

$$\text{H}_2\text{O} = \frac{3}{13.678} \times 100 = 21.93\%. \quad (\text{Ans.})$$

$$\text{N}_2 = \frac{8.678}{13.678} \times 100 = 63.45\%. \quad (\text{Ans.})$$

The total dry moles = 0.614 + 1.386 + 8.678 = 10.678

Hence dry analysis is :

$$\text{CO}_2 = \frac{0.614}{10.678} \times 100 = 5.75\%. \quad (\text{Ans.})$$

$$\text{CO} = \frac{1.386}{10.678} \times 100 = 12.98\%. \quad (\text{Ans.})$$

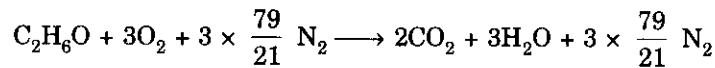
$$\text{N}_2 = \frac{8.678}{10.678} \times 100 = 81.27\%. \quad (\text{Ans.})$$

**Example 11.23.** For the stoichiometric mixture of example 11.22 calculate :

(i) The volume of the mixture per kg of fuel at a temperature of 50°C and a pressure of 1.013 bar.

(ii) The volume of the products of combustion per kg of fuel after cooling to a temperature of 130°C at a pressure of 1 bar.

**Solution.** As before,



$$\therefore \text{Total moles reactants} = 1 + 3 + 3 \times \frac{79}{21} = 15.3$$

From equation,  $pV = nR_0T$

$$V = \frac{nR_0T}{p} = \frac{15.3 \times 8.314 \times 10^3 \times (50 + 273)}{1.013 \times 10^5} = 405.6 \text{ m}^3/\text{mole of fuel}$$

In 1 mole of fuel there are  $(2 \times 12 + 6 + 16) = 46$  kg

$$(i) \therefore \text{Volume of reactants per kg of fuel} = \frac{405.6}{46} = 8.817 \text{ m}^3. \quad (\text{Ans.})$$

When the products are cooled to 130°C the H<sub>2</sub>O exists as steam, since the temperature is well above the saturation temperature corresponding to the partial pressure of the H<sub>2</sub>O. This must be so since the saturation temperature corresponding to the *total* pressure is 99.6°C, and the *saturation temperature decreases with pressure*. The total moles of the products is

$$= \left( 2 + 3 + 3 \times \frac{79}{21} \right) = 16.3$$

From equation,  $pV = nR_0T$

$$V = \frac{nR_0T}{p} = \frac{16.3 \times 8.314 \times 10^3 \times (130 + 273)}{1 \times 10^5} = 546.14 \text{ m}^3/\text{mole of fuel.}$$

$$(ii) \therefore \text{Volume of products per kg of fuel} = \frac{546.14}{46} = 11.87 \text{ m}^3. \quad (\text{Ans.})$$

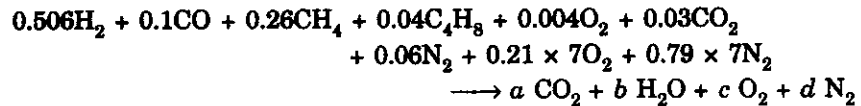
**Example 11.24.** The following is the composition of coal gas supplied to a gas engine :

H<sub>2</sub> = 50.6 per cent ; CO = 10 per cent ; CH<sub>4</sub> = 26 per cent ; C<sub>4</sub>H<sub>8</sub> = 4 per cent ; O<sub>2</sub> = 0.4 per cent ; CO<sub>2</sub> = 3 per cent ; N<sub>2</sub> = 6 per cent.

If the air-fuel ratio is 7/1 by volume, calculate the analysis of the dry products of combustion. It can be assumed that the stoichiometric A/F ratio is less than 7/1.

**Solution.** Since it is given that the actual A/F ratio is greater than the stoichiometric, therefore it follows that excess air has been supplied. The products will therefore consist of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$  and  $\text{N}_2$ .

The combustion equation can be written as follows :



Then,

$$\text{Carbon balance} : 0.1 + 0.26 + 4 \times 0.04 + 0.03 = a \quad \therefore a = 0.55$$

$$\text{Hydrogen balance} : 2 \times 0.506 + 4 \times 0.26 + 8 \times 0.04 = 2b \quad \therefore b = 1.186$$

$$\text{Oxygen balance} : 0.1 + 2 \times 0.004 + 2 \times 0.03 + 0.21 \times 7 \times 2 = 2a + b + 2c \quad \therefore c = 0.411$$

$$\text{Nitrogen balance} : 2 \times 0.06 + 2 \times 0.79 \times 7 = 2d \quad \therefore d = 5.59$$

$$\therefore \text{Total moles of dry products} = 0.55 + 0.411 + 5.59 = 6.65$$

Then analysis by volume is :

$$\text{CO}_2 = \frac{0.55}{6.65} \times 100 = 8.39\% \quad (\text{Ans.})$$

$$\text{O}_2 = \frac{0.411}{6.65} \times 100 = 6.27\% \quad (\text{Ans.})$$

$$\text{N}_2 = \frac{5.59}{6.65} \times 100 = 85.34\% \quad (\text{Ans.})$$

**Example 11.25.** The following is the analysis (by weight) of a chemical fuel :

Carbon = 60 per cent ; Hydrogen = 20 per cent ; Oxygen = 5 per cent ; Sulphur = 5 per cent and Nitrogen = 10 per cent.

Find the stoichiometric amount of air required for complete combustion of this fuel.

