



ENERGY BALANCES

Energy is the capacity/ability of a body to do work.

FORMS OF ENERGY

Forms of energy can be classified as :

Forms of energy related to the system : These include energy possessed by material of the system \Rightarrow energy, potential energy, flow/pressure energy, internal energy, surface energy and magnetic energy.

Forms of energy associated with the process : These include energy produced or transferred by the process \Rightarrow heat and work.

Kinetic energy : It is the energy which a substance/body possesses by virtue of its motion relative to some reference plane.

Potential energy : It is the energy that a substance possesses by virtue of its position in relation to some datum.

The sum of the kinetic energy and potential energy of a body is called the mechanical energy of the body.

Flow/pressure energy : It is the energy which a substance possesses by virtue of the space it occupies. It is the product of pressure and volume and is associated with flowing streams under pressure.

Internal energy : It is the energy which a substance possesses by virtue of the relative positions and motion of molecules.

Heat : It is the energy in transit between a hot source and a cold receiver. Heat is that form of energy which is transferred from one body to another as a result of a difference in temperature.

The driving force that produces a transfer of internal energy is termed as temperature and a form of energy which is transferred from a hot body to a cold body as a result of a difference in temperature is termed as heat.

Work : In mechanics, work done by a force is defined as the product of the force and the distance moved in the direction of the applied force. It is that form of energy which flows as a result of a driving force – a force, a torque or voltage. For example, if steam in a cylinder expands and moves a piston against a restraining force, the steam does work on the piston.

The exchange of energy between a system and its surroundings occurs either as heat or work (these forms of energy are dependent on the process).

Heat is considered to be positive when it is transferred from the surroundings to the system (Heat added to the system is taken as positive) and work done by the system is considered to be positive. Work has the units of joule (J), erg (dyne.cm) or foot.poundal (lbf.ft).

Industrially, thermal or electrical energy (indirectly) is produced by the combustion of a solid, liquid or gaseous fuel. One has to be very cautious during the production and utilisation of energy as its wastage leads to reduced profits. The energy requirement of a process can be calculated by making energy balances over the entire process (process units) in much the same way as we write material balances. An energy balance of a system accounts for the total amount of energy entering, leaving and accumulated within the system.

Heat is a form of energy that flows from a higher temperature to a lower temperature. The units of heat in the MKS, and CGS systems are joule (J), kilocalorie (kcal) and calorie (cal).

1 calorie (thermochemical) = 4.184 J

1 calorie (International steam tables) = 4.1868 J

Calorie is defined as the quantity of heat required to raise the temperature of one gram of water by 1°C in the vicinity of 15°C .

In this book, the terms 'energy', 'enthalpy' and 'heat' are used for thermal energy.

(0.1)

6.2 LAW OF CONSERVATION OF ENERGY

The basis of energy balances of a particular process is the **law of conservation of energy**. It states that energy can neither be created nor destroyed during a process although it can be converted from one form to another or the total energy of an isolated system remains constant. This law is also called as the **first law of thermodynamics**. According to this law, the total amount of energy entering any system must be exactly equal to that leaving plus any accumulation within the system or when a system gains or loses energy, it must be exactly equal to the loss from or gain of energy by the surroundings.

6.3 FLOW PROCESS

A process in which streams of materials continually enter and/or leave the system.

6.4 NON-FLOW/BATCH PROCESS

A process which is intermittent in character and wherein no material streams enter or leave continually during the course of operation.

While doing a general energy balance of a flow or continuous process, it is convenient to use a unit time of operation as a basis, e.g., one hour. In case of a non-flow or batch process, the convenient basis is one cycle of operation.

6.5 GENERAL ENERGY BALANCE PROCEDURE

- (1) Assume a suitable basis of calculations.
- (2) Draw a block diagram of the process and label the streams.
- (3) Determine the quantity or flow rates of all stream components with the help of material balances.
- (4) Determine the enthalpies of each stream component entering and leaving the process.
- (5) If a chemical reaction is involved (wherein heat is evolved or absorbed), it must be included in the energy balance equation.
- (6) If the heat capacity data are provided for the components involved, choose a reference temperature on which they are based for the convenience of calculations.

6.6 ENERGY BALANCES FOR CLOSED SYSTEMS

A system is said to be open when a mass crosses the system boundary and said to be closed when no mass crosses the system boundary during the period of time-covered by energy balance. Thus, a batch process is a closed system and a semibatch or continuous process is an open system.

Energy balance equation for the closed system is :

$$\left[\begin{array}{c} \text{Final system} \\ \text{energy} \end{array} \right] - \left[\begin{array}{c} \text{Initial system} \\ \text{energy} \end{array} \right] = \left[\begin{array}{c} \text{Net energy transferred} \\ \text{to the system} \end{array} \right] \quad \dots (6.1)$$

where,

$$\text{Energy transferred} = Q + W$$

$$\text{Initial system energy} = U_1 + E_{k1} + E_{p1}$$

$$\text{Final system energy} = U_2 + E_{k2} + E_{p2}$$

where the subscripts 1 and 2 refer to the initial and final states of the system and U , E_k , E_p , W and Q represent the internal energy, kinetic energy, potential energy, work done on the system by its surroundings and heat transferred to the system from its surroundings. Equation (6.1) becomes :

$$(U_2 - U_1) + (E_{k2} - E_{k1}) + (E_{p2} - E_{p1}) = Q + W \quad \dots (6.2)$$

$$\Delta U + \Delta E_k + \Delta E_p = Q + W \quad \dots (6.3)$$

The symbol Δ represents final condition minus initial condition.

6.7 ENERGY BALANCES FOR OPEN SYSTEMS

The steady-state open system energy balance - energy balance equation for the open system is :
Input energy = Output energy

Input energy is the total rate of transport of the kinetic, potential and internal energies by all process streams plus the rate at which energy is transferred as heat and work and output is the total rate of energy transport by all output streams.

$$Q + W + \sum E_1 = \sum E_2 \quad \dots (6.4)$$

Subscript 1 refers to the initial conditions and 2 refers to the final conditions.

$$W = W_s + W_f \quad \dots (6.5)$$

where,

W_s = shaft work and W_f = flow work

$$E_1 = U_1 + E_{K_1} + E_{P_1} \quad \dots (6.6)$$

$$E_2 = U_2 + E_{K_2} + E_{P_2} \quad \dots (6.7)$$

If V is the volumetric flow rate per unit mass and P is the pressure of the system, then

$$W_f = \sum P_1 V_1 - \sum P_2 V_2 \quad \dots (6.8)$$

W_f is P times V of all input streams minus P times V of all output streams.

