UNIT 5

First Law of Thermodynamics and Chemical Energetics

SYLLABUS

Some basic concepts—systems, surroundings, types of systems, types of processes, intensive and extensive properties, state functions, irreversible process.

Zeroth Law.

First Law of Thermodynamics—internal energy, enthalpy, work, heat capacity, specific heat capacity, molar heat capacity, enthalpy changes during phase transitions.

Enthalpy changes in chemical reactions—standard enthalpy of formation, Hess's law of constant heat summation, bond enthalpy, measurement of enthalpy of reactions, energy of combustion reactions.

Sources of energy—Sun as the primary source of energy, Alternative sources of energy.

SECTION I

SOME BASIC CONCEPTS USED IN THERMODYNAMICS

5.1. General Introduction

It is a well known fact that most of the physical changes and chemical changes are accompanied by energy changes. These energy changes may take place in the form of heat, light, work, electrical energy etc. All these forms of energy are convertible into one another and hence are related to each other quantitatively.

The branch of science which deals with the study of different forms of energy and the quantitative relationships between them is known as 'thermodynamics'.*

When we confine our study to chemical changes and chemical substances only, the restricted branch of thermodynamics is known as **Chemical Thermodynamics.**

The complete study of thermodynamics is based upon three generalizations called *First*, *Second* and *Third* laws of thermodynamics. In addition to these, another law was put forward after the enunciation of First Law of Thermodynamics. However as it was of primary importance, it was called as *Zeroth law.* These laws have been arrived at purely on the basis of human experience and there is no theotetical proof for any of these laws. However the validity of these laws is supported by the fact that nothing contrary to these laws has been found so far and nothing contrary is expected.

The **importance** of thermodynamics lies in the following two facts :–

(*i*) It helps us to predict whether any given chemical reaction can occur under the given set of conditions.

(*ii*) It helps in predicting the extent of reaction before the equilibrium is attained.

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*The name "thermodynamics" was given by mechanical engineers in the beginning who were interested only in the conversion of *heat* into *mechanical work (thermo* means *heat* and *dynamics* means *motion* resulting into mechanical work). The device used to bring about this conversion is called an *engine.*

The limitations of thermodynamics *i.e.* where it fails to give any information are as follows : –

(*i*) It helps to predict the *feasibility* of a process but does not tell anything about the rate at which the process takes place.

(*ii*) It deals only with the initial and final states of a system but does not tell anything about the *mechanism* of the process (*i.e.* the path followed by the process).

(*iii*) It deals with the properties like temperature, pressure etc. of the matter in bulk but does not tell anything about the individual atoms and molecules.

5.2. Some Basic Terms and Concepts

Some basic terms and concepts commonly used in thermodynamics are briefly explained below :

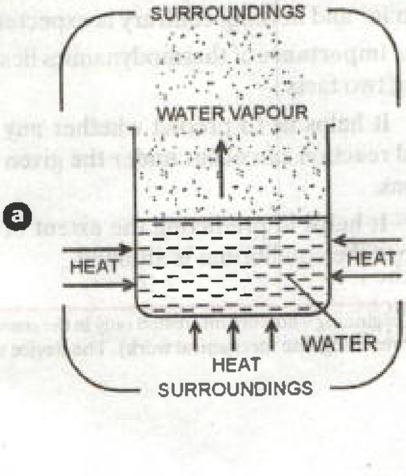
1. System and Surroundings. *The part of the universe chosen for thermodynamic consideration (i.e. to study the effect of temperature, pressure etc.) is called a system.*

The remaining portion of the universe, excluding the system, is called surroundings.

A system usually consists of a definite amount of one or more substances and is separated from the surroundings by a real or imaginary boundary through which matter and energy can flow from the system to the surroundings or *vice versa.*

2. Types of systems (Open, closed and isolated systems)

(*a*) **Open system.** *A system is said to be an open system if it can exchange both matter and energy with the surroundings.* For example, if some water is kept in an open vessel (Fig. 5.1. *a*) or if some reaction is allowed to take place in an open vessel (*e.g.* between a piece of marble and HCl) (Fig. 5.1. *b*), exchange of both matter and energy takes place between the system and the surroundings.



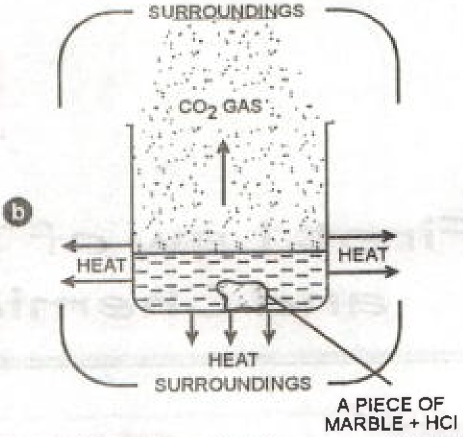


FIGURE 5.1. Examples of open system :
(a) Water kept in open vessel
(b) Reaction taking place in an open vessel.

Animals and plants are open systems from the thermodynamic point of view.

(*b*) **Closed system.** *If a system can exchange only energy with the surroundings but not matter, it is called a closed system.* For example, if some water is placed in a closed metallic vessel (Fig. 5.2. *a*) or if some reaction is allowed to take place in a cylinder enclosed by a piston (Fig. 5.2. *b*), then as the vessel is closed, no exchange of matter between the system and the surroundings can take place. However, as the vessel has conducting walls, exchange of energy can take place between the system and the surroundings.

If the reaction is exothermic, heat is given by the system to the surroundings. If the reaction is endothermic, heat is given by surroundings to the system. Further, if the reaction is accompanied by a decrease in volume, mechanical work is done by the surroundings on the system and if the reaction is accompanied by increase in volume, the mechanical work is done by the system on the surroundings. As mechanical work is also a type of energy, the movement of the piston in or out also amounts to an exchange of energy between the system and the surroundings.

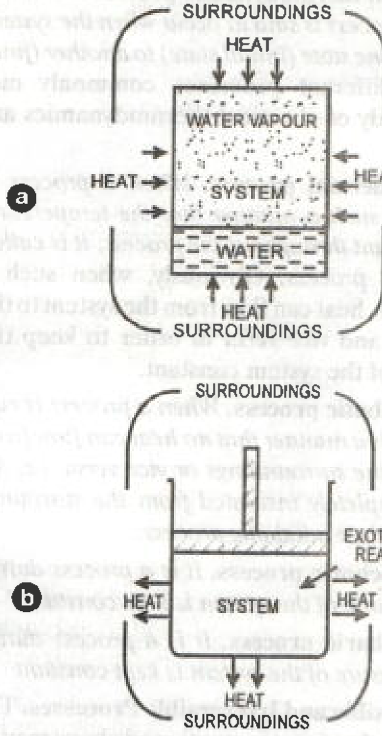


FIGURE 5.2. Examples of closed system : (a) Water placed in a closed vessel (b) A reaction taking place in an enclosed cylinder.

(c) **Isolated system.** *If a system can neither exchange matter nor energy with the surroundings, it is called an isolated system.* For example, if water is placed in a vessel which is closed as well as insulated, no exchange of matter or energy can take place between the system and the surroundings. This constitutes an isolated system (Fig. 5.3).

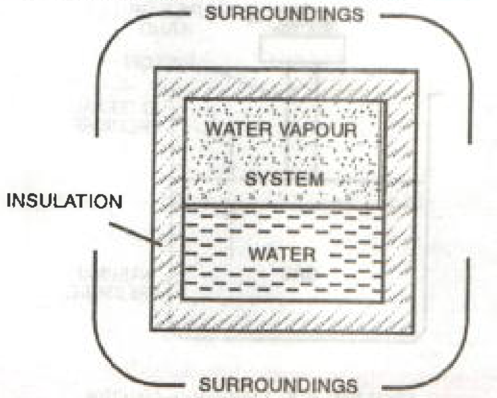


FIGURE 5.3. An example of an isolated system.

Tea placed in an open cup is an example of an open system whereas tea placed in a closed steel tea-pot is an example of a closed system and tea placed in thermos flask is an example of an isolated system. (Fig. 5.4)

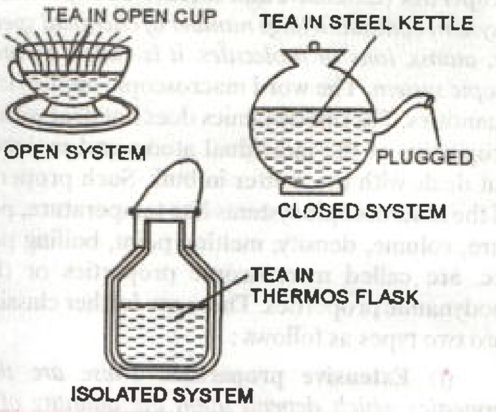


FIGURE 5.4. Examples to illustrate open, closed and isolated systems.

3. State of a system and State variables. *The state of a system means the condition of the system which is described in terms of certain observable (measurable) properties such as temperature (T), pressure (P), volume (V) etc. of the system.* If any of these properties of the system changes, the system is said to be in different state *i.e.* the state of the system changes. That is why these properties of a system are called *state variables*.

A process is said to occur when the state of the system changes. The first and the last state of a system are called the *initial state* and the *final state* respectively.

4. State function. *A physical quantity is said to be state function if its value depends only upon the state of the system and does not depend upon the path by which this state has been attained.* For example, a person standing on the roof of a five stroeyed building (*i.e.* at a particular height) has a fixed value of potential energy, irrespective of the fact whether he reached there by stairs or by a lift. Thus the potential energy of the person is a state function. On the other hand, the work done by the legs of the person to reach the same height is not same in the two cases *i.e.* whether he went by lift or by stairs. Hence work is not a state function. Instead, it is sometimes called a *'path function'*.

Alternatively, *a physical quantity is said to be a state function if the change in its value during the process depends only upon initial state and the final state of the system and does not depend upon the path by which this change has been brought about.*

5. Macroscopic system and Macroscopic Properties (Extensive and Intensive Properties). *If a system contains a large number of chemical species i.e. atoms, ions or molecules, it is called a macroscopic system.* The word macroscopic implies large quantities. Thermodynamics does not deal with the properties of the individual atoms and molecules but deals with the matter in bulk. Such properties of the macroscopic systems like temperature, pressure, volume, density, melting point, boiling point etc. are called macroscopic properties or thermodynamic properties. These are further classified into two types as follows :

(*i*) **Extensive properties.** *These are those properties which depend upon the quantity of the matter contained in the system.* The common examples of these properties are *mass, volume and heat capacity*. Besides these, some other properties discussed later in this unit include internal energy, enthalpy, entropy, Gibbs free energy etc. The total value of an extensive property is equal to the sum of the values for the separate parts into which the system may be divided for the sake of convenience.

(*ii*) **Intensive properties.** *These are those properties which depend only upon the nature of the substance and are independent of the amount of the substance present in the system.* The common examples of these properties are *temperature, pressure, refractive index, viscosity, density, surface tension, specific heat, freezing point, boiling point etc.* It is because pressure and temperature are intensive properties, independent of the quantity of the matter present in the system that they are frequently used as variables to describe the state of a system.

It is of interest to note that an extensive property may become intensive property by specifying unit amount of the substance concerned. Thus mass and volume are extensive properties but density and specific volume (*i.e.* mass per unit volume and volume per unit mass respectively) are intensive properties of the substance or the system. Similarly, heat capacity is an extensive property but specific heat is intensive (as will be discussed later).

Further, extensive properties are additive but intensive properties are not.

6. Types of thermodynamic processes. *A thermodynamic process is said to occur when the system changes from one state (initial state) to another (final state).* The different processes commonly met within the study of chemical thermodynamics are as follows :

(*i*) **Isothermal process.** *When a process is carried out in such a manner that the temperature remains constant throughout the process, it is called an isothermal process.* Obviously, when such a process occurs, heat can flow from the system to the surroundings and *vice versa* in order to keep the temperature of the system constant.