**Solution.** On the basis of 100 kg fuel let us assume an equivalent formula of the form :



From the given analysis by weight, we can write

$$12a = 60 \quad \text{or} \quad a = 5$$

$$1b = 20 \quad \text{or} \quad b = 20$$

$$16c = 5 \quad \text{or} \quad c = 0.3125$$

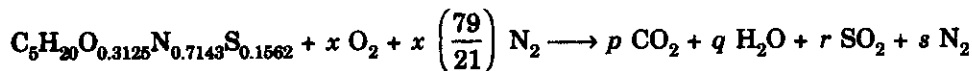
$$14d = 10 \quad \text{or} \quad d = 0.7143$$

$$32e = 5 \quad \text{or} \quad e = 0.1562$$

Then the formula of the fuel can be written as



The combustion equation is



Then,

$$\text{Carbon balance} : \quad \quad \quad 5 = p \quad \quad \quad \therefore p = 5$$

$$\text{Hydrogen balance} : \quad \quad \quad 20 = 2q \quad \quad \quad \therefore q = 10$$

$$\text{Sulphur balance} : \quad \quad \quad 0.1562 = r \quad \quad \quad \therefore r = 0.1562$$

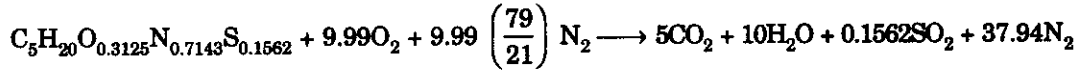
$$\text{Oxygen balance} : \quad \quad \quad 0.3125 + 2x = (2p + q + 2r)$$

i.e., 
$$x = p + \frac{q}{2} + r - \frac{0.3125}{2} = 5 + \frac{10}{2} + 0.1562 - \frac{0.3125}{2} = 9.99$$

**Nitrogen balance** :  $0.7143 + 2x \times \frac{79}{21} = 2s$

$$\therefore s = \frac{0.7143}{2} + x \times \frac{79}{21} = \frac{0.7143}{2} + 9.99 \times \frac{79}{21} = 37.94$$

Hence the combustion equation is written as follows :



$$\therefore \text{Stoichiometric air required} = \frac{9.92 \times 32 + 9.99 \times \left( \frac{79}{21} \right) \times 28}{100} = 13.7 \text{ kg/kg of fuel. (Ans.)}$$

(Note. This example can also be solved by tabular method as explained in example 11.20.).

**Example 11.26.** A sample of fuel has the following percentage composition by weight :

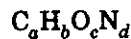
Carbon = 84 per cent	Hydrogen = 10 per cent
Oxygen = 3.5 per cent	Nitrogen = 1.5 per cent
Ash = 1 per cent	

(i) Determine the stoichiometric air-fuel ratio by mass.

(ii) If 20 per cent excess air is supplied, find the percentage composition of dry flue gases by volume.

**Solution.** (i) **Stoichiometric air fuel ratio :**

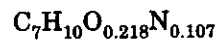
On the basis of 100 kg of fuel let us assume an equivalent formula of the form :



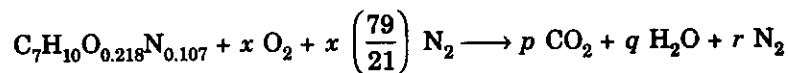
From the given analysis by weight, we can write

$12a = 84$	i.e.,	$a = 7$
$1b = 10$	i.e.,	$b = 10$
$16c = 3.5$	i.e.,	$c = 0.218$
$14d = 1.5$	i.e.,	$d = 0.107$

The formula of fuel is



The combustion equation is written as



Then,

**Carbon balance** :  $7 = p$  i.e.,  $p = 7$

**Hydrogen balance** :  $10 = 2q$  i.e.,  $q = 5$

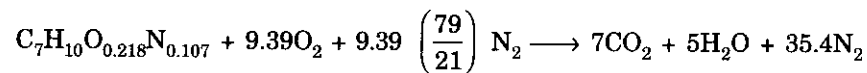
**Oxygen balance** :  $0.218 + 2x = (2p + q)$

or 
$$0.218 + 2x = 2 \times 7 + 5 \quad \text{i.e.,} \quad x = 9.39$$

**Nitrogen balance** :  $0.107 + 2x \left( \frac{79}{21} \right) = 2r$

or 
$$0.107 + 2 \times 9.39 \times \frac{79}{21} = 2r \quad \text{i.e.,} \quad r = 35.4$$

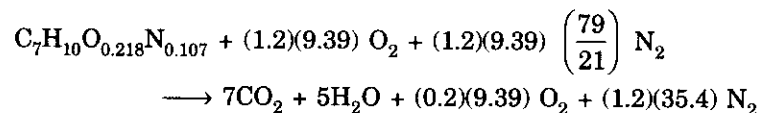
Hence the combustion equation becomes



$$\therefore \text{Stoichiometric A/F ratio} = \frac{9.39 \times 32 + 9.39 \times \frac{79}{21} \times 28}{100} = 12.89. \quad (\text{Ans.})$$

(ii) **Percentage composition of dry flue gases by volume with 20 per cent excess air :**

If 20 per cent excess air is used, the combustion equation becomes



Total number of moles of dry products of combustion

$$n = 7 + (0.2)(9.39) + (1.2)(35.4) \\ = 7 + 1.878 + 42.48 = 51.358$$

$\therefore$  **Percentage composition of dry flue gases by volume is as follows :**

$$CO_2 = \frac{7}{51.358} \times 100 = 13.63\%. \quad (\text{Ans.})$$

$$O_2 = \frac{1.878}{51.358} \times 100 = 3.66\%. \quad (\text{Ans.})$$

$$N_2 = \frac{42.48}{51.358} \times 100 = 82.71\%. \quad (\text{Ans.})$$

**Example 11.27.** Orsat analysis of the products of combustion of a hydrocarbon fuel of unknown composition is as follows :

Carbon dioxide ( $CO_2$ ) = 8%

Carbon monoxide (CO) = 0.5%

Oxygen ( $O_2$ ) = 6.3%

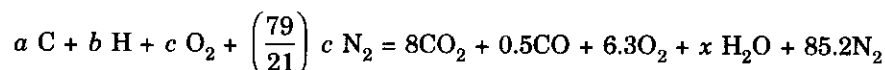
Nitrogen ( $N_2$ ) = 85.2%

Determine the following :

(i) Air-fuel ratio ;

(ii) Percent theoretical air required for combustion.

