline fuel.	Hydrocarbon which are poor gasoline are good diesel fuel.
Straight chain fuels are worst fuels. They give low octane no.	Straight chain fuels are best. They give high cetane no.

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking



L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Power Alcohol

- When Ethyl Alcohol is used as an additive
- to motor fuels to act as a fuel for internal
- combustion engines, called power alcohol

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Manufacture

- Saccharine material
- Cellulose material
- Starchy material
- Hydrocarbon gases

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

$C_{12}H_{22}O_{11}$ + H_2O

sucrose water

↓

$C_6H_{12}O_6$ + $C_6H_{12}O_6$

glucose fructose

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

- $C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + CO_2$

Glucose / fructose **Power alcohol**

Advantages

- **Alcohol –octane no. 90**
- **Petrol – octane no. 60-70 ,**
- **addition increases anti knocking property.**

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Combination

gives lesser difficulty in starting.

Alcohol is capable to absorb

any traces of moisture present in petrol

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Disadvantages

Calorific value of alcohol is 1/3than petrol so its lowers calorific value of petrol.

Alcohol easily oxidizes into acids and causes corrosion.

L-18 Petroleum, Chemical Composition Fractional distillation & Knocking

Analysis of flue gases by Orsat's Apparatus

L-19 Analysis of flue gases by Orsat's Apparatus

- **FLUE GAS ANALYSIS:-**
- An idea about the complete or incomplete combustion of fuel is given by 'Flue Gas Analysis'. Thus
- If the flue gases contain considerable amount of carbon monoxide, it shows incomplete combustion means short supply of oxygen.

L-19 Analysis of flue gases by Orsat's Apparatus

- If the flue gases contain considerable amount of oxygen, it shows complete combustion means or excess supply of oxygen.
- The analysis of flue gases is carried by Orsat's Apparatus.