Combining Equations (6.4) to (6.8), we get

$$\sum (U_2 + E_{K_2} + E_{P_2}) - \sum (U_1 + E_{K_1} + E_{P_1}) = Q + W_s + \sum (P_1 V_1 - P_2 V_2) \quad \dots (6.9)$$

$$\sum (U_2 + P_2 V_2) - \sum (U_1 + P_1 V_1) + \sum (E_{K_2} - E_{K_1}) + \sum (E_{P_2} - E_{P_1}) = Q + W_s \quad \dots (6.10)$$

A property that occurs in an energy balance equation is the enthalpy (H) and is defined as :

$$H = U + PV \quad \dots (6.11)$$

Combining Equations (6.10) and (6.11), we get

$$\sum H_2 - \sum H_1 + \sum (E_{K_2} - E_{K_1}) + \sum (E_{P_2} - E_{P_1}) = Q + W_s \quad \dots (6.12)$$

In industrial chemical processes, the kinetic energy, potential energy and work terms are negligible or cancel out and thus, heat added is equal to the increase in the enthalpy. Equation (6.12) thus reduces to

$$\sum H_2 - \sum H_1 = Q \quad \dots (6.13)$$

For the mass m or mass flow rate \dot{m} , Equation (6.13) becomes

$$Q = \sum \dot{m} H_2 - \sum \dot{m} H_1 \quad \dots (6.14)$$

$$Q = \sum m H_2 - \sum m H_1 \quad \dots (6.15)$$

Equation (6.14) or (6.15) is the heat balance equation which is a simplified form of the energy balance of all thermal processes.

6.8 SENSIBLE HEAT AND HEAT CAPACITIES

Sensible heat is the heat that must be transferred to raise or lower the temperature of a substance or mixture of substances.

The heat added or removed from a system to increase or decrease the temperature of the system. It is given by

$$Q = m C_p \Delta T$$

If m is a mass of substance then Q is a sensible heat in kJ.

$$Q' = m' C_p \Delta T$$

where m' is the mass flow rate of substance in kg/s and Q' is the heat transferred in kJ/s.

Heat Capacity :

It is the amount of heat required to increase the temperature of a substance by 1 K or 1 °C. Heat capacity is generally expressed on a unit mass or unit mole basis. When it is expressed on the unit mole basis, it is termed molal/molar heat capacity. It is denoted by the symbol 'C'. It has the units of kJ/(kmol·K). For pure water, the capacity on a mass basis is 4.1855 kJ/(kg·K) at 288 K (15°C).

The specific heat of a substance is the amount of heat required to raise the temperature of a unit mass (1 kg) of the substance by 1 °C or 1 K.

The heat capacity of a unit mass of a substance is known as the specific heat of the substance.

The heat capacity of a substance is expressed mathematically as :

$$C = \frac{dQ}{dT}$$

Heat capacity is of two types :

(i) Heat capacity at constant volume :

$$C_v = \frac{dQ}{dT}$$

$$\therefore dQ = C_v \cdot dT$$

Under constant volume, $dQ = dU$

$$\therefore dU = dQ = C_v \cdot dT$$

where, C_v - molal heat capacity at constant volume.

(ii) Heat capacity at constant pressure :

$$C_p = \frac{dQ}{dT}$$

$$\therefore dQ = C_p \cdot dT$$

$$\therefore dQ = dU + P \cdot dV$$

where C_p represents the molal heat capacity at constant pressure.

6.9 RELATIONSHIP BETWEEN C_p AND C_v FOR AN IDEAL GAS

The ideal gas equation for $n = 1$ mole is

$$PV = RT$$

$$dQ = C_p dT$$

$$\therefore dQ = dU + P dV$$

$$\therefore C_p = \left(\frac{\partial U}{\partial T} \right)_p + P \cdot \left(\frac{\partial V}{\partial T} \right)_p$$

$$C_v = \frac{dU}{dT} \text{ at constant volume}$$

$$\therefore C_v = \left(\frac{\partial U}{\partial T} \right)_v$$

For an ideal gas, internal energy is independent of volume or pressure.

$$\therefore \left(\frac{\partial U}{\partial T} \right)_p = \left(\frac{\partial U}{\partial T} \right)_v$$

Equation (6.24) becomes $C_p = C_v + P \left(\frac{\partial V}{\partial T} \right)_p$

The ideal gas equation for $n = 1$ is

$$PV = RT$$

Partial differentiation of the above equation with respect to T at constant P yields

$$P \left(\frac{\partial V}{\partial T} \right)_P = R$$

... (6.28)

Combining Equations (6.27) and (6.28), we get

$$C_p = C_v + R$$

... (6.29)

$$C_p - C_v = R$$

... (6.30)

6.10 HEAT CAPACITY OF GASES AT CONSTANT PRESSURE

The heat capacity at constant pressure is given by the equation :

$$dQ = C_p \cdot dT$$

... (6.31)

Integrating the above equation between two temperatures T_1 and T_2 , we get

$$Q = \int_{T_1}^{T_2} C_p \cdot dT$$

... (6.32)

6.11 EMPIRICAL EQUATION FOR HEAT CAPACITIES

Heat capacities are function of temperature and are frequently expressed in a polynomial form over a temperature range of 298 K to 1500 K.

For ideal gases, C_p at 101.325 kPa is denoted by the symbol C_p° and may be given by :

$$C_p^\circ = a + bT + cT^2 + dT^3$$

... (6.33)

where T is in kelvin (K), and a, b, c and d are constants. The values of these constants for the components under consideration are given in Appendix - II.

Equation (6.32) becomes :

$$Q = \int_{T_1}^{T_2} (a + bT + cT^2 + dT^3) dT$$

... (6.34)

$$\text{For 'n' moles: } Q = n \int_{T_1}^{T_2} (a + bT + cT^2 + dT^3) dT$$

... (6.35)

$$= n \left[a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) + \frac{d}{4}(T_2^4 - T_1^4) \right]$$

... (6.36)

6.12 MEAN MOLAL HEAT CAPACITIES OF GASES

To calculate the heat change during heating or cooling a gas between two temperatures with the help of Equation (6.36) is a lengthy procedure. To avoid this, it is convenient to use mean molal heat capacity data. Assume any arbitrary base temperature T_o (in K) and if T and T_o are the two temperatures between which a heat change is

desired, then C_{pm}° (mean molal heat capacity) is given as

$$C_{pm}^\circ = \frac{\int_{T_o}^T C_p^\circ dT}{(T - T_o)}$$

... (6.37)

... (6.38)

$$C_p^\circ = a + bT + cT^2 + dT^3$$

and

$$\therefore C_{pm}^{\circ} = \frac{a(T - T_0) + \frac{b}{2}(T^2 - T_0^2) + \frac{c}{3}(T^3 - T_0^3) + \frac{d}{4}(T^4 - T_0^4)}{(T - T_0)}$$

$$\text{or } C_{pm}^{\circ} = a + \left(\frac{b}{2}\right)(T + T_0) + \left(\frac{c}{3}\right)(T^2 + TT_0 + T_0^2) + \left(\frac{d}{4}\right)(T + T_0)(T^2 + T_0^2) \quad \dots (6.39)$$

In most cases, T_0 is selected as 298 K (25°C).