**Solution.** From the given Orsat analysis the combustion equation is written as follows :



Then,

**Carbon balance** :  $a = 8 + 0.5 = 8.5$      *i.e.*,  $a = 8.5$

**Nitrogen balance** :  $\frac{79}{21} C = 85.2$      *i.e.*,  $c = 22.65$

**Oxygen balance** :  $c = 8 + \frac{0.5}{2} + 6.3 + \frac{x}{2}$

or  $22.65 = 8 + 0.25 + 6.3 + \frac{x}{2}$      *i.e.*,  $x = 16.2$

**Hydrogen balance** :  $b = 2x = 2 \times 16.2 = 32.4$      *i.e.*,  $b = 32.4$

(i) **Air-fuel ratio :**

The air supplied per 100 moles of dry products is

$$= 22.65 \times 32 + \left(\frac{79}{21}\right) \times 22.65 \times 28 = 3110.6 \text{ kg}$$

$$\therefore \text{Air-fuel ratio} = \frac{3110.6}{8.5 \times 12 + 32.4 \times 1} = \mathbf{23.1 \text{ kg of air/kg of fuel. (Ans.)}$$

(ii) **Per cent theoretical air required for combustion :**

$$\text{Mass fraction of carbon} = \frac{12 \times 8.5}{12 \times 8.5 + 32.4 \times 1} = 0.759$$

$$\text{Mass fraction of hydrogen} = \frac{32.4 \times 1}{12 \times 8.5 + 32.4} = 0.241$$

Considering 1 kg of fuel, the *air required for complete combustion* is

$$= \left[0.759 \times \left(\frac{8}{3}\right) \times \frac{100}{23.3}\right] + \left[0.241 \times 8 \times \frac{100}{23.3}\right] = 16.96 \text{ kg}$$

$$\therefore \text{Per cent theoretical air required for combustion} = \frac{23.1}{16.96} \times 100 = \mathbf{136.2\% \text{ (Ans.)}}$$

**Example 11.28.** The following is the volumetric analysis of the dry exhaust from an internal combustion engine :

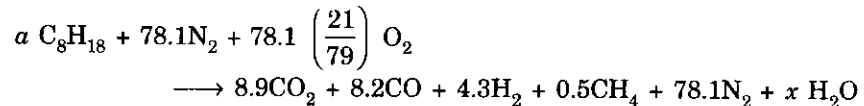
$CO_2 = 8.9\%$  ;  $CO = 8.2\%$  ;  $H_2 = 4.3\%$  ;  $CH_4 = 0.5\%$  and  $N_2 = 78.1\%$ .

If the fuel used is octane ( $C_8H_{18}$ ) determine air-fuel ratio on mass basis :

(i) By a carbon balance.

(ii) By a hydrogen-oxygen balance.

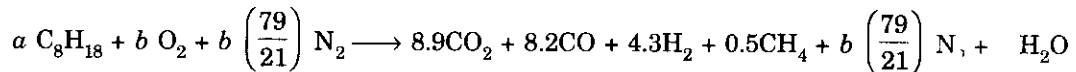
**Solution.** (i) As per analysis of dry products, the combustion equation is written as



**Carbon balance :**  $8a = 8.9 + 8.2 + 0.5 = 17.6$  i.e.,  $a = 2.2$

$$\begin{aligned} \therefore \text{Air-fuel (A/F) ratio} &= \frac{78.1 \times 28 + 78.1 \times \frac{21}{79} \times 32}{2.2(8 \times 12 + 1 \times 18)} \\ &= \frac{2186.8 + 664.3}{250.8} = \frac{2851.1}{250.8} = \mathbf{11.37 \text{ (Ans.)}} \end{aligned}$$

(ii) In this case the combustion equation is written as



**Carbon balance :**  $8a = 8.9 + 8.2 + 0.5 = 17.6$  i.e.,  $a = 2.2$

**Hydrogen balance :**  $18a = 4.3 \times 2 + 0.5 \times 4 + 2x$

$$\text{or } 18 \times 2.2 = 8.6 + 2 + 2x \quad \text{i.e., } x = 14.5$$

**Oxygen balance :**  $2b = 8.9 \times 2 + 8.2 + x$

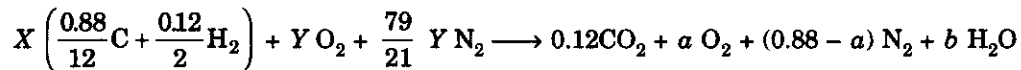
$$\text{or } 2b = 17.8 + 8.2 + 14.5 \text{ i.e., } b = 20.25$$

$$\therefore \text{Air-fuel (A/F) ratio} = \frac{(20.25 \times 32) + (20.25) \left(\frac{79}{21}\right) \times 28}{2.2(8 \times 12 + 1 \times 18)} = \frac{2781}{250.8} = \mathbf{11.09 \text{ (Ans.)}}$$

**Example 11.29.** The exhaust from an engine running on benzole was measured with the help of Orsat apparatus. Orsat analysis showed a  $\text{CO}_2$  content of 12%, but no CO. Assuming that the remainder of the exhaust contains only oxygen and nitrogen, calculate the air-fuel ratio of the engine.

The ultimate analysis of benzole is  $\text{C} = 88\%$  and  $\text{H}_2 = 12\%$ .

**Solution.** 1 kg of fuel, consisting of 0.88 kg C and 0.12 kg  $\text{H}_2$ , can be written as 0.88/2 moles C and 0.12/2 moles  $\text{H}_2$ . Therefore, considering 1 mole of dry exhaust gas (D.E.G.) we can write the combustion equation as follows :



[ Let the D.E.G. contain  $a$  moles of  $\text{O}_2$ . The moles of  $\text{CO}_2$  in 1 mole of D.E.G. are 0.12 ]  
 [ Therefore the D.E.G. contains  $(1 - a - 0.12) = (0.88 - a)$  moles of  $\text{N}_2$ . ]

where,  $X$  = Mass of fuel per mole D.E.G.,

$Y$  = Moles of  $\text{O}_2$  per mole D.E.G.,

$a$  = Moles of excess  $\text{O}_2$  per mole D.E.G., and

$b$  = Moles of  $\text{H}_2\text{O}$  per mole D.E.G.