(*ii*) **Adiabatic process.** *When a process is carried out in such a manner that no heat can flow from the system to the surroundings or vice versa. i.e. the system is completely insulated from the surroundings, it is called an adiabatic process.*

(*iii*) **Isochoric process.** *It is a process during which the volume of the system is kept constant.*

(*iv*) **Isobaric process.** *It is a process during which the pressure of the system is kept constant.*

7. Reversible and Irreversible Processes. The various types of processes mentioned above may be carried out *reversibly or irreversibly*. These terms may be understood as follows :

In order to understand a reversible process, imagine a gas confined within a cylinder provided with a frictionless piston upon which is piled some very fine sand (Fig. 5.5). Suppose the pressure exerted by the gas on the piston is equal to the combined pressure exerted by the weight of the piston, the pile of sand and the atmospheric pres-

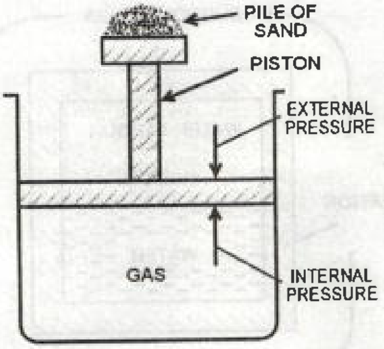


FIGURE 5.5. Understanding the concept of a reversible process.

sure. Thus under these conditions, the piston does not move at all and a state of equilibrium is said to exist. Now if one particle of sand is removed, the gas will expand very slightly but the equilibrium will be restored almost immediately. Such a change is called an *infinitestimal change*. If the particle of sand is replaced, the gas will return to its original volume. By the continued removal of the particles of sand, the gas can be allowed to undergo a finite expansion but each step in this expansion is an infinitesimal one and can be reversed by an infinitesimal change in the external conditions. At all times, the equilibrium is restored immediately.

A process carried out in the above manner is called a reversible process and may be defined as follows :

A reversible process is a process which is carried out infinitestimally slowly so that all changes occurring in the direct process can be exactly reversed and the system remains almost in a state of equilibrium with the surroundings at every stage of the process.

On the other hand, a process which does not meet the above requirements is called an irreversible process. In other words, an irreversible process is defined as that process which is not carried out infinitesimally slowly (instead, it is carried out rapidly) so that the successive steps of the direct process cannot be retraced and any change in the external conditions disturbs the equilibrium.

The main points of difference between a reversible and an irreversible process may be summed up as follows :

Reversible Process	Irreversible Process
1. The process is carried out infinitesimally slowly *i.e.* difference between the driving force and the opposing force is very very small.	1. This process is not carried out infinitesimally slowly but is carried out rapidly *i.e.* the difference between the driving force and the opposing force is quite large.
2. At any stage during the process, equilibrium is not disturbed.	2. Equilibrium may exist only after the completion of the process.
3. It takes infinite time for completion.	3. It takes a finite time for completion.
4. It is only imaginary and cannot be achieved in actual practice.	4. These processes actually occur in nature.
5. Work obtained in this process is maximum.	5. Work obtained in this process is not maximum.

SECTION II

ZEROTH LAW OF THERMODYNAMICS

5.3. Definition of Zeroth Law

As mentioned in the beginning of this unit, this law was put forward much after the enunciation of the first and second law of thermodynamics. However, it is of primary importance as it gives the basis of the measurement of temperatures. Hence it is called as *zeroth law of thermodynamics* or it is also called the *law of thermal equilibrium.*

To understand the origin of the law, consider two bodies A and B separately in thermal equilibrium with the third body C (*i.e.* bodies A and C have equality of temperature and bodies B and C also have equality of temperature), then if the bodies A and B are brought in contact with each other, they will also be in thermal equilibrium (*i.e.* bodies A and B will also have an equality of temperature with each other) (Fig. 5.6).

This leads to the following definitions for the zeroth law of thermodynamics :

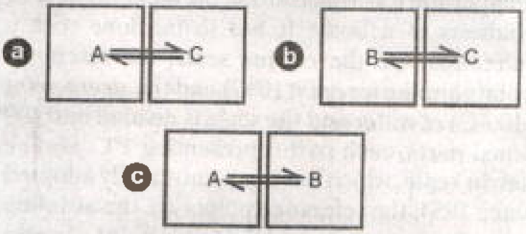


FIGURE 5.6. (a) Thermal equilibrium between bodies A and C
(b) Thermal equilibrium between bodies B and C
(c) Thermal equilibrium between bodies A and B.

When two bodies A and B are separately in thermal equilibrium with a third body C, they in turn are in thermal equilibrium with each other.

or

When two bodies A and B have equality of temperature with a third body C, they in turn have equality of temperature with each other.

5.4. Application of Zeroth Law in Measurement of Temperature

Suppose the body C is a thermometer. It is kept in contact with the body A till the temperature on the thermometer becomes constant. Now suppose the thermometer is removed from the body A and is brought in contact with body B. If the mercury level of the thermometer does not show any change, we say that the two bodies A and B are in thermal equilibrium with the given thermometer. In other words, bodies A and B have equality of temperature with each other. Thus for measurement of temperature, numbers can be marked on the mercury thermometer and every time a body has equality of temperature with the thermometer, we can say that the body has the temperature, we read on the thermometer.

The fact stated above is so simple and familiar that it does not need any further experiments for its support.

It may be pointed out that as thermometer is a very small body (as only the bulb comes in contact), it has negligible exchange of energy when it is brought in contact with large bodies like A and B. Hence the energies of the bodies A and B are supposed to remain almost unchanged during temperature measurement.

Thermodynamic scale of temperature. Temperature is a measure of the exact hotness or coldness of a body. It has to be done with a reference. On the **celsius scale**, the reference points are the *ice point* (0°C) and the *steam point* (100°C) of water and the scale is divided into 100 equal parts, each part representing 1°C. On the **kelvin scale**, which has been universally adopted since 1954, the reference points are the **absolute zero** of temperature and the **triple point** of water *i.e.* a fixed temperature and pressure (0·01°C, 4·58 torr) at which all the three phases of water *i.e.* ice, liquid water and water vapour exist together. The SI unit of temperature, called Kelvin (K) is based on this scale. *One kelvin is defined as 1/273·16 of the triple point temperature of water* (273·16 K). This is the scale most commonly used in thermodynamics and hence is called 'thermodynamic scale of temperature'. It is also called 'absolute scale' because on this scale, lowest possible temperature has been taken as zero, unlike celsius scale in which zero point has been taken arbitrarily.

SECTION III

FIRST LAW OF THERMODYNAMICS

5.5. Some Thermodynamic Quantities

A number of thermodynamic quantities appear during the study of thermodynamics *e.g.* internal energy, heat, work, enthalpy, entropy, free energy etc. The first three terms are briefly described below. The remaining terms will be discussed at +2 level.

(1) Internal energy. It is well known that whenever some process (physical or chemical) occurs, it is usually accompanied by some energy change. The energy may appear in different forms such as heat, light, work etc.

The evolution or absorption of energy in different processess clearly shows that every substance (or the system containing one or more substances) must be associated with some definite amount of energy, the actual value of which depends upon the nature of the substance and the conditions of temperature, pressure, volume and composition. It is the sum of different types of energies associated with atoms and molecules such as electronic energy (E_e), nuclear energy (E_n), chemical bond energy (E_c), potential energy (E_p) and kinetic energy (E_k) which is further the sum of translational energy (E_t), vibrational energy (E_v) and rotational energy (E_r). Thus

$$E = E_e + E_n + E_c + E_p + E_k$$

The energy thus stored within a substance (or a system) is called its internal energy and is usually denoted by the symbol 'E' or 'U'.

Internal energy is a state function. The internal energy of a definite amount of a particular substance under given conditions of temperature and pressure always has a definite value. For example, a certain amount of CO_2 under given conditions of temperature and pressure will always have the same internal energy, irrespective of the manner by which it has been produced. This is expressed by saying that *internal energy is a state function* (*i.e.* a property which depends only on the state of the system).

Internal energy change. The absolute or exact value of internal energy possessed by a substance cannot be determined. This is because it is impossible to determine accurately most of the quantities which contribute towards internal energy of the system. But it does not matter, since we are not interested in knowing the absolute value of internal energy of a substance. Rather, we are interested in the change in internal energy which accompanies a process and this can be determined. The change in internal energy, ΔE (or ΔU), accompanying a process is given by

$$\Delta E = E_2 - E_1$$

or $$\Delta U = U_2 - U_1$$

where E_1 (or U_1) is the internal energy of the system in the initial state and E_2 (or U_2) is the internal energy in the final state.

Since E_1 and E_2 are state functions, therefore, *ΔE is also a state function* (*i.e.* depends only on the initial state and the final state of the system).

In case of a reaction, if E_R (or U_R) is the internal energy of the reactants and E_p (or U_p) that of the products, the change in internal energy during the reaction is given by

$$\Delta E = E_p - E_R$$

or $$\Delta U = U_p - U_R$$

Two more important points about the internal energy are as follows :

(*i*) The internal energy depends upon the quantity of the substance contained in the system. Hence it is an *extensive property*.

(*ii*) The internal energy of ideal gases is a function of temperature only. Hence in isothermal processes, as the temperature remains constant, there is no change in internal energy *i.e.*

$$\Delta E = 0.$$

Sign of ΔE. Obviously, if $E_1 > E_2$ (or $E_R > E_p$), the extra energy possessed by the system in the initial state (or the reactants) would be given out and ΔE will be negative according to the above equations.

Similarly, if $E_1 < E_2$ (or $E_R < E_p$), energy will be absorbed in the process and ΔE will be positive. Hence

ΔE (or ΔU) is negative if energy is evolved and ΔE (or ΔU) is positive if energy is absorbed

Units of E or U. The units of energy are *ergs* (in CGS units) or *joules* (in SI units)

$$1 \text{ joule} = 10^7 \text{ ergs.}$$

(2) Work. As learnt from lessons in Physics, *work is said to have been done whenever the point of application of a force is displaced in the direction of the force*. If F is the magnitude of the force and dl is the displacement of the point of application in the direction in which the force acts, then the work done is given by $w = F \times dl$

The above type of work is called *mechanical work*. However, there are many other forms of work but in each of these forms

Work done = [A generalized force]
× [A generalized displacement]

Two main types of work used in themodynamics are briefly described below :

(*i*) **Electrical work.** The generalised force is the E.M.F. and the generalized displacement is the *quantity of electricity* flowing through the circuit. Hence

Electrical work done
= E.M.F. × Quantity of electricity.

This type of work is involved in case of reactions involving ions.

(*ii*) **Work of expansion or Pressure-volume work.** This type of work is involved in systems consisting of *gases*. This is the most important form of work used in the study of thermodynamics. *It is the work done when the gas expands or contracts against the external pressure* (usually, the atmospheric pressure). It is a kind of *mechanical work*. The expression for such a work may be derived as follows :

Consider a gas enclosed in a cylinder fitted with a frictionless piston (Fig. 5.7).

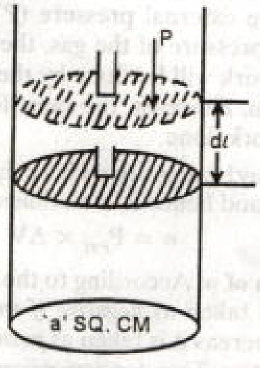


FIGURE 5.7. Expansion of a gas.