The heat change between two temperatures, T_1 and T_2 with the help of C_{pm}° data is calculated as follows:

Let $T_2 < T_1$.

Let C_{pm1}° and C_{pm2}° be the mean molal heat capacity of a gas between T_2 and T_0 and T_1 and T_0 . Let Q_1 be the heat change between T_1 and T_0 and Q_2 be the heat change between T_2 and T_0 . then net heat change for 'n' kmol of the gas is given as:

$$Q = Q_2 - Q_1$$

$$Q = n \left[C_{pm2}^{\circ} (T_2 - T_0) - C_{pm1}^{\circ} (T_1 - T_0) \right] \quad \dots (6.40)$$

If n in kmol, T in K, C_{pm}° in kJ/(kmol·K), then Q will be in kJ.

6.13 HEAT CAPACITIES OF GASEOUS MIXTURES

In case of heating or cooling a gas mixture of known composition, the heat change calculations may be simplified by calculating the heat capacity for the mixture by using in the following equation:

$$C_{p \text{ mix}}^{\circ} = \sum_{i=1}^n x_i C_{pi}^{\circ} \quad \dots (6.41)$$

x_i is the mass or mole fraction of i^{th} component in the gas mixture.

C_{pi}° and $C_{p \text{ mix}}^{\circ}$ are the heat capacities of i^{th} component and the mixture, respectively.

If C_{pi}° and $C_{p \text{ mix}}^{\circ}$ are expressed in the molar units then x_i be the mole fraction of i^{th} component.

The heat change for 'n' moles of the gas mixture is given by

$$Q = n \int_{T_1}^{T_2} C_{p \text{ mix}}^{\circ} (T) dT \quad \dots (6.42)$$

If mean molal heat capacity data of the components of a gas mixture are provided, then the mean molal heat capacity of the gas mixture is given by

$$C_{pm}^{\circ} (\text{mix}) = \sum_{i=1}^n x_i C_{pm i}^{\circ} \quad \dots (6.43)$$

where x_i is the mole fraction of i^{th} component in the gas mixture.

$C_{pm i}^{\circ}$ and $C_{pm}^{\circ} (\text{mix})$ be the mean molal heat capacity of i^{th} component and the gas mixture respectively.

The heat change between T_2 and T_1 for 'n' kmol of the gas mixture is calculated as follows:

$$Q = \Delta H = n \left[C_{pm}^{\circ} (\text{mix})_2 (T_2 - T_0) - C_{pm}^{\circ} (\text{mix})_1 (T_1 - T_0) \right] \quad \dots (6.44)$$

where $C_{pm}^{\circ} (\text{mix})_2$ and $C_{pm}^{\circ} (\text{mix})_1$ are the mean molal heat capacities of the gas mixture between T_2 and T_0 and T_1 and T_0 respectively.

In case of liquids, the sensible heat change may be given as follows :

$$dQ = mC dT$$

... (6.45)

where C is the heat capacity of liquid in $\text{kJ}/(\text{kg}\cdot\text{K})$, m is the mass of liquid in kg or mass flow rate of liquid in kg/h .
The heat change between temperatures T_1 and T_2 is given by

$$Q = \Delta H = m \int_{T_2}^{T_1} C \cdot dT$$

... (6.46)

where T is in K .

Molar heat capacity data for liquids is given in Appendix - III.

The calculation of enthalpy changes for heating or cooling of a mixture of known composition may be simplified by calculating the heat capacity for the mixture in the following manner :

$$C_{\text{mix}} = \sum x_i C_i$$

... (6.47)

where

x_i - the weight fraction of i^{th} component in liquid mixture.

C_i - heat capacity of i^{th} component.

C_{mix} - heat capacity of the liquid mixture

$$Q = m \int_{T_1}^{T_2} C_{\text{mix}}(T) dT$$

... (6.48)

14 ENTHALPY CHANGES ACCOMPANYING CHEMICAL REACTIONS

Whenever a chemical reaction takes place, heat may either be evolved or absorbed and this evolved or absorbed heat of reaction plays a major/vital role in the economics of a chemical process. When the enthalpy change associated with a reaction is positive, then heat must be added to keep the reaction temperature from dropping and if the enthalpy change is negative, then heat must be removed from the reaction zone/system to keep the reaction temperature from shooting.

Heat of Reaction (ΔH_R) :

It is the enthalpy change resulting due to a chemical reaction wherein

- (1) the reactants are fed in the stoichiometric amounts and the reaction proceeds to completion.
- (2) the reactants are fed at temperature T and pressure P , and the products emerge at the same temperature and pressure.

Chemical reactions can be carried out at different conditions of temperature and pressure. They are associated with the enthalpy changes. Since it is not possible to tabulate the enthalpy changes at all possible conditions of temperature and pressure, it is necessary to standardise the chemical reactions. For this purpose, the following standard states (of chemical species) at a given temperature T are widely accepted.

Gas : pure component gas in the ideal gas state at 0.1 MPa.

Liquid : pure liquid at 0.1 MPa.

Solid : pure solid in the most stable form at 0.1 MPa.

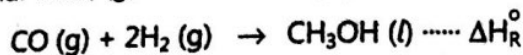
The enthalpy change associated with a chemical reaction wherein all the reactants and products are in their respective standard states is called the standard enthalpy change or standard heat of reaction. It is denoted by the symbol ΔH_{RT}^0 , where the superscript zero denotes that all the reactants and products are in their standard states and the subscript T denotes the temperature at which the reaction is carried out.

For tabulating heats of formation and heats of combustion data, the following standard states are commonly chosen.

Gas : pure component at 298 K and 0.1 MPa, Liquid : pure liquid at 298 K and 0.1 MPa and Solid : pure crystalline solid at 298 K and 0.1 MPa.

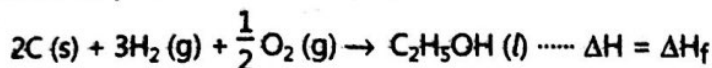
The **standard heat of reaction** is the enthalpy change associated with a chemical reaction when both the reactants and products are in their standard states, i.e., pure at a temperature of 298.15 K (25°C) and a pressure of 0.1 MPa. It is denoted by the symbol ΔH_R° and expressed in kJ/mol or J/mol. If the heat of reaction is positive (i.e., heat is absorbed), the reaction is said to be **endothermic** at temperature T and if heat of reaction is negative (i.e., heat is evolved), the reaction is said to be **exothermic** at temperature T.