Now,

$$\text{Carbon balance} : \frac{0.88}{12} X = 0.12 \quad \therefore X = 1.636$$

$$\text{Hydrogen balance} : 0.06X = b \quad \therefore b = 0.06 \times 1.636 = 0.098$$

$$\text{Oxygen balance} : 2Y = 2 \times 0.12 + 2a + b$$

$$\text{or} \quad 2Y = 0.24 + 2a + 0.098 \quad \therefore Y = 0.169 + a$$

$$\text{Nitrogen balance} : \frac{79}{21} Y = (0.88 - a) \quad \therefore Y = 0.234 - 0.266a$$

Equating the expressions for  $Y$  gives

$$0.234 - 0.266a = 0.169 + a \quad \therefore a = 0.0513$$

$$\text{i.e.,} \quad Y = 0.169 + 0.0513 = 0.2203$$

$$\therefore \text{O}_2 \text{ supplied} = 0.2203 \times 32 \text{ kg/mole D.E.G.}$$

$$\text{i.e.,} \quad \text{Air supplied} = \frac{0.2203 \times 32}{0.233} = 30.26 \text{ kg/mole D.E.G.}$$

Since  $X = 1.636$ , then, the fuel supplied per mole D.E.G. is 1.636 kg

$$\therefore \text{A/F ratio} = \frac{30.26}{1.636} = 18.5/1. \text{ (Ans.)}$$

**Example 11.30.** The analysis of the dry exhaust from an internal combustion engine is as follows :

Carbon dioxide ( $\text{CO}_2$ ) = 15 per cent

Carbon monoxide (CO) = 3 per cent

Methane ( $\text{CH}_4$ ) = 3 per cent

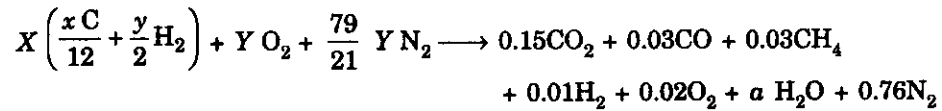
Hydrogen ( $\text{H}_2$ ) = 1 per cent

Oxygen ( $\text{O}_2$ ) = 2 per cent

Nitrogen ( $\text{N}_2$ ) = 76 per cent

Calculate the proportions by mass of carbon to hydrogen in the fuel, assuming it to be a pure hydrocarbon.

**Solution.** Let 1 kg of fuel contain  $x$  kg of carbon (C) and  $y$  kg hydrogen ( $\text{H}_2$ ). Then considering 1 mole of D.E.G. and introducing  $X$  and  $Y$ , we can write



Then,

**Nitrogen balance :**  $\frac{79}{21} Y = 0.76 \quad \therefore Y = 0.202$

**Oxygen balance :**  $Y = 0.15 + \frac{0.03}{2} + 0.02 + \frac{a}{2}$

or  $0.202 = 0.15 + 0.015 + 0.02 + \frac{a}{2} \quad \therefore a = 0.034$

**Carbon balance :**  $\frac{Xx}{12} = 0.15 + 0.03 + 0.03 \quad \therefore Xx = 2.52 \quad \dots(i)$

**Hydrogen balance :**  $\frac{Xy}{2} = 2 \times 0.03 + 0.01 + a = 0.06 + 0.01 + 0.034$

$\therefore Xy = 0.208 \quad \dots(ii)$

Dividing equations (i) and (ii), we get

$$\frac{Xx}{Xy} = \frac{2.52}{0.208} \quad \text{or} \quad \frac{x}{y} = 12.1$$

i.e., **Ratio of C to H<sub>2</sub> in fuel** =  $\frac{x}{y} = \frac{12.1}{1}$ . (Ans.)

**INTERNAL ENERGY AND ENTHALPY OF COMBUSTION**

**Example 11.31.**  $\Delta H_0$  (enthalpy of combustion at reference temperature  $T_0$ ) for benzene vapour ( $\text{C}_6\text{H}_6$ ) at  $25^\circ\text{C}$  is  $-3301000 \text{ kJ/mole}$  with the  $\text{H}_2\text{O}$  in the liquid phase. Calculate  $\Delta H_0$  for the  $\text{H}_2\text{O}$  in the vapour phase.

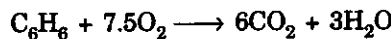
**Solution.** If  $\text{H}_2\text{O}$  remains as a vapour the heat transferred to the surroundings will be less than when the vapour condenses by the amount due to the change in enthalpy of the vapour during condensation at the reference temperature.

$$\Delta H_0 (\text{vapour}) = \Delta H_0 (\text{liquid}) + m_s h_{fg0}$$

where,  $m_s$  = Mass of  $\text{H}_2\text{O}$  formed, and

$$h_{fg0} = \text{Change in enthalpy of steam between saturated liquid and saturated vapour at the reference temperature } T_0 \\ = 2441.8 \text{ kJ at } 25^\circ\text{C}$$

For the reaction :



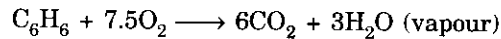
3 moles of  $\text{H}_2\text{O}$  are formed on combustion of 1 mole of  $\text{C}_6\text{H}_6$  ; 3 moles of  $\text{H}_2\text{O}$   
 $= 3 \times 18 = 54 \text{ kg H}_2\text{O}$

$\therefore \Delta H_0 (\text{vapour}) = -3301000 + 54 \times 2441.8 = -3169143 \text{ kJ/mole. (Ans.)}$

**Example 11.32.** Calculate  $\Delta U_0$  in  $\text{kJ/kg}$  for the combustion of benzene ( $\text{C}_6\text{H}_6$ ) vapour at  $25^\circ\text{C}$  given that  $\Delta H_0 = -3169100 \text{ kJ/mole}$  and the  $\text{H}_2\text{O}$  is in the vapour phase.