Suppose

Area of cross-section of cylinder = *a* sq. cm

Pressure on the piston = P

(which is slightly less than internal pressure of the gas so that the gas can expand)

Distance through which gas expands = dl cm

Then as pressure is force per unit area, force (f) acting on the piston will be $f = P \times a$

$\therefore$ Work done by the gas (*i.e.* the system)

$= \text{Force} \times \text{Distance} = f \times dl = P \times a \times dl.$

But $a \times dl = dV$, a small increase in the volume of the gas. Hence the small amount of work (δw) done by the gas can be written as

$$\delta w = P \times dV$$

If the gas expands from *initial volume* V_1 to the *final volume* V_2, then the total work done (w) will be given by

$$w = \int_{V_1}^{V_2} P dV$$

If the external pressure P against which the gas expands remains almost constant throughout the process (so that it is *irreversible expansion*), the above result may be written as

$$w = P \int_{V_1}^{V_2} dV = P\,(V_2 - V_1) = P\,.\,\Delta V$$

where $\Delta V = (V_2 - V_1)$ is the total change in volume of the gas (or the system). This is the expression for **work of irreversible expansion.**

If the external pressure (P) is slightly more than the pressure of the gas, the gas will contract *i.e.*, the work will be done by the surroundings on the system. However, the same formula will apply for the work done.

It may be mentioned here that P is the *external* pressure and hence is sometimes written as P_{ext} so that $\quad w = P_{ext} \times \Delta V$

Sign of w. According to the *latest S.I. convention, w* is taken as ***negative if work is done by the system*** whereas it is taken as ***positive if work is done on the system.*** Thus for expansion, we write

$$w = -P\,\Delta V$$

and for contraction, we have

$$w = P\,\Delta V$$

Units of w. The units of work are the same as those of energy *viz. ergs* or *joules* (1 J = 1 Nm = 1 kg m^2 s^{-2})*

Work done in isothermal reversible expansion of an ideal gas.** The small amount of work done, δw, when the gas expands through a small volume, dV, against the external pressure, P is given by $\quad \delta w = -PdV$

$\therefore$ Total work done when the gas expands from initial volume V_1 to final volume V_2, will be

$$w = -\int_{V_1}^{V_2} PdV$$

For an ideal gas, PV = nRT *i.e.*

$$P = \frac{nRT}{V}$$

$$\text{Hence} \quad w = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$$

For isothermal expansion, T = constant so that

$$w = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$= -nRT \ln \frac{V_2}{V_1}$$

$$= 2\cdot303\,nRT \log \frac{V_2}{V_1}$$

$$= -2\cdot303\,nRT \log \frac{P_1}{P_2}$$

$$\left(\text{At const. temp., } P_1V_1 = P_2V_2 \text{ or } \frac{V_2}{V_1} = \frac{P_1}{P_2}\right)$$

The –ve sign indicates work of expansion.

(3) Heat. Just as work is a form of energy which is exchanged between the system and the surroundings as a result of expansion or contraction of the gas because of the difference in the internal pressure of the gas and the external pressure, similarly *heat is* another *mode of energy exchanged between the system and the surroundings as*

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*Work = Force × distance = N × m = Nm = 1 J

Force = mass × acceleration. Hence work = kg × ms^{-2} × m = kg m^2 s^{-2}

**For reversible expansion, external pressure is not constant but is changed continuously so as to be infinitesimally smaller than the internal pressure of the gas.

a result of the difference of temperature between them. It is usually represented by the letter '*q*'.

It may be pointed out that *both heat and work appear only at the boundary of the system.*

Sign of 'q'. When heat is **given by the system** to the surroundings, it is given a **negative sign.**

When heat is **absorbed by the system** from the surroundings, it is **given a positive** sign.

Units of 'q'. Heat is usually measured in terms of **'calories'**. *A calorie is defined as the quantity of heat required to raise the temperature of one gram of water through 1°C (in the vicinity of 15°C).*

In the S.I. system, heat is expressed in terms of **joules**. The two types of units are related to each other as under :

$$1 \text{ calorie} = 4{\cdot}184 \text{ joules}$$

which means the same thing as

$$1 \text{ joule} = 0{\cdot}2390 \text{ calories}$$

It may be noted that whereas internal energy is a state function, work and heat are not state functions because their values do not depend merely on the initial and final states but depend upon the path followed.

Difference between heat and work. When heat is supplied to a gas in a system, the molecules start moving faster with greater randomness in different directions. However, when work is done on the system, then initially the molecules start moving down in the direction of the piston. **Thus** *whereas heat is a random form of energy, work is an organised form of energy.*

5.6. First Law of Thermodynamics

Definition. The first law of thermodynamics is simply the **law of conservation of energy** which states that

> ***Energy can neither be created nor destroyed although it may be converted from one form to another.***
>
> **or**
>
> ***The total energy of the universe (i.e. the system and the surroundings) remains constant, although it may undergo transformation from one form to the other.***

Justification for the First Law of Thermodynamics. This law is purely a result of experience. There is no theoretical proof for it. However, some of the following observations support the validity of this law.

(*i*) *Whenever a certain quantity of some form of energy disappears, an exactly equivalent amount of some other form of energy must be produced.* For example,

(*a*) In the operation of an electric fan, the electrical energy which is consumed is converted into mechanical work which moves the blades.

(*b*) The electrical energy supplied to a heater is converted into heat whereas electrical energy passing through the filament of a bulb is converted into light.

(*c*) Water can be decomposed by an electric current into gaseous hydrogen and oxygen. It is found that 286·2 kJ of electrical energy is used to decompose 1 mole of water.

$$H_2O(l) + \underset{\textbf{Electrical energy}}{286{\cdot}2\text{ kJ}} \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$$

This energy must have been stored in hydrogen and oxygen since same amount of energy in the form of heat is released when 1 mole of water (liquid) is obtained from gaseous hydrogen and oxygen.

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) + \underset{\textbf{Heat energy}}{286{\cdot}2\text{ kJ}}$$

Thus 286·2 kJ of electrical energy which was supplied to the system (*substance under observation*) has been recovered later as heat energy *i.e.*

Electrical energy supplied = Heat energy produced

Thus energy is conserved in one form or the other though one form of energy may change into the other form.

(*ii*) *It is impossible to construct a perpetual motion machine i.e. a machine which would produce work continuously without consuming energy* (Helmholtz, 1847).

(*iii*) *There is an exact equivalence between heat and mechanical work i.e. for every 4·184 joules of work done, 1 calorie of heat is produced and vice versa* (Joule 1840).

The above three observations are also sometimes taken as alternate statements of the first law of thermodynamics.

Mathematical formulation of the first law of thermodynamics (*i.e. Relationship between internal energy, work and heat*).

The internal energy of a system can be increased in two ways (Fig. 5.8) :

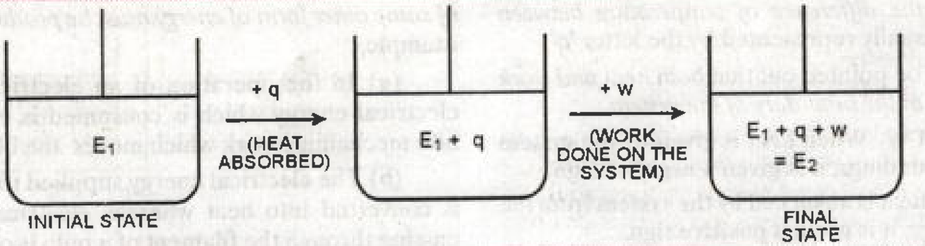


FIGURE 5.8. Increasing internal energy by absorption of heat and by doing work on the system.

(*i*) By supplying heat to the system

(*ii*) By doing work on the system.

Suppose the initial internal energy of the system = E_1

If it absorbs heat q, its internal energy will become = $E_1 + q$

If further work w is done on the system, the internal energy will further increase and become = $E_1 + q + w$. Let us call this final internal energy as E_2. Then $E_2 = E_1 + q + w$

or $E_2 - E_1 = q + w$

or $\boxed{\Delta E = q + w}$ ...(*i*)

This equation is the mathematical formulation of the first law of thermodynamics.

If the work done is the work of expansion, then $w = -P\Delta V$, where ΔV is the change in volume and P is the external pressure. Eqn. (*i*) can then be written as $\Delta E = q - P\Delta V$

or $\boxed{q = \Delta E + P\Delta V}$* ...(*ii*)

Two interesting results follow from the mathematical formulation of the first law of thermodynamics, as under :–

(*i*) Neither q nor w is a state function, yet the qunatity $q + w$ ($= \Delta E$) is a state function (because ΔE is a state function).

(*ii*) For an ideal gas undergoing an isothermal change, $\Delta E = 0$. Hence $q = -w$

i.e. the heat absorbed by the system is equal to work done by the system.

Internal enrregy is a state function – A deduction from the First law of Thermodynamics. Suppose the internal energy of a system under some conditions of temperature, pressure and volume is E_A (state A). Now suppose the conditions are changed so that the internal energy is E_B (state B) (Fig. 5.9). Then if internal energy is a state function, the difference $\Delta E = E_B - E_A$ must be same irrespective of the path from A to B. If not, then suppose in going from A to B by path I, the internal energy increases by ΔE but on returning from B to A by path II, internal energy decreases by $\Delta E'$. If $\Delta E > \Delta E'$, some energy has been created and if $\Delta E < \Delta E'$, some energy has been destroyed though we have returned to the same conditions. This is against the first law of thermodynamics. Hence ΔE must be equal to $\Delta E'$ *i.e.* internal energy is a state function.

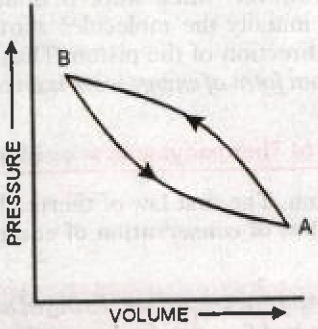


FIGURE 5.9. Changes in internal energy in direct and reverse paths.

Internal energy change in terms of heat evolved or absorbed. From first law of thermodynamics, $q = \Delta E + P\Delta V$

If the process is carried out at constant volume (say in a closed vessel), $\Delta V = 0$. The above equation then reduces to the form

$\Delta E = q_v$ (v indicating constant volume)

---

*or using the symbol U in place of E for internal energy, we can write

$\Delta U = q + w$ and $q = \Delta U + P\Delta V$

Hence

The internal energy change is the heat evolved or absorbed at constant volume.

Work and heat are not state functions. Unlike internal energy, the work done during a process does not depend merely on the initial and the final states of the system but it depends upon the path followed. Hence work is not a state function but a path function. This may be made clear as follows :

Suppose we wish to change the system from A to B. This may be done by following different paths as shown in Fig. 5.10. Confining ourselves to the work of expansion only, we know that the work done for a small change in volume dV is PdV where P is the external pressure. Thus the total work done is the sum of PdV terms and this is equivalent to the area under the curve in the P – V diagrams.

From Fig. 5.10, it is obvious that areas under the curve are different and hence the work done is different when different paths are followed.

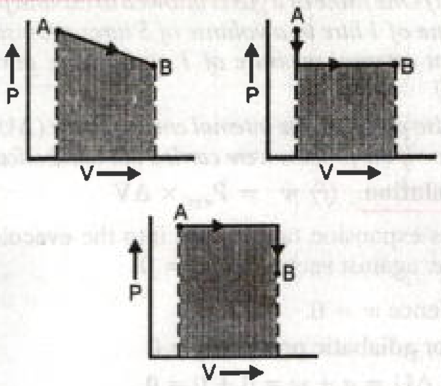


FIGURE 5.10. Different paths followed in going from state A to state B.

That heat is not a state function follows directly from the mathematical formulation of the first law of thermodynamics viz.

$$\Delta E = q + w \quad \text{or} \quad q = \Delta E - w$$

As ΔE is a state function but w is not a state function, hence q is also not a state function.