The value of heat of reaction depends on the state of aggregation (gas, liquid or solid) of the reactants and products. The state of aggregation of a reaction component is indicated by a letter in the parenthesis following its chemical formula. Thus, (g) indicates the gaseous state, (l) indicates the liquid state and (s) the solid. For example,



Heat of Formation (ΔH_f) :

It is the enthalpy change accompanying the formation of one mole of a compound from its element at a given temperature and pressure. For example,



Standard Heat of Formation (ΔH_f°) :

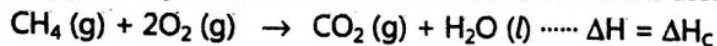
It is the heat of reaction when one mole of a compound is formed from its elements in a reaction beginning and ending at 298.15 K (25°C) and at pressure of 0.1 MPa (i.e., when all species of the chemical reaction are in their standard states). It is denoted by the symbol ΔH_f° . The superscript 'o' indicates the standard state - T = 298.15 K (25°C) and P = 0.1 MPa. The heat of formation of every element in its standard state is arbitrarily taken to be zero.

A compound is said to be exothermic when its heat of formation is negative and a compound is said to be endothermic when its heat of formation is positive.

Data of standard heat of formation for various components are given in Appendix - V.

Heat of Combustion (ΔH_c) :

It is the heat of reaction of one mole substance with molecular oxygen. The combustion reaction proceeds with a reduction in enthalpy of a system, hence heats of combustion are assigned negative signs. For example,



The standard heat of combustion of a substance (ΔH_c°) is the heat of reaction of the substance with molecular oxygen to yield specified products with both reactants and products are in their standard states, i.e., pure at 298.15 K (25°C) and 0.1 MPa.

Data of standard heats of combustion are listed in Appendix - VI.

The values of standard heats of combustion given in Appendix - VI are based on the assumptions that :

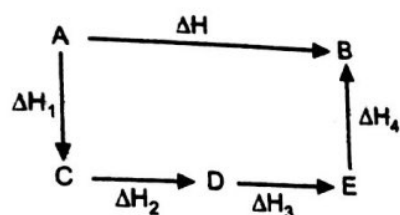
- (1) All carbon (of the substance under consideration) is converted to CO_2 (g).
- (2) All hydrogen to liquid water, H_2O (l).
- (3) All S to SO_2 (g) and
- (4) All nitrogen to N_2 (g).

6.15 HESS'S LAW OF CONSTANT HEAT SUMMATION

It states that the enthalpy change (i.e., heat evolved or absorbed) in a particular reaction is the same whether the reaction takes place in one or in several steps (i.e., in a series of steps). The total change in enthalpy depends on the pressure, temperature and state of aggregation and is independent of the number of intermediate reactions.

According to this law, the heats of reactions can be added or subtracted algebraically (i.e., this law permits us to treat all stoichiometric equations as algebraic equations). While applying this law, stoichiometric equations are treated as algebraic equations and the stoichiometric equation of a desired reaction can be obtained by algebraic operations (multiplication by constants, addition and subtraction) on the stoichiometric equations of a series of other reactions. To obtain the heat of desired reaction, the same algebraic operations are performed on the heats of reactions.

Using this law, we can calculate the heat of formation of a compound from a series of reactions that do not involve a direct formation of the compound from its elements.
For example,

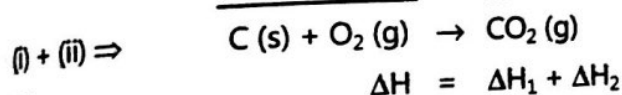
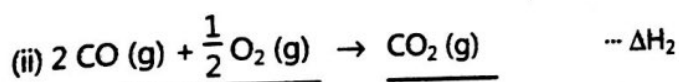
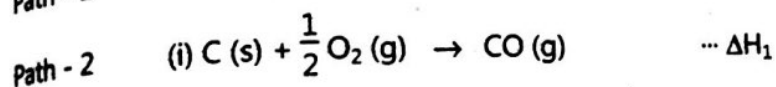
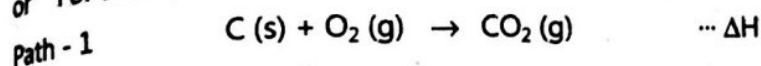


Path - 1 : A → B
Path - 2 : A → C
C → D
D → E
E → B

According to Hess's law,

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 \quad \dots (6.49)$$

or For example, carbon can be converted into CO_2 in two ways :



Thus,

With the help of this principle, it is possible to calculate the heats of formation of hydrocarbons as it is practically impossible to measure the same.

6.16 STANDARD HEAT OF REACTION FROM HEATS OF FORMATION

The standard heat of reaction may be calculated if the standard heats of formation of all components involved in the reaction are known.

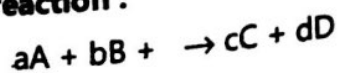
The standard heat of reaction is the difference between the algebraic sum of the standard heats of formation of the products and that of the reactants.

The standard heat of reaction is equal to the algebraic sum of the standard heats of formation of the products minus the algebraic sum of the standard heats of formation of the reactants.

... (6.50)

$$\Delta H_R^\circ = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants}) \quad \dots (6.51)$$

Consider the reaction :



where a, b, c and d are the stoichiometric coefficients of A, B, C and D. Let $\Delta H_f^\circ_A$, $\Delta H_f^\circ_B$, $\Delta H_f^\circ_C$ and $\Delta H_f^\circ_D$ be the standard heats of formation of components A, B, C and D respectively.

The standard heat of reaction is given by

$$\Delta H_R^\circ = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants}) \quad \dots (6.52)$$

$$\Delta H_R^\circ = (d \Delta H_f^\circ_D + c \Delta H_f^\circ_C) - (a \Delta H_f^\circ_A + b \Delta H_f^\circ_B)$$

When an element enters into a reaction, its heat of formation is zero if its state of aggregation is the one which is selected as the basis for heats of formation of its compounds.

When ΔH_R° is negative, the reaction is said to be exothermic, i.e., heat will be evolved during the course of the reaction. When ΔH_R° is positive, the reaction is said to be endothermic, i.e. it absorbs heat during the course of the reaction.

i. *The Steady-State Flow Process*

The application of Eqs. (2-4) and (2-5) is restricted to nonflow (constant mass) processes in which only internal-energy changes occur. Far more important industrially are processes which involve the steady-state flow of a fluid through equipment. For such processes the more general first-law expression [Eq. (2-3)] must be used. However, it may be put in more convenient form. The term *steady state* implies that conditions at all points in the apparatus are constant with time. For this to be the case, all rates must be constant, and there must be no accumulation of material or energy within the apparatus over the period of time considered. Moreover, the total mass flow rate must be the same at all points along the path of flow of the fluid.