**Solution.** Given :  $\Delta H_0 = -3169100 \text{ kJ}$

The combustion equation is written as



$$n_R = 1 + 7.5 = 8.5, n_P = 6 + 3 = 9$$

Using the relation,

$$\begin{aligned}\Delta U_0 &= \Delta H_0 - (n_P - n_R)R_0T_0 \\ &= -3169100 - (9 - 8.5) \times 8.314 \times (25 + 273) \\ &= -3169100 - 1239 = -3170339 \text{ kJ/mole}\end{aligned}$$

(It may be noted that  $\Delta U_0$  is negligibly different from  $\Delta H_0$ )

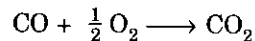
$$1 \text{ mole of } \text{C}_6\text{H}_6 = 6 \times 12 + 1 \times 6 = 78 \text{ kg}$$

$$\therefore \Delta U_0 = \frac{-3170339}{78} = -40645 \text{ kJ/kg. (Ans.)}$$

**Example 11.33.**  $\Delta H_0$  for CO at  $60^\circ\text{C}$  is given as  $-285200 \text{ kJ/mole}$ . Calculate  $\Delta H_0$  at  $2500^\circ\text{C}$  given that the enthalpies of gases concerned in kJ/mole are as follows :

Gas	$60^\circ\text{C}$	$2500^\circ\text{C}$
CO	9705	94080
O	9696	99790
CO <sub>2</sub>	10760	149100

**Solution.** The reaction equation is given by



Refer Fig. 11.7.

It can be seen from the property diagram of Fig. 11.7 that the enthalpy of combustion at temperature  $T$ ,  $\Delta H_T$  can be obtained from  $\Delta H_0$  and  $T_0$  by the relationship

$$-\Delta H_T = -\Delta H_0 + (H_{R_T} - H_{R_0}) - (H_{P_T} - H_{P_0}) \quad \dots(i)$$

where  $H_{R_T} - H_{R_0}$  = increase in enthalpy of the reactants from  $T_0$  to  $T$

and  $H_{P_T} - H_{P_0}$  = increase in enthalpy of the products from  $T_0$  to  $T$ .

Now, from the given data, we have

$$H_{R_0} = 1 \times 9705 + \frac{1}{2} \times 9696 = 14553 \text{ kJ}$$

$$H_{R_T} = 1 \times 94080 + \frac{1}{2} \times 99790 = 143975, \text{ kJ}$$

$$H_{P_0} = 1 \times 10760 = 10760 \text{ kJ}$$

$$H_{P_T} = 1 \times 149100 \text{ kJ} = 149100 \text{ kJ}$$

Using equation (i), we get

$$\begin{aligned}-\Delta H_T &= +285200 + (143975 - 14553) - (149100 - 10760) \\ &= 285200 + 129422 - 138340 = 276282\end{aligned}$$

$$\therefore \Delta H_T = -276282 \text{ kJ/mole. (Ans.)}$$

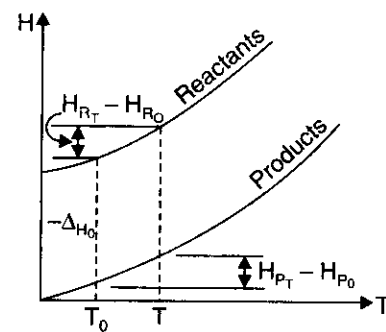


Fig. 11.7

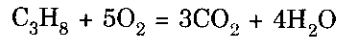


## HEATING VALUES OF FUELS

**Example 11.34.** The lower heating value of propane at constant pressure and 25°C is 2044009 kJ per kg mole. Find the higher heating value at constant pressure and at constant volume.

**Solution.** (i) **Higher heating value at constant pressure, (HHV)<sub>p</sub> :**

The combustion reaction for propane is written as



Now  $(\text{HHV})_p = (\text{LHV})_p + mh_{fg}$

where, HHV = Higher heating value at constant pressure,

LHV = Lower heating value,

$m$  = Mass of water formed by combustion

$$= 4 \times 18 = 72 \text{ kg per kg mole, and}$$

$h_{fg}$  = Latent heat of vaporisation at given temperature per unit mass of water  
= 2443 kJ/kg at 25°C.

$$\therefore (\text{HHV})_p = 2044009 + 72(2442) = \mathbf{2219833 \text{ kJ/kg. (Ans.)}}$$

(ii) **Higher heating value at constant volume, (HHV)<sub>v</sub> :**

Now  $(\Delta U) = \Delta H - \Delta nR_0T$

or  $-(\text{HHV})_v = -(\text{HHV})_p - \Delta nR_0T$

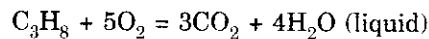
or  $(\text{HHV})_v = (\text{HHV})_p + \Delta nR_0T$

where  $R_0$  = universal gas constant = 8.3143 kJ/kg mol K

$$\Delta n = n_p - n_R$$

$$\left[ \begin{array}{l} n_p = \text{number of moles of gaseous products} \\ n_R = \text{number of moles of gaseous reactants} \end{array} \right]$$

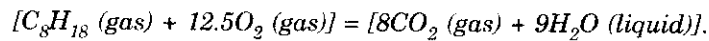
Now, the reaction for higher heating value is



$$\Delta n = 3 - (1 + 5) = -3$$

$$\therefore (\text{HHV})_v = 2219905 - 3(8.3143)(25 + 273) = \mathbf{2212472 \text{ kJ/kg. (Ans.)}}$$

**Example 11.35.** Calculate the lower heating value of gaseous octane at constant volume if  $(\Delta U)_{25^\circ\text{C}} = -5494977 \text{ kJ}$  for the reaction :



**Solution.** The given value of  $\Delta U$  corresponds to the higher heating value at constant volume because the water in the products is in liquid phase.

$$\text{HHV} = 5494977 \text{ kJ/kg}$$

$$(\text{LHV})_v = (\text{HHV})_v - m(u_g - u_f)$$

$$m = 9 \times 18 = 162 \text{ kg/kg mole C}_8\text{H}_{18}$$

$$(u_g - u_f) = 2305 \text{ kJ/kg at } 25^\circ\text{C}$$

$$\therefore (\text{LHV})_v = 5494977 - 162(2305) = \mathbf{5121567 \text{ kJ/kg. (Ans.)}}$$

**Example 11.36.** Calculate the lower and higher heating values at constant pressure per kg of mixture at 25°C, for the stoichiometric mixtures of :

(i) Air and benzene vapour ( $\text{C}_6\text{H}_6$ ), and

(ii) Air and octane vapour ( $\text{C}_8\text{H}_{18}$ ).