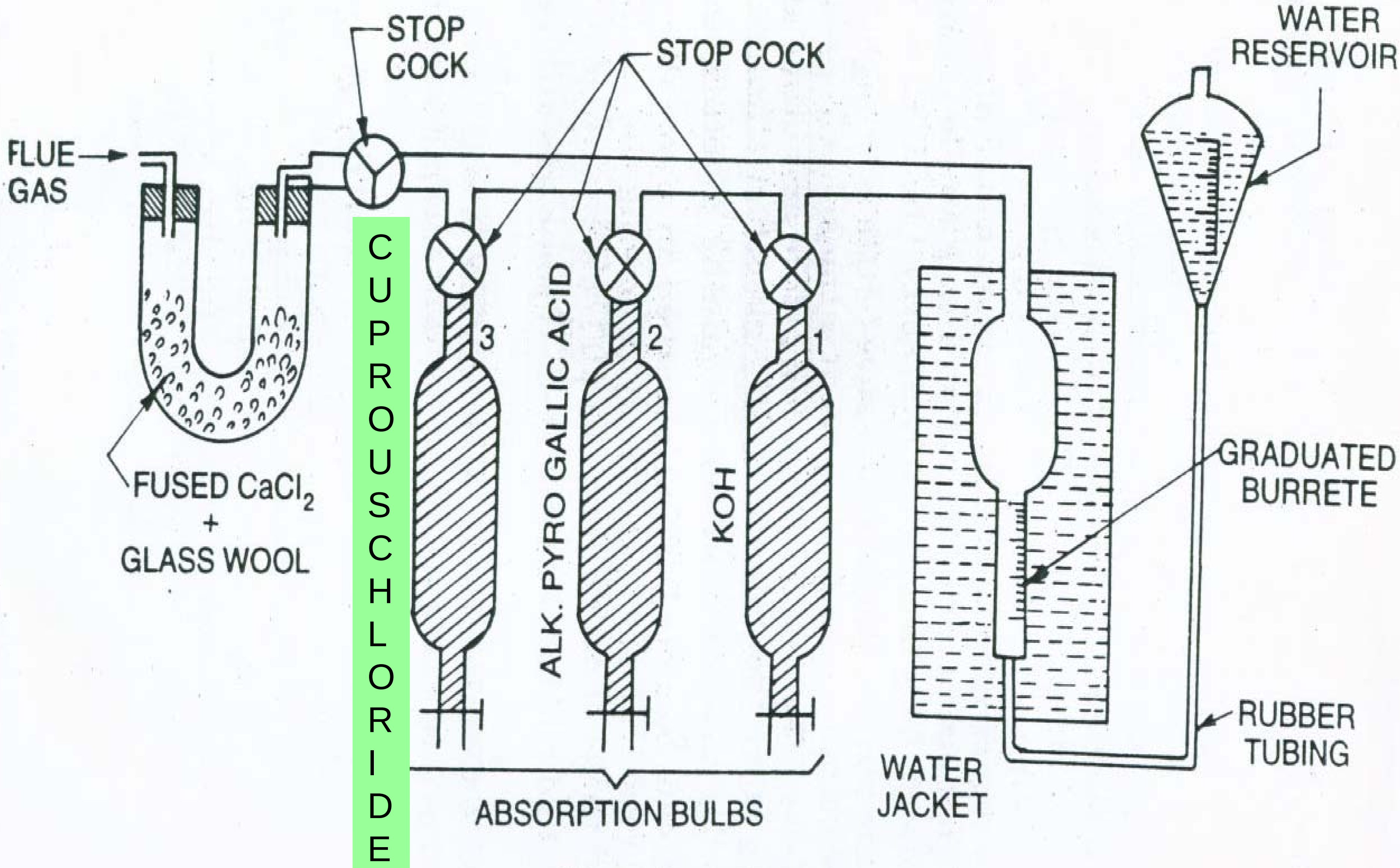


Fig. Orsats Apparatus

L-19 Analysis of flue gases by Orsat's Apparatus

CONSTRUCTION:-

- It consists of **horizontal tube** at the one end of this tube is **three way stop cock** and the other end is connected with **burette.**
- Burette is surrounded with a **water jacket** to keep the temperature constant of gas.

L-19 Analysis of flue gases by Orsat's Apparatus

- The lower end of the jacket burette is further connected to a water reservoir with the help of rubber tube.

- The water level in the burette can be raised or lowered by raising or lowering.

- The burette is connected in **series to a set of three absorption bulbs,** each through a separate stop cock.

L-19 Analysis of flue gases by Orsat's Apparatus

- The other end of horizontal tube is connected to a **U – tube.**
- U – tube is **packed with fused $CaCl_2$ and glass wool** for drying flue gas and avoiding for smoke particles.

L-19 Analysis of flue gases by Orsat's Apparatus

- Three absorption bulbs apart from having solution for absorbing CO_2, O_2 and CO.
- The first bulb **has KOH solution and it absorbs only CO_2.**
- The second bulb has **alkaline pyrogallic acid and it can absorb O_2 and CO_2.**

L-19 Analysis of flue gases by Orsat's Apparatus

- For proper analysis it is necessary that the flue gas is passed through first bulb having KOH, where CO_2 is absorbed.
- Then it is passed through second bulb having alkaline pyrogallic acid, where only O_2 will be absorbed.
- Finally flue gases are passed through third bulb having **$CuCl_2$ where only CO will be absorbed.**

L-19 Analysis of flue gases by Orsat's Apparatus

WORKING STEP – 1

- The whole apparatus is thoroughly cleaned.
- The absorption bulbs are filled with their respective solution and stop clock are closed.
- The water reservoir and jacket are filled with water.
- For the exclusion of air, the three way stop cock should be opened to the atmosphere.

L-19 Analysis of flue gases by Orsat's Apparatus

- Flue gas is analyzed by lowering the water reservoir and connecting the three way stop cock to flue gas supply.

- Air should be expelled by repeating the above process of sucking and expelling the flue gas by lowering and raising the water reservoir.