Consider the general case of a steady-state flow process as represented in Fig. 2-2. A fluid, either liquid or gas, flows through the apparatus from section 1 to section 2. At section 1, the entrance to the apparatus, conditions in the fluid are designated by the subscript 1. At this point the fluid has an elevation above an arbitrary datum level of z_1 , an average velocity u_1 , a specific volume V_1 , a pressure P_1 , an internal energy U_1 , etc. Similarly, the conditions in the fluid at section 2, the exit of the apparatus, are designated by the subscript 2.

The system will be taken as a unit mass of the fluid flowing, and we will consider the overall changes which occur in this unit mass of fluid as it flows through

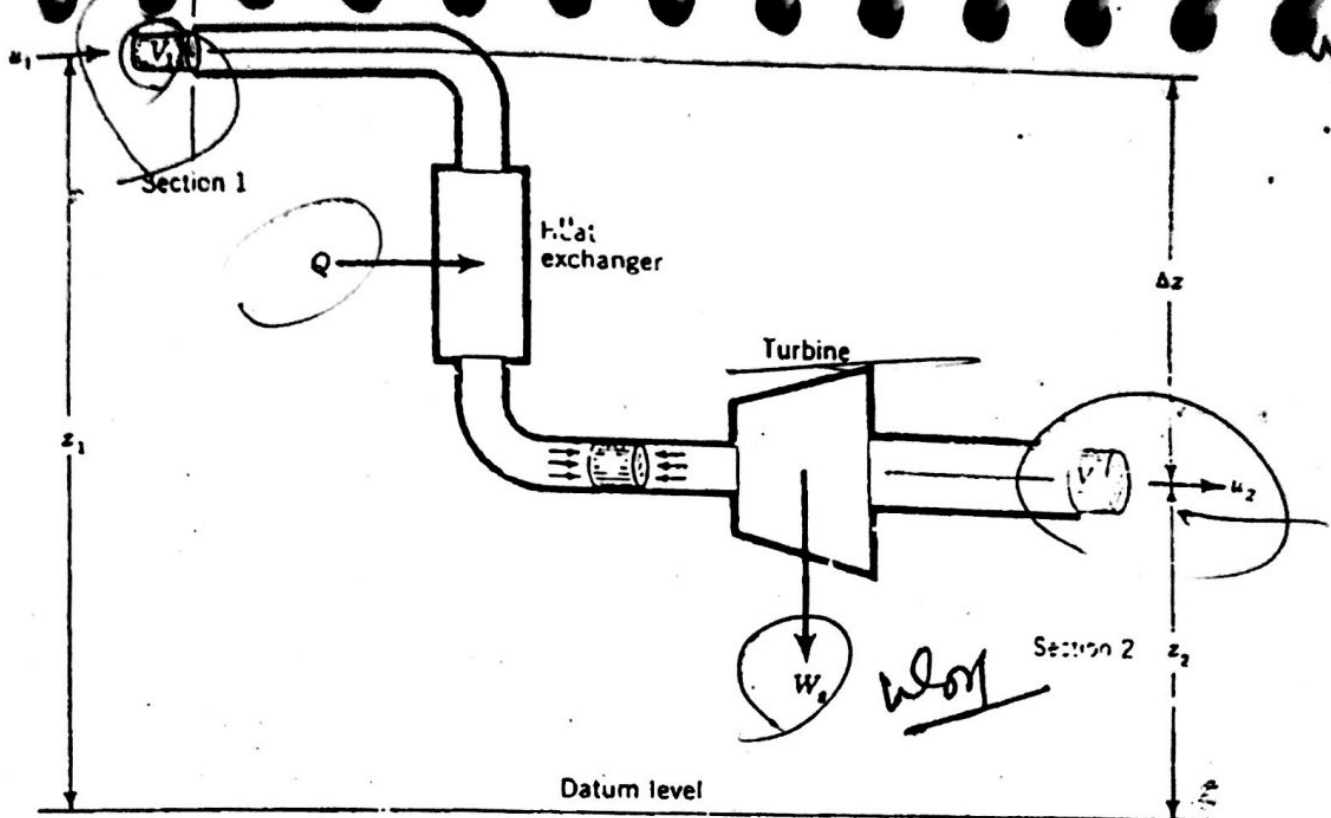


Fig. 2-2 Steady-state flow process.

the apparatus from section 1 to section 2. The energy of the unit mass may change in all three of the forms taken into account by Eq. (2-3), that is, potential, kinetic, and internal. By the definition of kinetic energy [Eq. (1-7)], its change between sections 1 and 2 is

$$\Delta E_k = \Delta \frac{mu^2}{2g_c} = \frac{\Delta u^2}{2g_c} = \frac{u_2^2 - u_1^2}{2g_c}$$

In this equation u represents the average velocity of the flowing fluid, defined as the volumetric flow rate divided by cross-sectional area. The development of the expression $u^2/2g_c$ for kinetic energy in terms of the average velocity is considered in detail in Chap. 10. Potential energy is defined by Eq. (1-9), and therefore its change is

$$\Delta E_p = \Delta \frac{mzg}{g_c} = \frac{g}{g_c} \Delta z = \frac{g}{g_c} (z_2 - z_1) = 2 \frac{h}{g_c} g$$

Note that m is the mass of the system and that it has been taken as unity. With these substitutions, Eq. (2-3) becomes

$$\Delta U + \frac{\Delta u^2}{2g_c} + \frac{g}{g_c} \Delta z = Q - W \quad (2-9)$$

where Q and W represent all the heat added and work extracted per unit mass of fluid flowing through the apparatus.

COMBUSTION

8.1 FUEL AND TYPES OF FUELS

- **Fuel** : A material such as coal, LPG, CNG, gasoline etc. is burned to produce heat or power.
- In the process industry, the fuel burnt in furnaces may be a solid, liquid or gas. The furnace is an enclosed space in which heat is produced by the chemical oxidation of a fuel. Fuels are of three main types. They are :
 1. **Solid fuels** : Principally coal which is a mixture of carbon, hydrogen, non-combustible ash, water and sulphur, coke, wood, bagasse, charcoal, etc.
 2. **Liquid fuels** : Principally hydrocarbons obtained by distillation of a crude oil (petroleum), such as kerosene, petrol, diesel, methanol, biodiesel, etc.
 3. **Gaseous fuels** : Principally natural gas which usually contains 80 to 95% methane, the balance being ethane, propane and small quantities of other gases, light hydrocarbons, acetylene, LPG, biogas, hydrogen etc.