Given that the enthalpies of combustion at 25°C are :

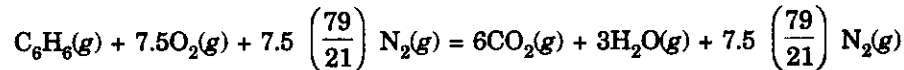
$$C_6H_6 = -3169500 \text{ kJ/mole}$$

$$C_8H_{18} = -5116200 \text{ kJ/mole}$$

Both the above figures are for the case where the water in the products is in the vapour phase.

**Solution. (i) Air and benzene vapour :**

For benzene, the combustion equation is as follows :



Since the water in the products is in *vapour phase*, therefore, the given value of enthalpy of combustion corresponds to the *lower heating value* at constant pressure.

i.e.,  $(LHV)_p = 3169500 \text{ kJ/mole}$

$$\begin{aligned} (LHV)_v \text{ per kg of mixture} &= \frac{3169500}{(12 \times 6 + 6 \times 1) + (7.5 \times 32) + 7.5 \left( \frac{79}{21} \right)} \quad (28) \\ &= \frac{3169500}{78 + 240 + 790} = \mathbf{2861 \text{ kJ/kg. (Ans.)}} \end{aligned}$$

Now,  $(HHV)_p = (LHV)_p + mh_{fg}$

where  $(HHV)_p$  = Higher heating value at constant pressure,

$(LHV)_p$  = Lower heating value at constant pressure,

$m$  = Mass of water formed by combustion.

$$= 3 \times 18 = 54 \text{ kg/kg mole of fuel, and}$$

$h_{fg}$  = Latent heat of vapourisation at given temperature per unit mass of water

$$= 2442 \text{ kJ/kg at } 25^\circ\text{C.}$$

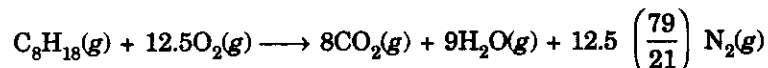
$$\therefore (HHV)_p = 3169500 + 54 \times 2442 = 3301368 \text{ kJ/mole}$$

$$\text{Thus, } (HHV)_p \text{ per kg of mixture} = \frac{3301368}{78 + 240 + 790} = \mathbf{2980 \text{ kJ/kg. (Ans.)}}$$

**(ii) Air and octane vapour :**

$$(LHV)_p = 5116200 \text{ kJ/mole of } C_8H_{18}$$

For octane, the combustion equation is written as follows :



$$\begin{aligned} (LHV)_p \text{ per kg of mixture} &= \frac{5116200}{(12 \times 8 + 18 \times 1) + 12.5 \times 32 + 12.5 \times \frac{79}{21} \times 28} \\ &= \frac{5116200}{114 + 400 + 1317} = \mathbf{2794 \text{ kJ/kg. (Ans.)}} \end{aligned}$$

$$(HHV)_p = (LHV)_p + mh_{fg}$$

$$m = 9 \times 18 = 162 \text{ kJ/kg mole of fuel}$$

$$\therefore (HHV)_p = 5116200 + 162 \times 2442 = 5511804$$

$$\text{Hence, } (HHV)_p \text{ per kg of mixture} = \frac{5511804}{114 + 400 + 1317} = \mathbf{3010 \text{ kJ/kg. (Ans.)}}$$

**Example 11.37.** The higher heating value of kerosene at constant volume whose ultimate analysis is 88% and 12% hydrogen, was found to be 45670 kJ/kg. Calculate the other three heating values.

**Solution.** Combustion of 1 kg of fuel produces the following products :

$$\text{CO}_2 = \frac{44}{12} \times 0.88 = 3.23 \text{ kg}$$

$$\text{H}_2\text{O} = \frac{18}{2} \times 0.12 = 1.08 \text{ kg}$$

At 25°C :  $(u_g - u_f)$  i.e.,  $u_{fg} = 2304 \text{ kJ/kg}$   
 $h_{fg} = 2442 \text{ kJ/kg}$

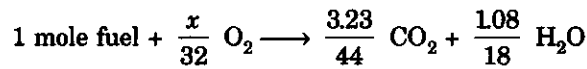
(i)  $(\text{LHV})_v$  :

$$\begin{aligned} (\text{LHV})_v &= (\text{HHV})_v - m(u_g - u_f) \\ &= 45670 - 1.08 \times 2304 = 43182 \text{ kJ/kg} \end{aligned}$$

Hence  $(\text{LHV})_v = 43182 \text{ kJ/kg. (Ans.)}$

(ii)  $(\text{HHV})_p$ ,  $(\text{LHV})_p$  :

The combustion equation is written as follows :



i.e.,  $\frac{x}{32} = \frac{3.23}{44} + \frac{1.08}{18 \times 2}$

or  $x = 3.31 \text{ kg}$

i.e.,  $1 \text{ kg fuel} + 3.31 \text{ kg O}_2 = 3.23\text{CO}_2 + 1.08\text{H}_2\text{O}$

Also,  $\Delta H = \Delta U + \Delta n R_0 T$

i.e.,  $-(\text{HHV})_p = -(\text{HHV})_v + \Delta n R_0 T$

or  $(\text{HHV})_p = (\text{HHV})_v - \Delta n R_0 T$

where  $\Delta n = n_p - n_R$

$$= \left( \frac{3.23}{44} - \frac{3.31}{32} \right) \left[ \begin{array}{l} n_p = \text{number of moles of gaseous products} \\ n_R = \text{number of moles of gaseous reactants} \end{array} \right]$$