L-19 Analysis of flue gases by Orsat's Apparatus

STEP – 2

- 100 ml of flue gas is carefully sucked in the burette for analysis. The three way stop cock is closed then.
- The flue gas is forced in the bulb 1 by opening its stop cock and raising the water reservoir.

L-19 Analysis of flue gases by Orsat's Apparatus

- Bulb 1 have KOH which absorbs CO_2 for complete absorption of CO_2 the flue gas is sent 2 or 3 times, again and again in bulb 1.

L-19 Analysis of flue gases by Orsat's Apparatus

- **STEP – 3**
- The unabsorbed gas is finally taken back in the burette and then stop cock for CO_2 absorption bulb is closed.
- The levels of water in the reservoir and burette are equalized and the value of residual gas is noted.

L-19 Analysis of flue gases by Orsat's Apparatus

- The decrease in volume gives the volume of CO_2 in 100 ml of the flue gas sample.

- The volumes of O_2 and CO are similarly determined by passing the flue gas through absorption bulbs 2 and 3.

L-19 Analysis of flue gases by Orsat's Apparatus

L-12 Numericals based on calorific values

Solved Numerical No.–1 (sim11)

- Calculate the weight and volume of air required for the combustion of one Kg of carbon.
- Solution : - carbon undergoes combustion by this –

$$C + O_2 \longrightarrow CO_2$$

12 32

- Thus wt. of O_2 required for combustion of 12g. of carbon = 32 gm.

L-12 Numericals based on calorific values

$\because$ 12 Kg of carbon require = 32 Kg of O_2

$\therefore$. **1 Kg of carbon** will require $= \frac{32}{12} \times 1$

$= 2.667$ Kg of O_2

$\therefore$. **weight of air required = 2.667** $\times \frac{100}{23}$

= 11.59 Kg

- **Now since 32 gm of O_2 occupies 22.4 L at NTP**

L-12 Numericals based on calorific values

Now since 32 gm of O_2 occupies 22.4 L at NTP

$\therefore$ 1 gm of O_2 of oxygen occupies = $\frac{22.4}{32}$ L

$\therefore$ **2.667 × 1000 gm O_2 will occupy =**

$$\frac{22.4}{32} \times 2.667 \times 1000 = 1866.9 \text{ L}$$

L-12 Numericals based on calorific values

... Volume of air required

$$=1866.9 \times \frac{100}{21}$$

= 8890 Liters or 8.890 m^3

Ans. 1 Kg of carbon will require**= 11.59 Kg of Air and/ 8890 Liters or 8.890 m^3 of Air**

L-12 Numericals based on calorific values

- **Numerical No. – 2**
- **Calculate the volume of air required for complete combustion of five liters of CO, given percentage of oxygen in air = 21%**

- **Solution : - Combustion reaction**

$$CO + 0.5O_2 \longrightarrow CO_2$$

L-12 Numericals based on calorific values

- **Solution : -** Combustion reaction

  $CO + 0.5O_2 \qquad\qquad CO_2$

  Vol. of O_2 needed

  5 liter × 0.5 = 2.5 liter

- **Given**- 21 part of oxygen found in 100part of air

L-12 Numericals based on calorific values

- Solution : - $CO + 0.5O_2 \longrightarrow CO_2$

Vol. of O_2 needed for 5 L CO = 5× 0.5 = 2.5 L

Given- 21 part of oxygen found in 100part of air

for 1L of O_2 --Volume of air required = 100/21

so for 2.5 L of O_2 -- Volume of air required

100/21 x 2.5 =11.9 liter

L-12 Numericals based on calorific values

- Hence, weight of air actually supplied per m^3 of the gas

-

=2142.8L(1mol/22.4)x(28.97/mol)

= 2771 gm

SOLVED NUMERICALS-13

- Ex. 13. Calculate the mass of air needed for complete combustion of 5 kg of coal containing C = 80%, H = 15%; O = rest.
- Slution: **5 kg coal contains C = 4 kg; H = 0.75 kg; and O = (5- 4.75) = 0.25 kg.**
- C + O2 = CO2 12 part of C needs
  12 32 44 32 parts of O
- **so 4 kg C need 32/12 x 4 = 13.333 kg O**