8.2 CALORIFIC VALUES OF FUELS (NCV AND GCV)

- The calorific value of a fuel also known as the heating value of the fuel is the negative of the standard heat of combustion, usually expressed per unit mass of the fuel. Since the standard heat of combustion is *always* negative, the calorific value (heating value) is positive. The calorific value of a fuel is defined as the *total heat produced when a unit mass of fuel is completely burnt with pure oxygen*.
- When a fuel is burnt, the hydrogen in the fuel reacts with oxygen to produce water. When water is present in the flue gases as vapour, the latent heat of vaporisation is lost (heat associated with water vapour) and hence this quantity of heat is not available for any useful purpose.
- The net calorific value (net heating value or low heating value) of a fuel is the calorific value of the fuel when the water in the combustion products is present in the vapour form i.e., it is $-\Delta H_c^\circ$ with H_2O (g or v) as one of the combustion products.
- The latent heat of vaporisation of water can be made available for useful purpose if water vapours are condensed. The gross-calorific value (higher heating value or gross heating value) of a fuel is the calorific value of the fuel when the water in the combustion products is present in the liquid form i.e. it is equal to the net calorific value of the fuel to which the latent heat of water vapours (latent heat of condensation of water vapour) is added. The gross calorific value is abbreviated as GCV, higher heating value as HHV, lower heating value as LHV, net calorific value as NCV and net heating value as NHV.
- The NCV and GCV of the fuels are usually reported at 298 K (25°C). These may be expressed in kJ/kg of fuel, kJ/mol of fuel or kJ/m³ of gaseous fuel.
- To calculate the net calorific value of a fuel from the gross calorific value of the fuel or vice-versa, we must calculate the moles of water produced when a unit mass of the fuel is burned.

Let n be the mol of water produced. Then,

$$GCV = NCV + n \Delta H_v [H_2O, 298 \text{ K } (25^\circ\text{C})] \text{ kJ/mol of fuel} \quad (8.1)$$

... (8.1)

SOLVED EXAMPLES

Example 8.1 : Crude oil is analysed to contain 87% carbon, 12.5% hydrogen and 0.5% sulphur (by weight). Calculate the net calorific value of the crude oil at 298 K (25 °C).

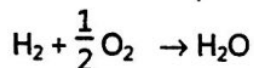
Data : Gross calorific value of crude oil at 298 K (25°C) is 45071 kJ/kg oil.

Latent heat of water vapour at 298 K (25°C) = 2442.5 kJ/kg.

Solution : Basis : 1 kg of crude oil.

It contains 0.87 kg carbon and 0.125 kg hydrogen.

Hydrogen burnt = Hydrogen in crude oil = 0.125 kg



1 kmol $\text{H}_2 \equiv$ 1 kmol H_2O

2 kg of $\text{H}_2 \equiv$ 18 kg of H_2O

Water produced = $\frac{18}{2} \times 0.125 = 1.125$ kg

Latent heat of water vapour at 298 K (25°C) = $1.125 \times \frac{2442.5}{1} = 2747.8$ kJ

Net calorific value = Gross calorific value – Latent heat of water vapours
= $45071 - 2747.8 = 42323.2$ kJ/kg oil

... Ans.

NCV of the crude oil is given by

$$\begin{aligned} \text{NCV} &= \text{GCV} - \frac{\% \text{ hydrogen by wt} \times 9 \times \lambda}{100} = 45071 - \frac{12.5 \times 9 \times 2442.5}{100} \\ &= 42323.2 \text{ kJ/kg of oil} \end{aligned}$$

... Ans.

Example 8.4 : The GHV (gross heating value) of gaseous n-butane is 2877.40 kJ/mol at 298 K (25 °C). Calculate its NHV (net heating value) in kJ/mol and kJ/kg. Latent heat of water vapour at 298 K (25 °C) = 2442.5 kJ/kg.

Solution : Basis : 1 mol of gaseous n-butane (C_4H_{10}).

The combustion reaction is $C_4H_{10} + 13.5 O_2 \rightarrow 4 CO_2 + 5 H_2O$

Thus, when 1 mol of n-butane is burnt, 5 mol of water are produced.

$$\text{Weight of water produced} = \frac{5}{1} \times 1 = 5 \text{ mol} = 5 \times 18 = 90 \text{ g} = 90 \times 10^{-3} \text{ kg}$$

Latent heat of water vapour at 298 K (25°C)

$$= 90 \times 10^{-3} \times 2442.5 = 219.825 \text{ kJ}$$

$$\text{NHV} = \text{GHV} - \text{Latent heat of water vapours}$$

$$= 2877.40 - 219.825 = 2657.575 \text{ kJ/mol } C_4H_{10}$$

... Ans.

$$\text{Moles of } C_4H_{10} = 1 \text{ mol}$$

$$\text{Molecular weight of } C_4H_{10} = 58 \text{ kg/kmol}$$

$$\text{Amount of } C_4H_{10} = 1 \times 10^{-3} \text{ kmol} \times 58 \text{ kg/kmol} = 0.058 \text{ kg}$$

$$\text{GHV of } C_4H_{10} = \frac{2877.40}{0.058} = 49610.3 \text{ kJ/kg}$$

From the reaction, 1 kmol C_4H_{10} \equiv 5 kmol H_2O ,

$$58 \text{ kg } C_4H_{10} \equiv 90 \text{ kg } H_2O$$

... (on weight basis)

$$\therefore \text{Water produced} = \frac{90}{58} \times 0.058 = 0.09 \text{ kg}$$

$$m = \text{mass of water produced} = 0.09 \text{ kg}$$

We have :

$$\text{NHV} = \text{GHV} - m\lambda = 49610.3 - 0.09 \times 2442.5$$

$$= 49390.475 \text{ kJ/kg } C_4H_{10}$$

Composition of Flue Gases :

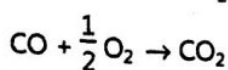
| Component | Quantity, kmol | Mole % |
|-----------------|----------------|----------|
| N ₂ | 122.43 | 77.88 |
| CO ₂ | 32.46 | 20.65 |
| CO | 0.54 | 0.343 |
| O ₂ | 1.77 | 1.126 |
| Total | 157.2 | ≈ 100.00 |

Whenever O₂ is present in the input stream, we have to find the net O₂ demand and then find O₂ entering using the percent excess air given. ... Ans.

Example 8.10 : Gas containing 25% CO, 5% CO₂, 2% O₂ and rest N₂ by volume is burnt with 25% excess air. If the combustion is 90% complete, calculate the composition by volume of flue gases.

Solution : Basis : 100 mol gas burnt.