NUMERICAL PROBLEMS ON FIRST LAW OF THERMODYNAMICS

FORMULAS AND UNITS

According to first law of thermodynamics $\Delta E = q + w$

q, ΔE and w are in joules

Heat absorbed by the system, q is + ve.

Heat given out by the system, q is —ve.

Energy absorbed by the system,

(*i.e.* internal energy of the system increases), ΔE is +ve

Energy given out by the system,

(*i.e.* internal energy of the system decreases), ΔE is —ve

Work done on the system, w is +ve.

Work done by the system, w is —ve.

EXAMPLE 1. *Calculate the internal energy change in each of the following cases :–*

(i) A system absorbs 15 kJ of heat and does 5 kJ of work.

(ii) 5 kJ of work is done on the system and 15 kJ of heat is given out by the system.

Solution. (*i*) Here $q = +15$ kJ

$w = -5$ kJ

∴ According to first law of thermodynamics,

$$\Delta E = q + w = 15 + (-5) = 10 \text{ kJ}$$

Thus the internal energy of the system increases by 10 kJ

(*ii*) Here $w = +5$ kJ

$q = -15$ kJ

∴ According to first law of thermodynamics

$$\Delta E = q + w = -15 + (+5) = -10 \text{ kJ}$$

i.e. the internal energy of the system decreases by 10 kJ.

EXAMPLE 2. *Calculate the amount of work done in each of the following cases :–*

(i) One mole of an ideal gas contained in a bulb of 10 litre capacity at 1 atm is allowed to enter into an evacuated bulb of 100 litre capacity.

(ii) One mole of a gas is allowed to expand from a volume of 1 litre to a volume of 5 litres against the constant external pressure of 1 atm (1 litre atm = 101.3 J)

Also calculate the internal energy charge (ΔU) in each case if the process were carried out adiabatically.

Solution. (i) $w = P_{ext} \times \Delta V$

As expansion takes place into the evacuated bulb, *i.e.* against vacuum, $P_{ext} = 0$.

Hence $w = 0$.

For adiabatic process, $q = 0$

$\therefore \Delta U = q + w = 0 + 0 = 0$

(ii) $\Delta V = V_2 - V_1 = 5 - 1 = 4$ litres

$P = 1$ atm

$\therefore \quad w = -P\Delta V$

$= -1 \times 4$ litre atm $= -4$ litre atm

$= -4 \times 101.3\text{ J} = \mathbf{-405.2\text{ J}}$

Alternatively, using the SI units directly

$P = 1\text{ atm} = 101325\text{ Pa}$

$\Delta V = 4\text{L} = 4 \times 10^{-3}\text{ m}^3$

$\therefore \quad w = -P \times \Delta V$

$= -101325 \times 4 \times 10^{-3}\text{ J} = \mathbf{-405 \cdot 3\text{ J}}$

The negative sign implies that the work is done by the system.

For adiabatic process

$\Delta U = q + w = 0 - 405 \cdot 3\text{ J}$

$= \mathbf{-405 \cdot 3\text{ J}}$

EXAMPLE 3. *Calculate the maximum work obtained when 0·75 mol of an ideal gas expands isothermally and reversibly at 27°C from a volume of 15 L to 25 L. Also calculate the value of q and ΔU accompanying the process.*

Solution. For isothermal reversible expansion of an ideal gas.

$$w = -nRT \ln \frac{V_2}{V_1} = -2 \cdot 303\, nRT \log \frac{V_2}{V_1}$$

Putting $n = 0 \cdot 75$ mol, $V_1 = 15$ L,

$V_2 = 25$ L, $T = 27 + 273 = 300$ K and

$R = 8 \cdot 314\text{ J K}^{-1}\text{ mol}^{-1}$, we get

$$w = -2 \cdot 303 \times 0 \cdot 75 \times 8 \cdot 314 \times 300 \log \frac{25}{15}$$

$= \mathbf{-955 \cdot 5\text{ J}}$

(– ve sign represents work of expansion)

For isothermal expansion of an ideal gas, $\Delta U = 0$

$\therefore \Delta U = q + w$ gives $q = -w = \mathbf{+955 \cdot 5\text{ J}}$

EXAMPLE 4. *Carbon monoxide is allowed to expand isothermally and reversibly from 10 m³ to 20 m³ at 300 K and work obtained is 4·754 kJ. Calculate the number of moles of carbon monoxide.*

Solution. $w = 2 \cdot 303\, n\, RT \log \frac{V_2}{V_1}$

$$4754 = 2 \cdot 303 \times n \times 8 \cdot 314 \times 300 \times \log \frac{20}{10}.$$

This gives $n = \mathbf{2 \cdot 75}$ **moles.**

EXAMPLE 5. *A 5-moles cylinder contained 10 moles of oxygen gas at 27°C. Due to sudden leakage through the hole, all the gas escaped into the atmosphere and the cylinder got empty. If the atmospheric pressure is 1·0 atmosphere, calculate the work done by the gas.*

Solution. $V_{initial} = 5\text{L}$,

$T = 27°\text{C} = 27 + 273\text{ K} = 300\text{ K}$

$$V_{final} = \frac{nRT}{P} = \frac{10 \times 0 \cdot 0821 \times 300}{1 \cdot 0} = 246 \cdot 3\text{ L}$$

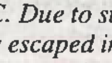
$\Delta V = V_{final} - V_{initial} = 246 \cdot 3 - 5 = 241 \cdot 3\text{ L}$

$w_{exp} = -P\Delta V = -1 \times 241 \cdot 3$ L atm

$= -241 \cdot 3 \times 101 \cdot 3\text{ J}$

$= \mathbf{-24443 \cdot 7\text{ J}}$.

PROBLEMS FOR PRACTICE



1. 500 joule of heat was supplied to a system at constant volume. It resulted in the increase of temperature of the system from 20°C to 25° C. What is the change in internal energy of the system? [Ans. ΔE = 500 J]
2. What would be the work done on/by the system if the internal energy of the system falls by 100 joules even when 200 joules of heat is supplied to it ? [Ans. Work done by the system = 300 J]
3. Calculate the work done when 1·0 mol of water at 373 K vaporizes against an atmospheric pressure of 1·0 atmosphere. Assume ideal gas behaviour. [Ans. 3100 J]

HINTS FOR DIFFICULT PROBLEMS

1. At constant volume, $\Delta V = 0$. Applying $\Delta E = q + w = q + P\Delta V$, we get $\Delta E = q = 500$ J.

3. $PV = nRT$ or $V = n\frac{RT}{P}$

$$= \frac{1 \times 0{\cdot}0821 \times 373}{1} = 30{\cdot}6\ L$$

Taking volume of liquid water to be negligible,

$$\Delta V = V_{vap} - V_{H_2O(l)} = 30{\cdot}6\ L.$$

5.7. Enthalpy or Heat Content

If a process is carried out at constant pressure (as is usually the case, because most of the reactions are studied in vessels open to the atmosphere or if a system consists of a gas confined in a cylinder fitted with a piston, the external pressure acting on the piston is the atmospheric pressure), the work of expansion is given by

$$w = -P\Delta V \qquad ...(i)$$

where ΔV is the increase in volume and P is the constant pressure.

According to first law of thermodynamics, we know that

$$q = \Delta E - w \qquad ...(ii)$$

where q is the heat absorbed by the system, ΔE is the increase in internal energy of the system and w is the work done by the system.

Under condition of constant pressure, putting $w = -P\Delta V$ and representing the heat absorbed by q_p, we get

$$q_p = \Delta E + P\Delta V \qquad ...(iii)$$

Suppose when the system absorbs q_p joules of heat, its internal energy increases from E_1 to E_2 and the volume increases from V_1 to V_2. Then we have

$$\Delta E = E_2 - E_1 \qquad ...(iv)$$

$$\text{and} \quad \Delta V = V_2 - V_1 \qquad ...(v)$$

Putting these values in equation (*iii*) above, we get

$$q_p = (E_2 - E_1) + P(V_2 - V_1)$$

$$\text{or} \quad q_p = (E_2 + PV_2) - (E_1 + PV_1) \qquad ...(vi)$$

Now as E, P and V are the functions of state, therefore the quantity E + PV must also be a state function. *The thermodynamic quantity E + PV is called the* **heat content or enthalpy** *of the system* and is represented by the symbol H *i.e.* the enthalpy may be defined mathematically by the equation

$$\boxed{H = E + PV}$$

Thus if H_2 is the enthalpy of the system in the final state and H_1 is the value in the initial state, then

$$H_2 = E_2 + PV_2$$

$$\text{and} \quad H_1 = E_1 + PV_1$$

Putting these values in equation (*vi*), we get

$$q_p = H_2 - H_1$$

$$\text{or} \quad \boxed{q_p = \Delta H} \qquad ...(vii)$$

where $\Delta H = H_2 - H_1$ is the enthalpy change of the system.

Hence enthalpy change of a system is equal to the heat absorbed or evolved by the system at constant pressure.

It may be remembered that as most of the reactions are carried out at constant pressure (*i.e.* in the open vessels), the measured value of the heat evolved or absorbed is the enthalpy change.

Further, putting the value of q_p from equation (*vii*) in equation (*iii*), we get

$$\boxed{\Delta H = \Delta E + P\Delta V} \qquad ...(viii)$$

Hence the enthalpy change accompanying a process may also be defined as the sum of the increase in internal energy of the system and the pressure-volume work done i.e. the work of expansion.

Physical concept of enthalpy or heat content. In the above discussion, the enthalpy has been defined by the mathematical expression, H = E + PV. Let us try to understand what this quantity really is.

It has been described earlier that every substance or system has some definite energy stored in it, called the internal energy. This energy may be of many kinds.

The energy stored within the substance or the system that is available for conversion into heat is called the heat content or enthalpy of the substance or the system.

As $H = E + PV$ and absolute value of E cannot be determined, therefore, the absolute value of the heat content or enthalpy of a substance or a system cannot be measured. Fortunately, this is not required also. In the thermodynamic processes, we are concerned only with the changes in enthalpy (ΔH) which can be easily measured experimentally. Further, it may be mentioned here that as E and V are extensive properties, therefore the *enthalpy is also an extensive property*.

SUMMING UP MAIN POINTS ABOUT INTERNAL ENERGY AND ENTHALPY

1. Both internal energy and enthalpy are state functions.
2. Both are extensive properties.
3. The absolute value of neither internal energy nor enthalpy can be determined.
4. Internal energy change is the heat evolved or absorbed at constant volume while enthalpy change is that at constant pressure *i.e.* $\Delta E = q_v$, $\Delta H = q_p$.
5. In a cyclic process *i.e.* when the system returns to original state after a number of changes, ΔE or $\Delta H = 0$.

5.8. Relationship Between Heat of Reaction at Constant Pressure and that at Constant Volume

It has already been discussed that

$$q_p = \Delta H \text{ and } q_v = \Delta E \qquad \text{...}(i)$$

It has also been derived already that at constant pressure

$$\Delta H = \Delta E + P\,\Delta V \qquad \text{...}(ii)$$

where ΔV is the change in volume

Eqn. (*ii*) can be rewritten as

$$\Delta H = \Delta E + P(V_2 - V_1)$$

$$= \Delta E + (PV_2 - PV_1) \qquad \text{...}(iii)$$

where V_1 is the initial volume and V_2 is the final volume of the system.

But for ideal gases, $PV = nRT$ so that we have

$$PV_1 = n_1RT \qquad \text{...}(iv)$$

$$\text{and} \qquad PV_2 = n_2RT \qquad \text{...}(v)$$

where n_1 is the number of moles of the gaseous reactants and n_2 is the number of moles of the gaseous products.