SOLVED NUMERICALS-13

- $H2 + ½ O2 = H2O$ 2 parts of H need
- 2 16 18 16 part of O

so 0.75 kg H need 16/2 x 0.75 = 6.000kg O

Minimum O_2 required for combustion = Theoretical O_2 required – O_2 present in fuel.

soMin.O required = [13.333+ 6.000- 0.25] = ……….kg

when 23 kg O is found in 100kg air

then ……kg O will be found in $\frac{100 \text{ x….}}{23}$

Numericals based on calorific values-15

- **Numerical No. –1 3**
- A gaseous fuel has the following composition by volume H_2 = 20%, CH_4 = 5%, CO = 25%, CO_2 = 6%, O_2 = 5% and
- Rest of N_2 If 20% excess air is used- find
- the weight of air actually supplied per m^3 (molecular weight of air =28.97) of the fuel and
- composition of dry flue gases.

Numericals based on calorific values-15

Solution (i) : - In one m_3 of the gas

Composition (x/100)	Volume of O_2 needed
$H_2 + 0.5O_2 \longrightarrow$	H_2O
H_2 (20%) = 0.20 m^3	$0.2 \times 0.5 = 0.10\ m^3$
$CH_4 + 2O_2 \longrightarrow$	$CO_2 + H_2O$
CH_4 (5%) = 0.05 m^3	$0.05 \times 2 = 0.1\ m^3$
$CO + 0.5O_2 \longrightarrow$	CO_2
CO (25%) = 0.25 m^3	$0.25 \times 0.5 = 0.125\ m^3$

- Total O_2 req.(min) = 0.325 m^3

Numericals based on calorific values-13

- **Solution (i) : - In one m^3 of the gas**

Composition (x/100)	Vol. of O_2 needed	Vol. of dry gas(m^3)
$H_2 + 0.5O_2 \rightarrow H_2O$		
H_2 (20%) = 0.20 m^3	$0.2 \times 0.5 = 0.10$ m^3	
$CH_4 + 2O_2 \rightarrow CO_2 + H_2O$		
CH_4 (5%) = 0.05 m^3	$0.05 \times 2 = 0.1$ m^3	CO_2 = 0.05 x 1= 0.05
$CO + 0.5O_2 \rightarrow CO_2$		
CO (25%) = 0.25 m^3	$0.25 \times 0.5 = 0.125$ m^3	CO_2 = 0.25 x 1= 0.25
		CO_2 = 0.06, N_2 = 0.46 } from fuel
•	Total = 0.325 m^3	CO_2 = 0.36; N_2 = 0.46

Numericals based on calorific values-15

Sol: (ii) Volume of air required for 1 m^3 of gas using 20% excess air

$1\ m^3 = 1000\ L$

$0.325\ m^3\ (O_2) = 1000 \times 0.325 = 325\ L$

- **Volume of air** required for **1 m^3** of gas using **20%** excess air = **325 x 100/21 x 120/100**