It contains 25 mol CO, 5 mol CO₂, 2 mol O₂ and 68 mol N₂.



$$1 \text{ mol CO} = 0.5 \text{ mol O}_2$$

$$\text{Theoretical O}_2 \text{ requirement} = \frac{0.5}{1} \times 25 = 12.5 \text{ mol}$$

$$\text{Net demand of O}_2 = 12.5 - 2 = 10.5 \text{ mol}$$

25% excess air is used.

$$\therefore \text{O}_2 \text{ in the air supplied} = 1.25 \times 10.5 = 13.125 \text{ mol}$$

$$\text{N}_2 \text{ in the air supplied} = \frac{79}{21} \times 13.125 = 49.375 \text{ mol}$$

$$\text{CO reacted} = 0.9 \times 25 = 17.5 \text{ mol}$$

$$\text{CO unreacted} = 25 - 17.5 = 7.5 \text{ mol}$$

$$\text{CO}_2 \text{ produced} = 17.5 \text{ mol}$$

$$\text{Total CO}_2 \text{ in the gas leaving} = 17.5 + 5 = 22.5 \text{ mol}$$

$$\text{O}_2 \text{ reacted} = \frac{1}{2} \times 17.5 = 8.75 \text{ mol}$$

$$\text{O}_2 \text{ unreacted} = 13.125 - 8.75 = 4.375 \text{ mol}$$

$$\text{N}_2 \text{ in the gas leaving} = 49.375 + 68 = 117.375 \text{ mol}$$

Analysis of Flue Gases :

| Component | Quantity, mol | Mole % (Volume %) |
|-----------------|---------------|-------------------|
| CO ₂ | 22.5 | 14.83 |
| O ₂ | 4.375 | 2.88 |
| N ₂ | 117.375 | 77.35 |
| CO | 7.5 | 4.94 |
| Total | 151.75 | 100.00 |

... Ans.

Example 8.11 : A gas containing 25% CO, 5% CO₂, 2% O₂ and the rest N₂ is burnt with 20% excess air. If the combustion is 80% complete, calculate the composition by volume of the flue gases considering the given compositions of gas to be on mole basis.

Solution : Basis : 100 mol gas.

It contains 25 mol CO, 5 mol CO₂, 2 mol O₂ and 68 mol N₂.

unit-4

COMBUSTION

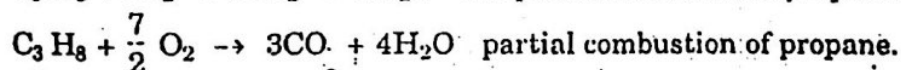
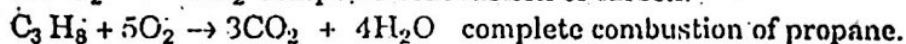
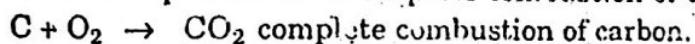
In process industry the fuel burnt in furnaces may be solid, liquid or gas. The furnace is a enclosed space in which heat is produced by chemical oxidation of fuel. Some of the more common fuels are :

1. **Solid fuels** : Principally coal which is a mixture of carbon, hydrogen, non-combustible ash, water and sulphur, coke and to some extent wood, bagasse.

2. **Liquid fuels** : Principally hydrocarbons obtained by distillation of crude oil (petroleum).

3. **Gaseous fuels** : Principally natural gas which usually contains 80 to 95 methane, the balance ethane, propane and small quantities of other gases, light hydrocarbons, acetylene etc.

The rapid reaction of a fuel with oxygen is known as **combustion**. In combustion operation, the union of carbon, hydrogen and sulphur of fuel takes place with oxygen. When a fuel is burned, the carbon in the fuel reacts to form either CO_2 or CO , hydrogen reacts to form H_2O and sulphur reacts to form SO_2 . The combustion is termed as complete combustion if the products of combustion are CO_2 , H_2O and SO_2 . A combustion reaction in which CO is formed from a fuel is referred to as partial or incomplete combustion of the hydrocarbon. Examples :



The combustion products of fuel (CO_2 , H_2O and frequently CO and SO_2) are relatively worthless as compared to fuels burned to obtain them.

The significance of combustion reactions lies in the tremendous quantities of heat released during course of combustion process. The heat released is used to produce steam, which is then used to drive the turbines to produce electricity. In process industry, the heat released by burning fuel is used to supply thermal energy.

For economic reasons, air is the source of oxygen in most combustion operations. The product gas that leaves a combustion chamber (containing CO_2 , CO , H_2O , O_2 , SO_2 (SO_3) and N_2) is referred to as the stack gas or flue gas. In analysis of flue gas, the term composition on wet basis is used to denote the component mole fractions of a gas that contains water and composition on a dry basis is used to denote the component mole fractions of a gas without water.

Calorific Values of Fuels :

The calorific value of a fuel also known as the heating value of a fuel is the negative of the standard heat of combustion, usually expressed per unit mass of a fuel. Since the standard heat of combustion is always negative, the calorific value (heating value) is positive. The calorific value of a fuel is defined as the total heat produced when a unit mass of fuel is completely burnt with pure oxygen.

When a fuel is burnt, the hydrogen in a fuel reacts with oxygen to produce water. When water is present in flue gas as vapour, the latent heat of vaporisation is lost and hence this quantity of heat is not available for any useful purpose.

The net calorific value (net heating value or low heating value of a fuel) is the calorific value of a fuel which is determined by considering that the water is present in the vapour form i.e. it is $-\Delta H_c^\circ$ with H_2O (g or v) as a combustion product.

The latent heat of vaporisation of water can be made available for useful purpose if water vapours are condensed. The gross-calorific value (higher heating value or gross heating value) of a fuel is the negative of standard heat of combustion with $H_2O(l)$ as a combustion product. i.e. it is equal to the net calorific value of a fuel to which latent heat of water vapours is added. The gross calorific value is abbreviated as GCV, higher heating value as HHV, lower heating value as LHV, net calorific value as NCV and net heating value as NHV.

The NCV and GCV of the fuels are usually reported at 298 K (25 °C). These may be expressed in kJ/kg of fuel, kJ/mol of fuel or kJ/m³ of fuel.

To calculate net calorific value of a fuel from a gross calorific value of a fuel or vice-versa, we must calculate the moles of water produced when a unit mass of the fuel is burned.