Substituting these values in eqn. (*iii*), we get

$$\Delta H = \Delta E + (n_2RT - n_1RT)$$

$$= \Delta E + (n_2 - n_1)\,RT$$

$$\text{or} \qquad \Delta H = \Delta E + \Delta n_g RT \qquad \text{...}(vi)$$

where $\Delta n_g = n_2 - n_1$ is the difference between the number of moles of the gaseous products and those of the gaseous reactants

Putting the values of ΔE from eqn. (*i*), eqn. (*vi*) becomes

$$\boxed{q_p = q_v + \Delta n_g RT} \qquad \text{...}(vii)$$

Conditions under which $q_p = q_v$ or $\Delta H = \Delta E$

(*i*) *When reaction is carried out in a closed vessel* so that volume remains constant *i.e.* $\Delta V = 0$

(*ii*) *When reaction involves only solids or liquids or solutions but no gaseous reactant or product*. This is because the volume changes of the solids and liquids during a chemical reaction are negligible.

(*iii*) *When reaction involves gaseous reactants and products but their number of moles are equal (i.e. $n_p = n_r$) e.g.* in the reactions

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl\,(g)$$

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

Thus q_p is different from q_v only in those reactions which involve gaseous reactants and products and $\left(n_p\right)_{gaseous} \neq \left(n_r\right)_{gaseous}$.

NUMERICAL PROBLEMS ON RELATIONSHIP BETWEEN q_p AND q_v

FORMULAS AND UNITS

$$q_p = q_v + \Delta n_g \, RT$$

or $$\Delta H = \Delta E + \Delta n_g \, RT$$

or $$\Delta H = \Delta U + \Delta n_g \, RT$$

Here $$\Delta n_g = (n_p - n_r)_{gaseous}$$

If q_p and q_v (or ΔH and ΔE or ΔU) are in calories,
R = 1·987 ≃ 2 cal/degree/mole.

If they are in kcals,
R = 0·002 kcal/degree/mole.

If they are in joules, R = 8·314 J K^{-1} $mole^{-1}$ and if they are in kJ,
R = 0·008314 kJ K^{-1} $mole^{-1}$. T is temperature in K.

EXAMPLE. *The heat of combustion of benzene in a bomb calorimeter (i.e. constant volume) was found to be 3263·9 kJ mol^{-1} at 25°C. Calculate the heat of combustion of benzene at constant pressure.*

Solution. The reaction is

$$C_6H_6(l) + 7\tfrac{1}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$$

In this reaction, O_2 is the only gaseous reactant and CO_2 is the only gaseous product.

$$\therefore \quad \Delta n_g = n_p - n_r$$

$$= 6 - 7\tfrac{1}{2} = -1\tfrac{1}{2} = -3/2$$

Also, we are given

$$\Delta E \text{ (or } q_v) = -3263 \cdot 9 \text{ kJ mol}^{-1}$$

$$T = 25°C = 298K$$

$$R = 8 \cdot 314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= \frac{8 \cdot 314}{1000} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

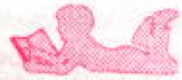
$$\Delta H \text{ (or } q_p) = \Delta E + \Delta n_g \, RT$$

$$= -3263 \cdot 9 + \left(-\frac{3}{2}\right)\left(\frac{8 \cdot 314}{1000}\right)(298)$$

$$= -3263 \cdot 9 - 3 \cdot 7$$

$$= \mathbf{-3267 \cdot 6 \text{ kJ mol}^{-1}}.$$

PROBLEMS FOR PRACTICE



1. The heat of combustion of CH_4 (g) at constant volume is measured in a bomb calorimeter at 298·2 K and found to be —885389 J/mol. Find the value of enthalpy change. **[Ans. —890347 J mol^{-1}]**
2. The enthalpy change (ΔH) for the reaction $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ is —92·38 kJ at 298 K. What is ΔU at 298K ? *(A.I.S.B. 1991 S, 2001, P.S.B. 95, N.C.E.R.T.)* **[Ans. —87·42 kJ]**
3. The internal energy change (ΔE) for the reaction $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ is −885 kJ mol^{-1} at 298 K. What is ΔH at 298 K ? *(H.P.S.B. 1994)* **[Ans. −889·96 kJ mol^{-1}]**
4. When NH_4NO_2(s) decomposes at 373 K, it forms N_2 (g) and H_2O (g). The ΔH for the reaction at one atmospheric pressure and 373 K is —223·6 kJ mol^{-1} of NH_4NO_2(s) decomposed. What is the value of ΔU for the reaction under the same conditions ? (Given R = 8·31 JK^{-1} mol^{-1}) *(A.I.S.B. 1998)* **[Ans. —232·9 kJ mol^{-1}]**
5. When 0·532 g of benzene (C_6H_6), boiling point 353 K is burnt with excess of oxygen in a constant volume system, 22·3 kJ of heat is given out. Calculate ΔH for the combustion process (R = 8·31 JK^{-1} mol^{-1}) *(A.I.S.B. 1999)* **[Ans. −3274·2 kJ mol^{-1}]**
6. The heat of combustion of naphthalene ($C_{10}H_8$ (s)) at constant volume was found to be − 5133 kJ mol^{-1}. Calculate the value of enthalpy change. **[Ans. − 5128·04 kJ mol^{-1}]**

HINTS FOR DIFFICULT PROBLEMS

4. $NH_4NO_2(s) \longrightarrow N_2(g) + 2H_2O(g)$,

$$\Delta n_g = 3 - 0 = 3$$

$$\Delta E = \Delta H - \Delta n_g RT$$

$$= -223{\cdot}6 - 3 \times (8{\cdot}314/1000) \times 373$$

$$= -232{\cdot}9 \text{ kJ mol}^{-1}.$$

5. $0{\cdot}532$ g $C_6H_6 = 0{\cdot}532/78$ mole

$$= 0{\cdot}00682 \text{ mole}$$

$$\therefore \quad \Delta E = -\frac{22{\cdot}3}{0{\cdot}00682} \text{ kJ mol}^{-1}$$

$$= -3269{\cdot}8 \text{ kJ mol}^{-1}$$

Calculate ΔH as in solved example above.

6. $C_{10}H_8(s) + 12O_2(g) \longrightarrow 10CO_2(g) + 4H_2O(l)$,

$$\Delta E = -5133 \text{ kJ mol}^{-1}$$

$$\Delta n = 10 - 12 = -2$$

ADD TO YOUR KNOWLEDGE

1. 1 cal > 1 joule > 1 erg.
2. When a real gas is allowed to expand adiabatically from a region of high pressure to a region of low pressure through a fine hole, it is accompanied by cooling except H_2 and He which get warmed up. This phenomenon is known as **Joule-Thomson effect.**
3. During adiabatic expansion of a real gas, enthalpy (but not internal energy) remains constant. It is, therefore, called **isenthalpic process.**
4. The temperature at which a real gas shows no cooling or heating effect on adiabatic expansion is called **inversion temperature.** Below this temperature it shows cooling effect while above this temperature., it shows heating effect.
5. H_2 and He have very low inversion temperatures. That is why they show heating effect at room temperature during adiabatic expansion.
6. During isothermal expansion of an ideal gas $\Delta E = 0, \Delta T = 0$

$\therefore \quad H = E + PV$ or $\Delta H = \Delta E + \Delta(PV) = \Delta E + PnR\Delta T = 0 + 0 = 0$. Hence enthalpy remains constant.

5.9. Heat Capacity, Specific Heat Capacity and Molar Heat Capacity

5.9.1. Definitions.

The heat capacity of a system is defined as the amount of heat required to raise the temperature of the system through 1°C.

Thus if q is the amount of heat supplied to a system and as a result, if the temperature of the system rises from T_1 and T_2, then the heat capacity (C) of the system is given by

$$C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T} \qquad \text{...}(i)$$

However since the heat capacity varies with temperature, therefore the value of C has to be considered over a very narrow temperature range. Thus if δq is small amount of heat absorbed by a system which raises the temperature of the system by a small amount dT (say from T to T + dT), then the heat capacity of the system will be given by

$$C = \frac{\delta q}{dT} \qquad \text{...}(ii)$$

The specific heat capacity (or specific heat) of a substance is defined as the amount of heat required to raise the temperature of 1 gram of the substance through 1°C.

If instead of 1 g, 1 mole of the substance is taken, the term used is called 'molar heat capacity'. Thus

Molar heat capacity of a substance is defined as the amount of heat required to raise the temperature of one mole of the substance through 1°C.

Example. To understand the difference between heat capacity, specific heat capacity and molar heat capacity, let us take the following example :

A piece of Al metal weighing 3 g requires 5·4 J of heat to raise the temperature from 298 K to 300 K. Then

Heat capacity of the piece of Al

$$= \frac{5\cdot 4\ \text{J}}{2\ \text{K}} = 2\cdot 7\ \text{JK}^{-1}$$

Specific heat capacity of Al

$$= \frac{5\cdot 4\ \text{J}}{3\ \text{g} \times 2\ \text{K}} = 0\cdot 9\ \text{Jg}^{-1}\text{K}^{-1}$$

Molar heat capacity of Al

$$= \frac{5\cdot 4}{3 \times 2} \times 27 = 24\cdot 3\ \text{J mol}^{-1}\ \text{K}^{-1}$$

$$(\because 1 \text{ mol of Al} = 27 \text{ g of Al})$$

Evidently, the amount of heat, q required to raise the temperature from T_1 to T_2 of mass m gram of a sample and having specific heat C, can be calculated from the expression

$$q = m \times C \times (T_2 - T_1)$$

$$= m \times C \times \Delta T$$

It is useful to remember that the specific heat capacity of water is 1 cal g^{-1} K^{-1} or $4\cdot 18\ Jg^{-1}\ K^{-1}$.

5.9.2. Types of heat capacities or molar heat capacities. Since 'q' is not a state function and depends upon the path followed, therefore C is also not a state function. Hence to know the value of C, the conditions, such as *constant volume or constant pressure* have to be specified which define the path. Thus there are two types of heat capacities, which are

(*i*) Heat capacity at constant volume (represented by C_v).

(*ii*) Heat capacity at constant pressure (represented by C_p).

The heat supplied to a system to raise its temperature through 1°C keeping the volume of the system constant is called heat capacity at constant volume. Similarly, the heat supplied to a system to raise its temperature through 1°C keeping the external pressure constant is called heat capacity at constant pressure.

Now, according to first law of thermodynamics, we know that

$$\delta q = dE + PdV \qquad ...(iii)$$

$$C = \frac{dE + PdV}{dT} \qquad ...(iv)$$

When the volume is kept constant, $dV = 0$ and, therefore, equation (*iv*) becomes

$$\boxed{C_v = \left(\frac{\partial E}{\partial T}\right)_v^{*}} \qquad ...(v)$$

or *for an ideal gas***, this equation may simply be written as

$$\boxed{C_v = \frac{dE}{dT}} \qquad ...(vi)$$

Thus the heat capacity at constant volume may be defined as the rate of change of internal energy with temperature at constant volume.

When the pressure is kept constant during the absorption of heat, equation (*iv*) becomes

$$C_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \qquad ...(vii)$$

Also, we know that the heat content or enthalpy of a system is given by

$$H = E + PV$$

Differentiating w.r.t. T at constant P, we get

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \qquad ...(viii)$$

Combining equations (*vii*) and (*viii*), we get

$$\boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P} \qquad ....(x)$$

or *for any ideal gas*, this equation may simply be put in the form

$$\boxed{C_P = \frac{dH}{dT}} \qquad ....(x)$$

Thus the heat capacity at constant pressure may be defined as the rate of change of enthalpy with temperature at constant pressure.

---

*This is called *partial differentiation* and the equation is read as C_v is equal to δE by δT at constant volume.

**For an ideal gas, it can be shown that the internal energy is independent of volume and depends only on the temperature.