= 1.857 m^3

Numericals based on calorific values-15

Sol: (iii) Calculation of dry products of combustion

$CO_2 = 0.36\ cm^3$ $\quad O_2 = 20\%$ of $0.325\ m^3$

$= (20/100) \times 0.325 = 0.065\ m^3$

$N_2 = 0.46\ m^3 + (77/100) \times 1.857\ m^3 = 1.927\ m^3$

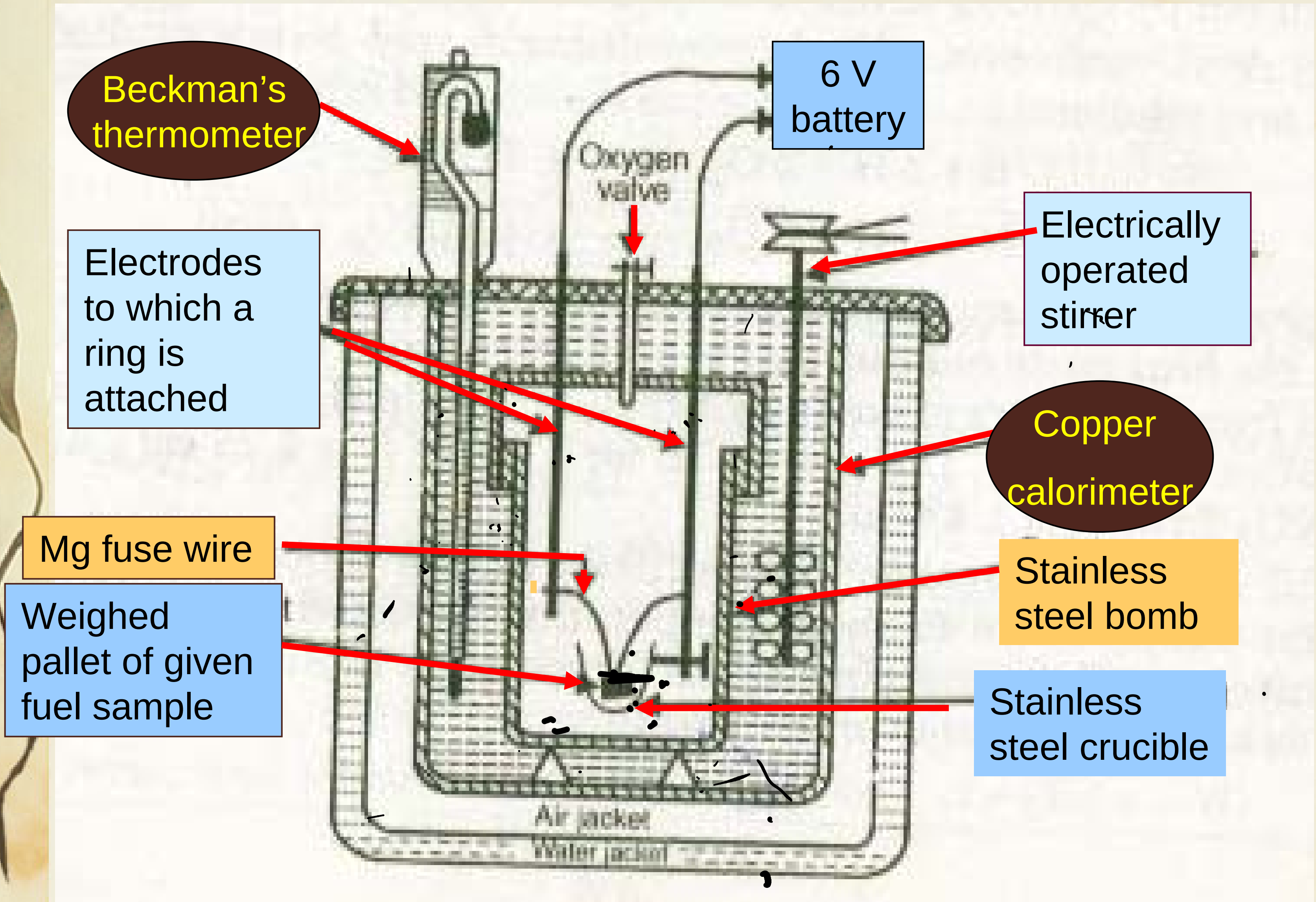
Total volume of dry products =

$(0.36 + 0.065 + 1.927) = 2.325\ m^3$

iv) Composition:

$CO_2 = \frac{0.36 \times 100}{2.325} = 15.306\%$; $\quad N_2 = \frac{1.927 \times 100}{2.325} = 81.93\%$