Since in case of higher heating value,  $\text{H}_2\text{O}$  will appear in liquid phase

$$\begin{aligned} (\text{HHV})_p &= 45670 - \left( \frac{3.23}{44} - \frac{3.31}{32} \right) \times 8.3143 \times (25 + 273) \\ &= 45744 \text{ kJ/kg. (Ans.)} \end{aligned}$$

$$\begin{aligned} (\text{LHV})_p &= (\text{HHV})_p - 1.08 \times 2442 = 45744 - 1.08 \times 2442 \\ &= 43107 \text{ kJ/kg. (Ans.)} \end{aligned}$$

## HIGHLIGHTS

1. A chemical reaction may be defined as the rearrangement of atoms due to redistribution of electrons. 'Reactants' comprise of initial constituents which start the reaction while 'products' comprise of final constituents which are formed by the chemical reaction.
2. A chemical fuel is a substance which releases heat energy on combustion.
3. The total number of atoms of each element concerned in the combustion remains constant, but the atoms are rearranged into groups having different chemical properties.

4. The amount of excess air supplied varies with the type of the fuel and the firing conditions. It may approach a value of 100 per cent but modern practice is to use 25% to 50% excess air.
5. *Stoichiometric* (or chemically correct) *mixture* of air and fuel is one that contains just sufficient oxygen for complete combustion of the fuel.
6. Mixture strength =  $\frac{\text{Stoichiometric } A/F \text{ ratio}}{\text{Actual } A/F \text{ ratio}}$ .
7. When analysis of combustion products is known air fuel ratio can be calculated by the following methods :
  - (a) Fuel composition known
    - (i) Carbon balance method
    - (ii) Hydrogen balance method
    - (iii) Carbon hydrogen balance method
  - (b) Fuel composition unknown
    - (i) Carbon hydrogen balance method.
8. The most common means of analysis of the combustion products is Orsat apparatus.
9. The *enthalpy of formation* ( $\Delta H_f$ ) is the increase in enthalpy when a compound is formed from its constituent elements in their natural form and in a standard state. The standard state is 25°C and 1 atm. pressure (but it must be borne in mind that not all substances can exist in natural form, e.g. H<sub>2</sub>O cannot be a vapour at 1 atm. and 25°C).
10.
 
$$\begin{aligned} (\text{HHV})_p &= (\text{LHV})_p + m h_{fg} \\ (\text{HHV})_v &= (\text{LHV})_v + m(u_g - u_f) \end{aligned}$$
 where HHV = Higher heating value,  
 LHV = Lower heating value,  
 m = Mass of water formed by combustion,  
 h<sub>fg</sub> = Enthalpy of vapourisation of water, kJ/kg,  
 u<sub>g</sub> = Specific internal energy of vapour, kJ/kg, and  
 u<sub>f</sub> = Specific internal energy of liquid, kJ/kg.
11. In a given combustion process, that takes place adiabatically and with no work or changes in kinetic or potential energy involved, the temperature of the products is referred to as the '*adiabatic flame temperature*'.
12. For a given fuel and given pressure and temperature of the reactants, the maximum adiabatic flame temperature that can be achieved is with a '*stoichiometric*' mixture.

**OBJECTIVE TYPE QUESTIONS**
**Choose the Correct Answer :**

1. The smallest particle which can take part in a chemical change is called
  - (a) atom
  - (b) molecule
  - (c) electron
  - (d) compound.
2. A chemical fuel is a substance which releases ..... on combustion.
  - (a) chemical energy
  - (b) heat energy
  - (c) sound energy
  - (d) magnetic energy.
3. The most important solid fuel is
  - (a) wood
  - (b) charcoal
  - (c) coal
  - (d) all of the above.
4. For each mole of oxygen, number of moles of nitrogen required for complete combustion of carbon are
  - (a) 20/21
  - (b) 2/21
  - (c) 77/21
  - (d) 79/21.
5. Modern practice is to use ..... excess air.
  - (a) 5 to 10 per cent
  - (b) 15 to 20 per cent
  - (c) 20 to 25 per cent
  - (d) 25 to 50 per cent.

6. Stoichiometric air-fuel ratio by mass for combustion of petrol is  
(a) 5 (b) 10  
(c) 12 (d) 15.05.
7. An analysis which includes the steam in the exhaust is called  
(a) dry analysis (b) wet analysis  
(c) dry and wet analysis (d) none of the above.
8. The Orsat apparatus gives  
(a) volumetric analysis of the dry products of combustion  
(b) gravimetric analysis of the dry products of combustion  
(c) gravimetric analysis of products of combustion including  $H_2O$   
(d) volumetric analysis of products of combustion including  $H_2O$ .
9. In the Orsat apparatus KOH solution is used to absorb  
(a) carbon monoxide (b) carbon dioxide  
(c) oxygen (d) none of the above.
10. Enthalpy of formation is defined as enthalpy of compounds at  
(a)  $25^\circ C$  and 10 atmospheres (b)  $25^\circ C$  and 1 atmosphere  
(c)  $0^\circ C$  and 1 atmosphere (d)  $100^\circ C$  and 1 atmosphere.
11. Bomb calorimeter is used to find the calorific value of ..... fuels.  
(a) solid (b) gaseous  
(c) solid and gaseous (d) none of the above.
12. When the fuel is burned and the water appears in the vapour phase, the heating value of fuel is called  
(a) enthalpy of formation (b) lower heating value  
(c) higher heating value (d) none of the above.
13. Heat released in a reaction at constant pressure is called  
(a) entropy change (b) enthalpy of reaction  
(c) internal energy of reaction (d) none of the above  
(e) all of the above.
14. When the fuel is burned and water is released in the liquid phase, the heating value of fuel is called  
(a) higher heating value (b) lower heating value  
(c) enthalpy of formation (d) none of the above.
15. Choose the *correct* statement :  
(a) Number of atoms of each constituent are not conserved in a chemical reaction.  
(b) The mass of all the substances on one side of the equation may not be equal to the mass of all the substances on the other side.  
(c) The number of atoms of each constituent are conserved in a chemical reaction.  
(d) The number of moles of the reactants in a chemical equation are equal to the number of moles of the products.