Alternatively, from equation (*ii*), we can directly say that

$$C_p = \frac{(\delta q)_p}{dT}$$

But $(\delta q)_P = dH$

(according to def. of enthalpy change)

$$\therefore \quad C_p = \frac{dH}{dT}$$

Note. Heat capacities C_v and C_p as defined above are the heat capacities per mole. These are therefore, sometimes represented by $\overline{C}_v$ and $\overline{C}_p$. Hence for *n* moles of the substance, we have

$$C_v = n\,\overline{C}_v \quad \text{and} \quad C_p = n\,\overline{C}_p$$

5.9.3. Relationship between C_p and C_v. If the volume of the system is kept constant and the heat is added to a system, then no work is done by the system. Thus the heat absorbed by the system is used up completely to increase the internal energy of the system. Again if the pressure of the system is kept constant and heat is supplied to the system, then some work of expansion is also done by the system in addition to the increase in internal energy. Thus if at constant pressure, the temperature of the system is to be raised through the same value as at constant volume, then some extra heat is required for doing the work of expansion. Hence $C_p > C_v$.

The difference between the heat capacities of an ideal gas can be obtained by subtracting equation (*vi*) from equation (*x*). So we have

$$C_p - C_v = \frac{dH}{dT} - \frac{dE}{dT} \qquad \text{...(xi)}$$

But $\quad H = E + PV \quad$ (by definition)

and $\quad PV = RT \quad$ (for 1 mole of an ideal gas)

$\therefore \quad H = E + RT.$

Differentiating this equation w.r.t. T, we get

$$\frac{dH}{dT} = \frac{dE}{dT} + R \qquad \text{...(xii)}$$

$$\text{or} \quad \frac{dH}{dT} - \frac{dE}{dT} = R \qquad \text{...(xiii)}$$

Combining equation (*xi*) and (*xiii*), we get

$\boxed{C_p - C_v = R}$ for 1 mole of an ideal gas.

Thus C_p is greater than C_v by the gas constant R, *i.e.*, approximately 2 calories or 8·314 joules.

PROBLEMS ON USE OF SPECIFIC HEAT

EXAMPLE. *(a) Calculate the energy needed to raise the temperature of 10·0 g of iron from 25°C to 500°C if specific heat capacity of iron is 0·45 J $(°C)^{-1}\,g^{-1}$.*

(b) What mass of gold of specific heat capacity 0·13 J $(°C)^{-1}\,g^{-1}$ can be heated through the same temperature difference when supplied with the same amount of energy as in (a) ? **(N.C.E.R.T.)**

Solution. (*a*) Energy needed (*q*)

$$= m \times C \times \Delta T$$
$$= 10·0 \times 0·45 \times (500 - 25)\ J$$
$$= \mathbf{2137·5\ J}$$

(*b*) $q = m \times C \times \Delta T$

$$2137·5 = m \times 0·13 \times (500 - 25)$$

or $\quad m = \mathbf{34·6\ g}$

SECTION IV

ENERGY CHANGES DURING CHEMICAL REACTIONS

5.10. General Introduction

A chemical reaction involves rearrangement of atoms *i.e.* some bonds within each of the reactant molecule are broken while some new bonds in each molecule of the products are formed. Energy is required for the dissociation of bonds while energy is evolved when the bonds are formed. If the total energy evolved is greater than the total energy required, the net result is the *release of energy* and the process is called *'exothermic'*. On the other hand, if the energy required is greater than the energy evolved, the net result is the *absorption of energy* and the process is called *'endothermic'*.

Thus all chemical reactions are usually accompanied by energy changes. Ordinarily, these energy changes appear in the form of absorption or evolution of heat. However, under certain conditions, these may also appear in the form of light, work, electricity etc. These energy changes are of great practical utility both for domestic and industrial purposes. A few such reactions alongwith the form in which the accompanying energy changes manifest and the use to which they are put are given below :

(*i*) *Burning of coal in* air produces *heat*. That is why it is used as a fuel.

$$C(s) + O_2(g) \longrightarrow CO_2(g) + \text{heat.}$$

(*ii*) *Burning of natural gas* (a mixture of lower hydrocarbons) produces *heat and light*. Therefore, it is also used as a fuel.

$$\underset{\text{Methane}}{CH_4(g)} + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) + \text{heat} + \text{light}$$

$$\underset{\text{Ethane}}{2C_2H_6(g)} + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l) + \text{heat} + \text{light}$$

(*iii*) *Combustion of petrol* ($C_{10}H_{22}$) in an automobile engine produces *heat and mechanical work*. It is, therefore, used as a fuel for automobile engines.

$$2C_{10}H_{22}(l) + 31O_2(g) \longrightarrow 20CO_2(g) + 22H_2O(g)$$

(*iv*) *Slow combustion of carbohydrates* in biological systems produces *heat* which maintains the body temperature.

$$\underset{\text{Glucose}}{C_6H_{12}O_6(s)} + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) + \text{heat}$$

(*v*) *Burning of candle in air* produces heat and light. It is, therefore, used as a source of light. Taking wax as $C_{15}H_{32}$, we have

$$C_{15}H_{32}(s) + 23O_2(g) \longrightarrow 15CO_2(g) + 16H_2O(g)$$

(*vi*) *Reaction taking place in a galvanic cell* produces *electrical energy* which may be used to run an electrical motor or to ring a bell, etc.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

The branch of chemistry which deals with the study of energy changes accompanying chemical reactions is called chemical energetics.

Modes of transference of energy between the system and the surroundings. The two most common forms of energy transferred between the system and the surroundings are :

(*i*) **Heat** which is due to the difference of temperature between the system and the surroundings and flows from higher temperature to lower temperature.

(*ii*) **Work** which is due to the difference of pressure between the system and the surroundings. If pressure inside the system is higher, work is said to be done *by* the system and if pressure of the surroundings is higher, the work is said to be done *on* the system.

5.11. Exothermic and Endothermic Reactions

Exothermic Reaction. ***These are those reactions which are accompanied by the evolution of heat.***

The quantity of heat produced is shown alongwith the products with a 'plus' sign. A few examples of exothermic reactions are given below :

$$C(s) + O_2(g) \longrightarrow CO_2(g) + 393 \cdot 5 \text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) + 285 \cdot 8 \text{ kJ}$$

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) + 92 \cdot 4 \text{ kJ}$$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + 890 \cdot 4 \text{ kJ}$$

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(g) + 2658 \text{ kJ}$$

Endothermic Reactions. ***Those reactions in which heat is absorbed are called endothermic reactions.***

Although the heat absorbed can be written with a plus sign alongwith with reactants, however, it is usually shown alongwith the products with a minus sign. A few examples of endothermic reactions are given below :–

$$N_2(g) + O_2(g) \longrightarrow 2NO(g) - 180 \cdot 7 \text{ kJ}$$

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g) - 131 \cdot 4 \text{ kJ}$$

$$C(s) + 2S(s) \longrightarrow CS_2(g) - 92 \cdot 0 \text{ kJ}$$

$$H_2(g) + I_2(g) \longrightarrow 2HI(g) - 52 \cdot 5 \text{ kJ}$$

$$2HgO(s) \longrightarrow 2Hg(l) + O_2(g) - 181 \cdot 6 \text{ kJ}$$

Exothermic and Endothermic reactions in terms of ΔH. The enthalpy change (ΔH) accompanying a reaction is given by

$$\Delta H = \text{Heat content of products} - \text{Heat content of reactants}$$

$$= H_P - H_R$$

A reaction is exothermic *i.e.*, heat is given out in a reaction if the total heat content of the reactants is more than that of the products, *i.e.*,

$$H_R > H_P$$

But if it is so, then according to the above equation ΔH will be negative. Hence

ΔH is negative for exothermic reactions.

Thus the exothermic reactions given above may be written in terms of ΔH as

$$C\,(s) + O_2(g) \longrightarrow CO_2\,(g), \quad \Delta H = -393\cdot5 \text{ kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O(l), \quad \Delta H = -285\cdot8 \text{ kJ mol}^{-1}$$

$$N_2(g) + 3H_2\,(g) \longrightarrow 2NH_3(g), \quad \Delta H = -92\cdot4 \text{ kJ mol}^{-1}$$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l), \quad \Delta H = -\,890\cdot4 \text{ kJ mol}^{-1}$$

$$C_4H_{10}\,(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(g), \quad \Delta H = -2658 \text{ kJ mol}^{-1}$$

A reaction is endothermic *i.e.* heat is absorbed in a reaction if the total heat content of reactants is less than that of the products, *i.e.*, $H_R < H_P$

Then, according to the equation

$\Delta H = H_P - H_R$, ΔH will be positive. Hence

ΔH is positive for endothermic reactions.

Thus the endothermic reactions given earlier may be written in terms of ΔH as

$$N_2(g) + O_2(g) \longrightarrow 2NO(g), \quad \Delta H = +180\cdot7 \text{ kJ mol}^{-1}$$

$$C(s) + H_2O(g) \longrightarrow CO\,(g) + H_2(g), \quad \Delta H = +131\cdot4 \text{ kJ mol}^{-1}$$

$$C(s) + 2S(s) \longrightarrow CS_2(l), \quad \Delta H = +92\cdot0 \text{ kJ mol}^{-1}$$

$$H_2(g) + I_2(g) \longrightarrow 2HI(g), \quad \Delta H = +52\cdot5 \text{ kJ mol}^{-1}$$

$$2HgO(s) \longrightarrow 2Hg(l) + O_2(g), \quad \Delta H = +181\cdot6 \text{ kJ mol}^{-1}$$

Graphically, the exothermic and endothermic reactions may be represented as shown in Fig. 5.11.

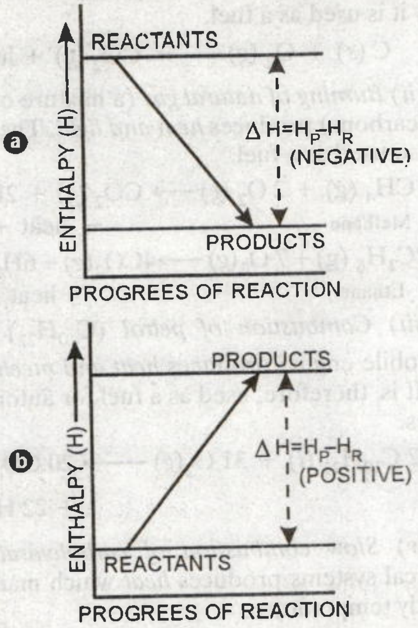


FIGURE 5.11. (a) Exothermic rection
(b) Endothermic reaciton.

5.12. Thermochemical Equation

When a balanced chemical equation not only indicates the quantities of the different reactants and products but also indicates the amount of heat evolved or absorbed (as in the above reactions), it is called a thermochemical equation.

However, contrary to the usual practice about the balanced equations, fractional coefficients may be used in writing a thermochemical equation. For example, the formation of water is written as

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) + 285\cdot8 \text{ kJ mol}^{-1}$$

$$\text{or} \quad H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O\,(l), \quad \Delta H = -285\cdot8 \text{ kJ mol}^{-1}$$

Thus 285·8 kJ of heat is produced when 1 mole of hydrogen reacts with 0·5 mole of oxygen. If the quantities of reactants are doubled, the heat produced will also be doubled. For example, in the above case, we may write

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) + 571{\cdot}6 \text{ kJ mol}^{-1}$$

or $$2H_2(g) + O_2(g) \longrightarrow 2H_2O\,(l), \quad \Delta H = -571{\cdot}6 \text{ kJ mol}^{-1}$$

Some Conventions about Thermochemical Equations

(*i*) For exothermic reactions, ΔH is negative whereas for endothermic reactions, ΔH is positive.

(*ii*) Unless otherwise mentioned, ΔH values are for the standard state of the substances (*i.e.* 298 K and 1 bar pressure).

(*iii*) The coefficients of different substances represent the number of moles reacted and formed for the heat change represented in the equation.