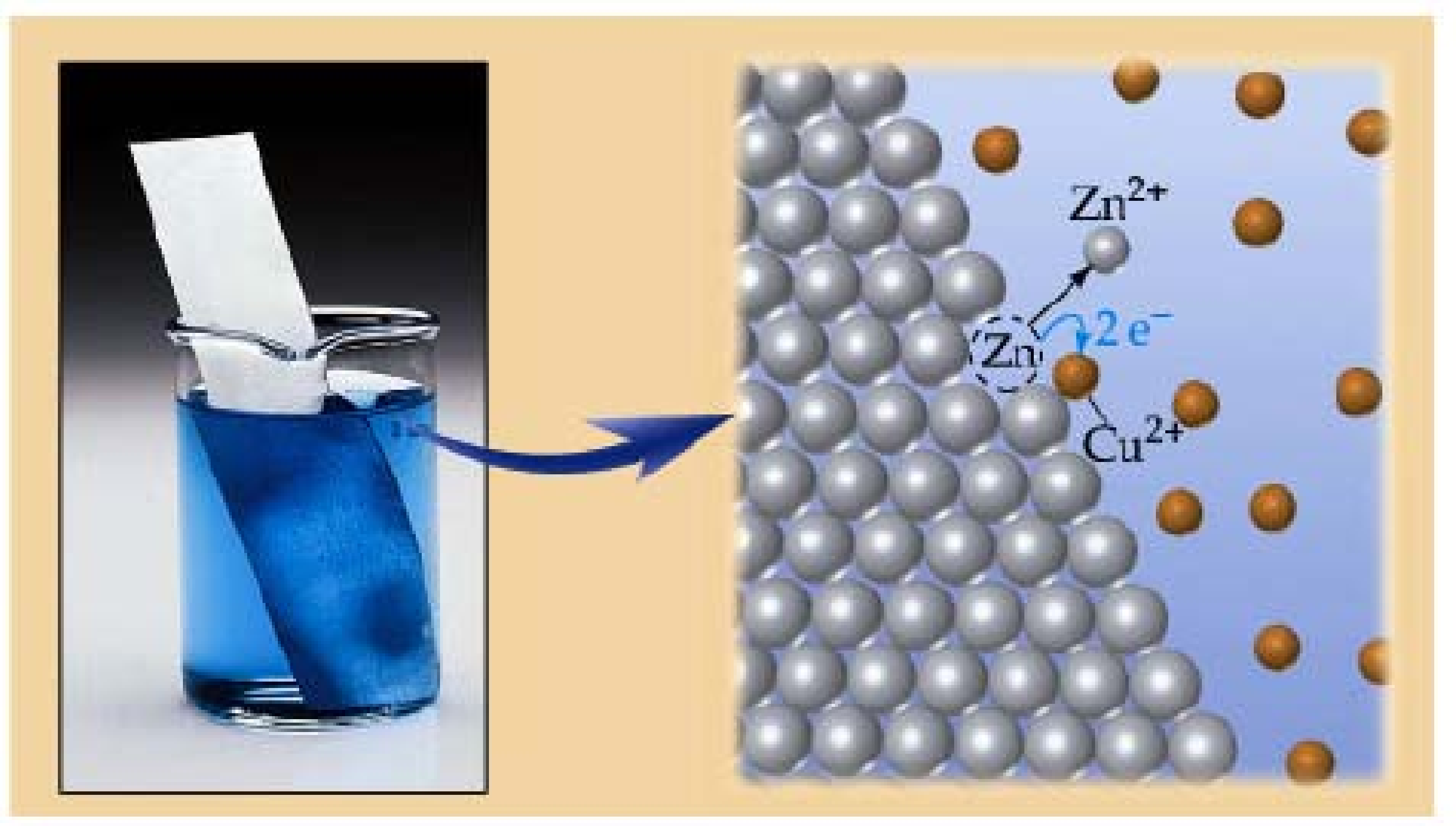
$O_2 = \frac{0.065 \times 100}{2.325} = 2.764\%$