### ANSWERS

- |          |        |         |         |         |         |         |
|----------|--------|---------|---------|---------|---------|---------|
| 1. (a)   | 2. (b) | 3. (c)  | 4. (d)  | 5. (d)  | 6. (d)  | 7. (b)  |
| 8. (a)   | 9. (b) | 10. (b) | 11. (a) | 12. (b) | 13. (b) | 14. (a) |
| 15. (c). |        |         |         |         |         |         |

### THEORETICAL QUESTIONS

1. What is chemical thermodynamics ?
2. What is a chemical fuel ?
3. What are primary fuels ? List some important primary fuels.

4. What are secondary fuels? List some important secondary fuels.
5. Write a short note on 'excess air'.
6. What do you mean by stoichiometric air-fuel (A/F) ratio?
7. Enumerate the methods by which air fuel ratio can be calculated when analysis of combustion products is known.
8. How is analysis of exhaust and flue gas carried out?
9. Derive relations for internal energy and enthalpy of reaction.
10. What is enthalpy of formation ( $\Delta H_f$ ) = ?
11. Define heating value of fuel.
12. What is the difference between higher heating value (HHV) and lower heating value (LHV) of the fuel?
13. Describe with the help of neat sketches the following calorimeters used for the determination of heating values :
  - (i) Bomb calorimeter
  - (ii) Junkers gas calorimeter.
14. What is 'adiabatic flame temperature'?
15. Write a short note on chemical equilibrium.

**UNSOLVED EXAMPLES**

1. A fuel has the following composition by weight : Carbon = 86% ; hydrogen = 11.75% and oxygen = 2.25%. Calculate the theoretical air supply per kg of fuel, and the weight of products of combustion per kg of fuel.  
 [(Ans.) 13.98 kg ; 4.21 kg]
2. The volumetric analysis of a fuel gas is :  $\text{CO}_2 = 14\%$  ;  $\text{CO} = 1\%$  ;  $\text{O}_2 = 5\%$  and  $\text{N}_2 = 80\%$ . Calculate the fuel gas composition by weight.  
 [(Ans.) 20.24% ; 0.93% ; 5.25% ; 73.58%]
3. The ultimate analysis of a dry coal burnt in a boiler gauge C = 84% ;  $\text{H}_2 = 9\%$  and incombustibles 7% by weight. Determine the weight of dry flue gases per kg of coal burnt, if volumetric combustion of the flue gas is :  
 $\text{CO}_2 = 8.75\%$  ,  $\text{CO} = 2.25\%$  ;  $\text{O}_2 = 80\%$  and  $\text{N}_2 = 81\%$ .  
 [(Ans.) 18.92 kg]
4. During a trial in a boiler, the dry flue gas analysis by volume was obtained as  $\text{CO}_2 = 13\%$  ,  $\text{CO} = 0.3\%$  ,  $\text{O}_2 = 6\%$  ,  $\text{N}_2 = 80.7\%$ . The coal analysis by weight was reported as C = 62.4% ,  $\text{H}_2 = 4.2\%$  ,  $\text{O}_2 = 4.5\%$  , moisture = 15% and ash 13.9%. Estimate :
  - (a) Theoretical air required to burn 1 kg of coal.
  - (b) Weight of air actually supplied per kg of coal.
  - (c) The amount of excess air supplied per kg of coal burnt.  
 [Ans. 8.5 kg ; 11.5 kg ; 3 kg]
5. A steam boiler uses pulverised coal in the furnace. The ultimate analysis of coal (by weight) as received is : C = 78% ;  $\text{H}_2 = 3\%$  ;  $\text{O}_2 = 3\%$  ; ash 10% and moisture 5%. Excess air supplied is 30%. Calculate the weight of air to be supplied and weight of gaseous product formed per kg of coal burnt.  
 [Ans. 13 kg ;  $\text{CO}_2 = 2.86$  kg ;  $\text{H}_2 = 0.27$  kg ; excess  $\text{O}_2 = 0.69$  kg and  $\text{N}_2 = 9.81$  kg per kg of coal]
6. The percentage composition by mass of a crude oil is given as follows : C = 90% ;  $\text{H}_2 = 3.3\%$  ;  $\text{O}_2 = 3\%$  ,  $\text{N}_2 = 0.8\%$  ; S = 0.9% and remaining incombustible. If 50% excess air is supplied find the percentage of dry exhaust gases found by volume.  
 [Ans.  $\text{CO}_2 = 12.7\%$  ;  $\text{SO}_2 = 0.05\%$  ;  $\text{O}_2 = 7\%$  ,  $\text{N}_2 = 80.25\%$ ]
7. In a boiler trial, the analysis of the coal used is as follows : C = 20% ,  $\text{H}_2 = 4.5\%$  ,  $\text{O}_2 = 7.5\%$  , remainder— incombustible matter.  
 The dry flue gas has the following composition by volume :  
 $\text{CO}_2 = 8.5\%$  ,  $\text{CO} = 1.2\%$  ,  $\text{N}_2 = 80.3\%$  ,  $\text{O}_2 = 10\%$ . Determine :
  - (i) Minimum weight of air required per kg of coal.
  - (ii) Percentage excess air.  
 [Ans. (i) 3.56 kg, (ii) 63.2%]
8. The ultimate analysis of a sample of petrol by weight is : Carbon 0.835 ; hydrogen 0.165. Calculate the ratio of air to petrol consumption by weight, if the volumetric analysis of the dry exhaust gas is : Carbon dioxide 12.1 ; Carbon monoxide 1.1 ; Oxygen 0.8 ; Nitrogen 85.4 per cent. Also find the percentage excess air.  
 [Ans. 16.265 : 1 ; 5.6%]