If n is the mol of water produced, then

$$GCV = NCV + n \Delta H_v [H_2O, 298 K (25^\circ C)] \text{ kJ/mol of fuel} \quad \dots (8.1)$$

where $\Delta H_v [H_2O, 298 K (25^\circ C)]$ is the heat of vaporisation of water at 298 K (25 °C) in kJ/mol. The GCV calculated will be kJ/mol. If 'm' is the quantity of water produced in kg when a unit mass of a fuel is burned and ' λ ' is the latent heat of water vapours at 298 K (25 °C) in kJ/kg, then GCV and NCV of a fuel in kJ/kg of a fuel are related by equation :

$$GCV = NCV + m\lambda \quad \dots (8.2)$$

Latent heat of water vapours, λ , at 298 K (25 °C) is 2442.5 kJ/kg.

$$GCV = NCV + \frac{(\text{wt \% hydrogen}) (9) (\lambda)}{100} \text{ kJ/kg} \quad \dots (8.3)$$

If a fuel contains a mixture of combustible substances, its heating value (HV) is

$$HV = \sum x_i (HV)_i \quad \dots (8.4)$$

where $(HV)_i$ is the heating value of the i^{th} combustible substance. When the heating values are expressed in units of energy per unit mass, then the x_i 's are the weight fractions of the fuel components, and when they are expressed in units of energy per mole then the x_i 's are the mole fractions of the fuel components.

Proximate analysis of coal involves determination of moisture, volatile matter, ash and fixed carbon (obtained by deducting % moisture, % VM and % ash from 100). Ultimate analysis of coal involves determination of carbon, hydrogen, nitrogen, sulphur, and oxygen of coal. The oxygen content of coal is obtained by deducting sum of % of elements other than oxygen from 100.

Air Requirement:

For any combustion process i.e. for chemical oxidation of a fuel, oxygen is must which will combine with carbon, hydrogen and sulphur. In normal practice, air is used for burning the fuel as it being the inexpensive source of oxygen. Air contains about 21% oxygen and 79% nitrogen by volume. It is normal practice to feed less expensive reactant in excess of valuable one to increase the conversion of a valuable reactant. Hence, combustion reactions are invariably run with more air than needed to supply oxygen in stoichiometric proportion to the fuel.

Handwritten note: Air = 21% O₂, 79% N₂

Handwritten note: by vol.

Handwritten note: less expensive reactant

Amount of O₂ needed for complete combustion

Theoretical oxygen : It is the amount of oxygen needed for complete combustion of all the fuel fed to the combustion chamber, assuming that all carbon in the fuel reacts with oxygen to form CO₂, all hydrogen reacts to form H₂O and all sulphur reacts to form SO₂. *O₂ → CO₂, H₂ → H₂O, S → SO₂*

Theoretical air : It is the quantity of air that contains the theoretical oxygen i.e. it is the minimum air required to burn the fuel completely so that all carbon gets converted into CO₂, all hydrogen into H₂O and all sulphur into SO₂. *→ min. Air reqd to burn fuel completely*

Theoretical air demand of a fuel is calculated as

$$\text{Theoretical air demand in moles} = \frac{\text{Theoretical oxygen demand in moles}}{0.21} \quad \dots (8.5)$$

In actual combustion practice, air is used in excess of that theoretically required to assure complete combustion.

Excess air : It is the amount by which the air fed to combustion chamber exceeds the theoretical air.

$$\text{Percent excess air} = \left(\frac{\text{Moles air supply} - \text{Moles air theoretical}}{\text{Moles air theoretical}} \right) \times 100 \quad \dots (8.6)$$

The quantity of actual air supply and theoretical air can be used either in weight units or in molar units in the formula cited above.

The actual air supply is obtained knowing % excess and theoretical demand by the relation :

$$\text{Actual air supply} = \text{Theoretical air} \left[1 + \frac{\% \text{ excess}}{100} \right] \quad \dots (8.7)$$

If you know the feed rate of the fuel and the stoichiometric equation for complete combustion of the fuel, you can calculate the theoretical oxygen demand and air feed rate. The equation for calculation of % excess air cited above is applicable for calculation of % excess oxygen. The % excess air and % excess oxygen are one and the same terms. The theoretical air required to burn a given quantity of fuel does not depend on how much is actually burned and the value of the percent air depends only on a theoretical air and the air supply rate and not on the quantity of O₂ actually consumed or whether the combustion is complete or partial. The theoretical as well as actual air requirements are expressed in different units for the sake of convenience e.g. kg per kg fuel or m³ per kg fuel. For converting amount of air expressed in kmol into amount of air in kg, the average molecular weight of air can be taken as 29. For converting amount of air from kmol/mol into l/m³ (volume units), we have to use the ideal gas law.

The excess air requirement depends upon the type of fuel burnt. The gaseous fuel required very less excess air. The liquid fuels require more excess air than for gaseous fuel and solid fuels require higher amounts of excess air than that required for liquid fuels. Gaseous fuels are burnt with 5 to 15% excess air while liquid and solid fuels are burnt with 10 to 50% excess air.

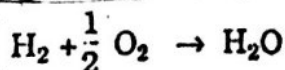
Ex. 8.1 : Crude oil is found to contain 87% carbon, 12.5% hydrogen and 0.5% sulphur. Calculate the net calorific value of crude oil at 298 K (25 °C).

Data : Gross calorific value of crude oil at 298 K (25 °C) is 45071 kJ/kg oil.

Latent heat of water vapour at 298 K (25 °C) = 2442.5 kJ/kg.

Sol. : Basis : 1 kg of crude oil.

$$\text{Hydrogen burnt} = \text{Hydrogen in crude oil} = 0.125 \text{ kg}$$



Calculations. Simple combustion calculations can be studied in three categories :—

- (a) Burning of solids or liquids.
- (b) Burning of gases.
- (c) Calculation of air supplied.

When the composition of the fuel is known, the theoretical amount of air needed for its combustion and the products of combustion can be easily calculated with the help of a simple chemical equation. For this purpose the composition of air is taken to be :.

| | By weight | By volume |
|----------|-----------|-----------|
| Oxygen | 23% | 21% |
| Nitrogen | 77% | 79% |

This means that when 1 kg of O_2 is needed for a reaction $\frac{1 \times 100}{23} = 4.35$ kg of air is to be supplied. In the same manner for

1 m³ of O_2 , $\frac{1 \times 100}{21} = 4.76$ m³ of air is to be supplied.. This gives the amount of N_2 that will go along with the products of combustion.

Hydrogen burns to give water which is supposed to be in a liquid state and the volume, being comparatively very small, is neglected. The volumes of solids are also neglected.

If the analysis of fuel shows O_2 , it is supposed to be in chemical combination; therefore, its amount is to be subtracted from the calculated total requirement.

Some useful conversions are :—

- (i) Gram molecule of gases occupy 22.4 litres at N. T. P.
- (ii) Pound molecule of gases occupy 359 cu. ft. at N. T. P.
- (iii) 1 lb. of air occupies 12.39 cu. ft. at N. T. P.

Since air contains 23% by weight of oxygen, the weight of air needed is the weight of oxygen divided by 0.23. Let C, H, O and S represent the weights of the elements in kg per kg of fuel, the weight of air theoretically needed is :

$$W = 11.6 C + 34.8 (H - O/8) + 4.35 S$$