BOMB CALORIMETER

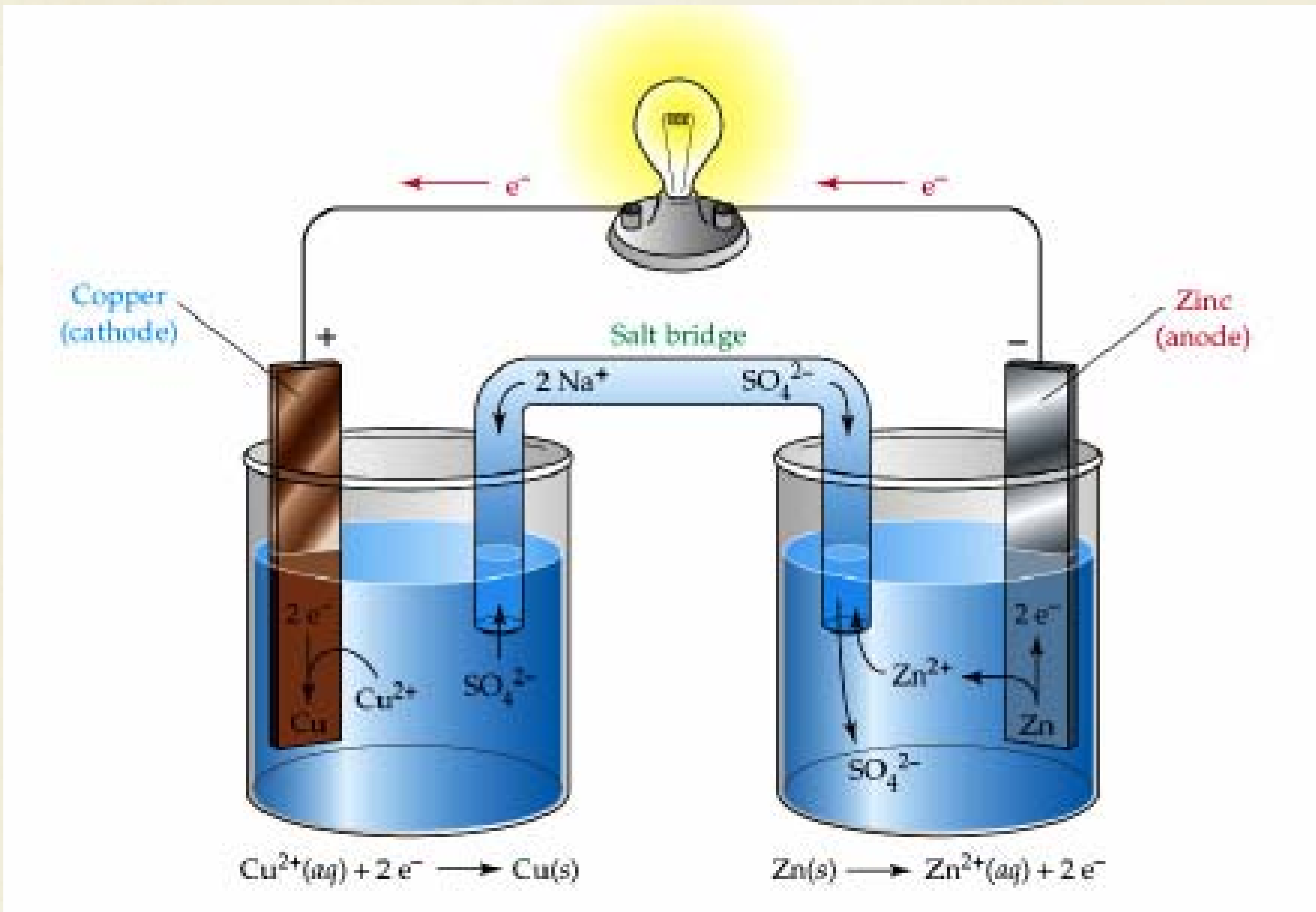
Redox Reactions

- **Oxidation Half-Reaction:** Zn(*s*) ® Zn2+(*aq*) + 2 e–.
- The Zn loses two electrons to form Zn2+.



Redox Reactions

Overall: Zn(*s*) + Cu2+(*aq*)® Zn2+(*aq*) + Cu(*s*)



SOLVED NUMERICALS

SOLVED NUMERICALS