(*iv*) The physical state (*s, l, g* etc.) of the different substances must be mentioned as the heat evolved or absorbed depends upon the physical state (as discussed in the next section).

(*v*) If the coefficients of the susbtances are multiplied or divided by some number, the value of ΔH is multiplied or divided by the same number.

(*vi*) If the reaction is reversed, the sign of ΔH changes but the magnitude remains the same.

5.13. Heat of Reaction or Enthapy of Reaction

The amount of heat evolved or absorbed in a chemical reaction when the number of moles of the reactants as represented by the chemical equation have completely reacted, is called the heat of reaction.

Let us consider the following two examples :

$$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g), \quad \Delta H = -\ 393.5 \text{ kJ mol}^{-1}$$

$$C\,(s) + H_2O\,(g) \longrightarrow CO\,(g) + H_2\,(g), \quad \Delta H = +131{\cdot}4 \text{ kJ mol}^{-1}$$

The first equation indicates that when 1 mole of solid carbon (*i.e.* 12 g) combines completely with 1 mole of oxygen gas (*i.e.* 32 g), 393·5 kJ of heat of produced. Similarly, the second equation tells that when 1 mole of solid carbon (*i.e.* 12 g) reacts completely with 1 mole of steam (*i.e.* 18 g) 131·4 kJ of heat is absorbed.

It is interesting to note that

Heat of reaction, ΔH = Heat content of products − Heat content of reactants.

If the reaction is reversed, the sign of ΔH changes *e.g.*,

For $$H_2(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l), \quad \Delta H = -\ 285.8 \text{ kJ mol}^{-1}$$

For $$H_2O\,(l) \longrightarrow H_2\,(g) + \frac{1}{2}O_2\,(g), \quad \Delta H = +285{\cdot}8 \text{ kJ mol}^{-1}$$

Factors on which the heat of reaction depends. The heat of a reaction depends upon a number of factors as explained below :

(i) Quantities of the reactants involved. If the quantities of the reactants are doubled, the heat of reaction is also doubled. An example of this has already been given in section 5.12.

(ii) Physical state of the reactants and products. Since latent heat is involved in the change of state, therefore the physical state of the reactants and products (*i.e.,* whether they are solids, liquids or gaseous) affects the heat of reaction. For example, when hydrogen and oxygen gases combine to form liquid water, the heat of reaction is different than when they combine to form water in the gaseous state *i.e.*,

$$H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l), \quad \Delta H = -285.8 \text{ kJ mol}^{-1}$$

$$H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(g), \quad \Delta H = -248.8 \text{ kJ mol}^{-1}$$

Hence it is essential to write the symbols *s, l, g* or *aq.* to indicate whether a particular substance is solid, liquid, gaseous or an aqueous solution.

(iii) Allotropic modifications. For elements like sulphur and carbon which exist in different allotropic modifications, the heat of reaction is different if different allotropic form is involved in the reaction. For example,

$$C\,(\text{diamond}) + O_2\,(g) \longrightarrow CO_2\,(g), \quad \Delta H = -395.4 \text{ kJ mol}^{-1}$$

$$C\,(\text{graphite}) + O_2\,(g) \longrightarrow CO_2\,(g), \quad \Delta H = -393.5 \text{ kJ mol}^{-1}$$

(iv) Concentration of solutions. Heat change occurs when a solute is dissolved in a solvent to form a solution or when a solution is diluted. Therefore, if the solutions are involved in a reaction, their concentrations affect the heat of reaction.

(v) Temperature. The heat of reaction depends upon the temperature at which the reactants and products are taken. The values are usually reported at 298 K.

(vi) Conditions of constant pressure or constant volume *i.e.* whether the reaction takes place at constant pressure or at constant volume.

Standard enthalpy change. A substance in its most stable form at 25°C or 298 K under a pressure of one bar is said to be in its standard state.

The enthalpy change of a reaction when all the reactants and the products are in their standard states *i.e.* at 25° C or 298 K and under a pressure of one bar is known as the standard enthalpy change. It is usually represented by $\Delta H°_r$ or ΔH_r^{298}.

Origin of enthalpy change in a reaction. It has already been stated in the beginning of sec 5.10 that energy is required to break the bonds present between the atoms in a molecule while energy is released when bonds are formed between the atoms. Now as a chemical reaction involves breaking of bonds of the reactants and the formation of new bonds in the products, some net energy change (called the enthalpy of reaction) takes place. The simplest case is that of gaseous reactions. In case of solutions, there are interactions of the solvent with the reactants and the products and that makes the situation complicated. Thus for a gaseous reaction, we have

Enthalpy change of a reaction

$$= \begin{bmatrix} \textit{Energy required to} \\ \textit{break the bonds of} \\ \textit{the reactants} \end{bmatrix} - \begin{bmatrix} \textit{Energy released in the} \\ \textit{formation of bonds in} \\ \textit{the products} \end{bmatrix}$$

If energy required > energy released, the net result is the absorption of energy and the reaction is *endothermic*.

If energy released > energy required, the net result is the release of energy and the reaction is *exothermic*.

The above point of view is further explained with solved examples in section 5.18.

5.14. Different Types of Heats/Enthalpies of Reaction or Phase Changes

'Heat of reaction' or 'Enthalpy of reaction' is a general term used for the heat change (enthalpy change) accompanying any reaction. However, depending upon the nature of the reaction (*i.e.* combustion, neutralization etc.), the enthalpy of reaction is named accordingly (*i.e.* enthalpy of combustion, enthalpy of neutralization etc). Similarly, depending upon the type of process involving a phase change such as fusion, vaporisation, sublimation etc., the enthalpy change involved is named accordingly (*i.e.*, enthalpy of fusion, enthalpy of vaporisation etc.). A few important heats of reactions are as follows :

1. Enthalpy of combustion.

The enthalpy of combustion of a substance is defined as the heat change (usually the heat evolved) when 1 mole of substance is completely burnt or oxidized in oxygen.

e.g. $CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(g),$

$$\Delta H = -890.4 \text{ kJ mol}^{-1}$$

This reaction shows that 890.4 kJ of heat is produced when 1 mole of methane is completely burnt. Hence enthalpy of combustion of methane is 890.4 kJ mol^{-1}.

The significance of the words *'completely oxidized'* must be clearly understood. For example, carbon may be oxidized to carbon monoxide (CO) or carbon dioxide (CO_2). The heats evolved in the two cases are different, viz.,

$$C\,(s) + \frac{1}{2}O_2\,(g) \longrightarrow CO\,(g), \quad \Delta H = -110.5 \text{ kJ mol}^{-1}$$

$$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g), \quad \Delta H = -393.5 \text{ kJ mol}^{-1}$$

Complete oxidation means oxidation to CO_2 and not to CO. Hence heat of combustion of carbon is 393.5 kJ mol^{-1}.

Standard heat of combustion ***is the amount of heat evolved when one mole of the substance under standard conditions (298 K, 1 bar pressure) is completely burnt to form the products also under standard conditions. It is represented by*** $\Delta H°_c$.

Note carefully *that it is not the combustion that is taking place at 298 K, which, in fact, cannot happen. It is the total heat change that occurs when the initial reactants and final products are at 298 K irrespective of the fact that during combustion, temperature is higher than 298 K.*

Calorific values of foods and fuels. Just as the fuels like coal, kerosene oil, gasoline (petrol), diesel oil etc. are burnt to produce energy for the running of machines, similarly for the working of the human machine, we eat carbohydrates, fats etc. in the form of food. The carbohydrates are first decomposed in our body by the enzymes to form glucose which then undergoes oxidation by the oxygen that we inhale to produce energy.

$$C_6H_{12}O_6\,(s) + 6O_2\,(g) \longrightarrow 6CO_2\,(g) + 6H_2O\,(g) + 2840\text{ kJ mol}^{-1}$$

This oxidation reaction is usually called *'combustion of food'*.

Different fuels and foods produce different amounts of heat on combustion. These are usually expressed in terms of their calorific values which is defined as follows :—

The calorific value of a fuel or food is the amount of heat in calories or joules produced from the complete combustion of one gram of the fuel or the food.

Thus according to the above reaction, 1 mole of glucose *i.e.* 180 g of glucose produce heat = 2840 kJ. Hence calorific value of glucose $= \frac{2840}{180} = 15{\cdot}78\text{ kJ g}^{-1}$

A normal person needs about 3000 kcal (*i.e.* about 12000 – 13000 kJ) per day. *The food consisting of carbohydrates, oils, fats, vitamins, proteins, mineral salts etc. which provides the necessary calories is called a* **balanced diet.**

2. Enthalpy of formation.

The enthalpy of formation of a substance is defined as the heat change i.e. heat evolved or absorbed when 1 mole of the substance is formed from its elements under given conditions of temperature and pressure. It is usually represented by ΔH_f

The conditions of temperature and pressure usually chosen are 298 K and 1 bar pressure. This is called standard state. The enthalpy of formation under these conditions is called standard enthalpy of formation.

Standard enthalpy of formation ***of a substance is defined as the heat change accompanying the formation of 1 mole of the subtance in the standard state from its elements, also taken in the standard state (i.e. 298K and 1 bar pressure).*** It is usually represented by ΔH°_f.

For example, in the reaction

$$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g), \qquad \Delta H^\circ_f = -393.5\text{ kJ mol}^{-1}$$

when 1 mole of CO_2 (*g*) is formed from its elements viz C (*s*) and O_2 (*g*) (all substances being taken in the standard state), 393.5 kJ of heat is produced. Hence standard enthalpy of formation of gaseous CO_2 is 393.5 kJ mol^{-1}.

Similarly, in the reaction

$$2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(l), \qquad \Delta H^\circ_f = -571.6\text{ kJ mol}^{-1}$$

we observe that 571.6 kJ of heat is evolved when 2 moles of H_2O (*l*) are formed from the elements, all substances being taken in the standard state. Thus the heat evolved when 1 mole of liquid water is formed from its elements, would be 571.6/2 = 285.8 kJ. Hence standard enthalpy of formation of liquid water is 285.8 kJ mol^{-1}.

In many cases, however, the heat of formation cannot be determined directly. Methane (CH_4), for example, cannot be made directly from carbon and hydrogen. In such cases, the heat of formation is calculated from some other heats of reaction, using Hess's law, as will be discussed later in section 5.17.

Importance of standard enthalpies of formation. Knowing the standard enthalpies of formation of the different compounds involved in a chemical reaction, the standard enthaply change of the given reaction can be calculated using the formula*

$$\Delta H^\circ_{reaction} = \begin{bmatrix}\text{Sum of the standard enthalpies}\\ \text{of formation of products}\end{bmatrix} - \begin{bmatrix}\text{Sum of the standard enthalpies}\\ \text{of formation of reactants}\end{bmatrix}$$

i.e. $\Delta H^\circ_{reaction} = \Sigma\,\Delta H^\circ_f\,(\text{Products}) - \Sigma\,\Delta H^\circ_f\,(\text{Reactants})$

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*Actually, $\Delta H^\circ_{reaction} = \begin{bmatrix}\text{Sum of enthalpies}\\ \text{of products}\end{bmatrix} - \begin{bmatrix}\text{Sum of enthalpies}\\ \text{of reactants}\end{bmatrix}$

But if enthalpies of the elements are taken as zero, then enthalpy of any compound = its enthalpy of formation.

Thus for a general reaction

$$aA + bB \longrightarrow cC + dD$$

$$\Delta H^\circ_{reaction} = [c\Delta H^\circ_f(C) + d\,\Delta H^\circ_f(D)] - [a\,\Delta H^\circ_f(A) + b\,\Delta H^\circ_f(B)]$$

REMEMBER

For elementary substances in the standard state, the standard enthalpy of formation (ΔH_f°) is taken as zero. The standard state of an elementary substance means the most stable form of that substance at 298 K and one atmospheric pressure. It refers to the normal physical state in which it exists under these conditions and in case of elements showing allotropy, it refers to the most stable allotropic form. For example, the standard states of oxygen, bromine and iodine are O_2 (*g*), Br_2 (*l*) and I_2 (*s*) whereas standard states for carbon and sulphur are C (graphite) and S_8 (rhombic).

For example, suppose we want to predict the enthalpy of combustion of methane. The reaction is

$$CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(l)$$

$$\therefore\quad \Delta H^\circ_{reaction} = [\Delta H^\circ_f \text{ for } CO_2 + 2 \times \Delta H^\circ_f \text{ for } H_2O] - [\Delta H^\circ_f \text{ for } CH_4 + 2 \times \Delta H^\circ_f \text{ for } O_2]$$

Putting the values of enthalpies of formation in the standard state

$$\Delta H^\circ_{reaction} = [-393{\cdot}5 + 2 \times (-285{\cdot}8)] - [-74{\cdot}9 + 0]$$

$$= -965{\cdot}1 + 74{\cdot}9 = -890{\cdot}2 \text{ kJ}$$

$$[\because\ \Delta H^\circ_f \text{ for any element like } O_2 = 0]$$

3. Enthalpy of Neutralization.

The enthalpy of neutralization of an acid by a base is defined as the heat change (usually the heat evolved) when one gram equivalent of the acid is neutralized by a base, the reaction being carried out in dilute aqueous solution.

The enthalpy of neutralization of a base by an acid is defined in a similar manner.

For example, when one gram equivalent of HCl is neutralized by NaOH or one gram equivalent of NaOH is neutralized by HCl, both solutions being dilute and aqueous, 57.1 kJ of heat is produced. Thus we may write

$$NaOH + HCl \longrightarrow NaCl + H_2O, \quad \Delta H = -57.1 \text{ kJ mol}^{-1}$$

Hence enthalpy of neutralization of HCl with NaOH or NaOH with HCl is 57.1 kJ.

The enthalpy of neutralization of any strong acid (HCl, HNO_3, H_2SO_4) with a strong base (LiOH, NaOH, KOH) or vice versa, is always the same *i.e.* 57.1 kJ. This is because the strong acids, strong bases and the salts that they form, are all completely ionized in dilute aqueous solution. Thus the reaction between any strong acid and strong base *e.g.* in the above case may be written as

$$Na^+ + OH^- + H^+ + Cl^- \longrightarrow Na^+ + Cl^- + H_2O, \Delta H = -57.1 \text{ kJ mol}^{-1}$$

$$\text{or}\quad H^+\,(aq) + OH^-\,(aq) \longrightarrow H_2O\,(l), \quad \Delta H = -57.1 \text{ kJ mol}^{-1}$$

Thus neutralization is simply a reaction between the H^+ ions given by the acid with the OH^- ions given by the base to form one mole of H_2O*.

Since strong acids and strong bases ionize completely in dilute aqueous solution, the number of H^+ ions and OH^- ions produced by one gram equivalent of the strong acid and the strong base is always the same. Hence the enthalpy of neutralization between a strong acid and a strong base is always constant.

In case either the acid or the base or both are weak, the enthalpy of neutralization is usually less than 57.1 kJ. The reason for this may be understood by considering the neutralization of a weak acid like acetic acid with a strong base like NaOH. Acetic acid ionizes to a small extent whereas NaOH ionizes completely as

$$(i)\quad CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$(ii)\quad NaOH \longrightarrow Na^+ + OH^-$$

When H^+ ions given by the acid combine with the OH^- ions given by the base, the equilibrium (*i*) shifts to the right *i.e.,* more of acetic acid dissociates. A part of the heat produced during the combination of H^+ ions and OH^- ions is used up for the complete dissociation of acetic acid. The heat thus used up is called *enthalpy of dissociation* or *enthalpy of ionization*. It is 1.9 kJ for the acetic acid. Hence the net heat evolved in the above reaction is 57.1 − 1.9 = 55.2 kJ.

Similarly, in the neutralization of NH_4OH with HCl, 5.6 kJ of heat is used up for the dissociation of the weak base *i.e.* NH_4OH. Hence the enthalpy of neutralization in this case is only 57.1 − 5.6 = 51.5 kJ.

---

*The units are kJ mol^{-1} because it is for the formation of 1 mole of H_2O for the neutralisation of acid with base.

Note. The heat of neutralisation is taken for 1 **gram equivalent** of the acid and base. This is because neutralisation involves combination of 1 mol of H^+ ions with 1 mol of OH^- ions (as explained above) to form one mol of H_2O. One gram equivalent of any acid on complete dissociation gives 1 mol of H^+ ions. But 1 mol of an acid on dissociation may not give 1 mol of H^+ ions *e.g.* 1 mol H_2SO_4 gives 2 moles of H^+ ions on complete dissociation. However one gram equivalent of H_2SO_4 (= 0·5 mol) gives 1 mol of H^+ ions.

4. Enthalpy of Solution.

The enthalpy of solution of a substance in a particular solvent is defined as the enthalpy change (i.e. amount of heat evolved or absorbed) when 1 mole of the substance is dissolved in such a large volume of the solvent that further addition of the solvent does not produce any more heat change.

Water is usually used as the solvent and the symbol aq (aqueous) is used to represent it at large dilutions (infinite dilutions). Thus the thermochemical equations for the dissolution of KCl and $CuSO_4$ may be represented as

$$KCl\,(s) + aq \longrightarrow KCl\,(aq), \qquad \Delta H = +18.6 \text{ kJ mol}^{-1}$$

$$CuSO_4\,(s) + aq \longrightarrow CuSO_4\,(aq), \qquad \Delta H = -66.5 \text{ kJ mol}^{-1}$$

Thus the first case is endothermic and enthalpy of solution = + 18·6 kJ mol^{-1}

The second case is exothermic and enthalpy of solution = − 66·5 kJ mol^{-1}

It is interesting to note that the salts like copper sulphate, calcium chloride etc., when present in the hydrated state (*i.e.* $CuSO_4.5H_2O$, $CaCl_2.6H_2O$ etc.) dissolve with the absorption of heat. For example,

$$CuSO_4.5H_2O + aq \longrightarrow CuSO_4\,(aq), \qquad \Delta H = +11.7 \text{ kJ}$$

Thus it can be generalized that the process of dissolution is usually endothermic for

(*i*) salts which do not form hydrates like NaCl, KCl, KNO_3 etc.

(*ii*) hydrated salts like $CuSO_4.5H_2O$, $CaCl_2 . 6H_2O$ etc.

5. Enthalpy of Hydration.

The amount of enthalpy change (i.e. the heat evolved or absorbed) when one mole of the anhydrous salt combines with the required number of moles of water so as to change into the hydrated salt, is called the enthalpy of hydration or heat of hydration.

For example, the heat of hydration of copper sulphate is −78·2 kJ mol^{-1}. This may be represented as

$$CuSO_4\,(s) + 5H_2O \longrightarrow CuSO_4.5H_2O\,(s), \qquad \Delta H = -78\cdot2 \text{ kJ mol}^{-1}$$

IMPORTANT

It is interesting to note that the magnitude of enthalpy change represented alongwith the balanced equation is for the number of moles of different reactants reacted and the number of moles of different products formed, yet the units of $\Delta H^\circ_{reaction}$ are always written as kJ mol^{-1}. This is because if an equation is multiplied by a number, the units do not change. For example,

$$H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l), \qquad \Delta H^\circ = -285\cdot8 \text{ kJ mol}^{-1}$$

The units of ΔH° are kJ mol^{-1}. If we mutiply this equation by 2, we get

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(l), \qquad \Delta H^\circ = -571\cdot6 \text{ kJ mol}^{-1}$$

The units of ΔH° are again kJ mol^{-1}.

5.15. Measurement of Enthalpy of Reactions

5.15.1. Measurement of enthalpy of combustion at constant volume (q_v or ΔE). The heat of combustion at constant volume *i.e.* internal energy change is measured experimentally using an apparatus called **Bomb calorimeter,** as shown in Fig. 5.12.

It consists of a strong vessel (called *'bomb'*) which can stand high pressures. It is surrounded by a bigger vessel which contains water and is insulated. A thermometer and a stirrer are suspended in it. The procedure consists of the following two steps :

(*i*) *Combustion of known mass of a compound whose heat of combustion is known.* A known mass of the compound is taken in the platinum cup. Oxygen under high pressure is introduced into the bomb. A current is passed through the filament

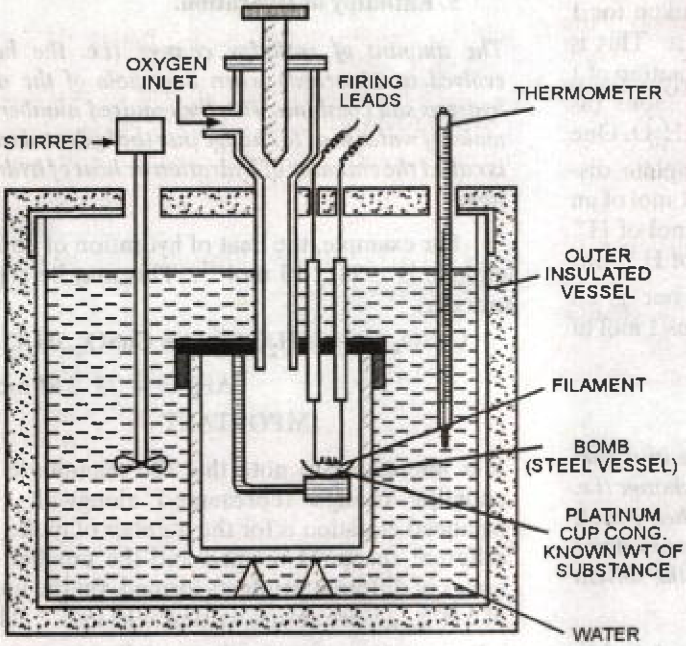

FIGURE 5.12. Bomb calorimeter.

immersed in the compound. Combustion of the compound takes place. The increase in the temperature of water is noted. From this the heat capacity of the apparatus (*i.e.* heat absorbed per degree rise of temperature) can be calculated.

(*ii*) *Combustion of known mass of the experimental compound.* The experiment is repeated as in step (*i*)

In the above case, as the reaction is carried out in a closed vessel, therefore heat evolved is the heat of combustion at constant volume and hence is equal to the internal energy change.

The value of ΔE can be calculated using the formula

$$\Delta E = Q \times \Delta t \times \frac{M}{m}$$

where Q = heat capacity of the calorimeter
Δt = rise in temperature
m = mass of the substance taken
and M = molecular mass of the substance

Note. $\Delta H = \Delta E + P\Delta V$. In a bomb calorimeter, $\Delta V = 0$. Hence we should have $\Delta H = \Delta E$. However, this is not true because the relation $\Delta H = \Delta E + P\Delta V$ holds good only at constant pressure. This may be seen as follows :

$$H = E + PV$$

$$\therefore \quad \Delta H = \Delta E + P\Delta V + V\Delta P$$

At constant pressure, $\Delta P = 0$. Hence

$$\Delta H = \Delta E + P\Delta V$$

At constant volume, $\Delta V = 0$. Hence $\Delta H = \Delta E + V\Delta P$.

5.15.2. Measurement of Heat of neutralisation. The heat of neutralisation of an acid with a base or vice versa can be determined using a simple calorimeter consisting of a polythene bottle* fitted with a cork having two holes, one for the thermometer and the other for the stirrer, as shown in Fig. 5.13. Taking the example of neutralisation of HCl with NaOH, the method consists of the following steps :

(*i*) A known volume of HCl of known concentration (say 100 cm^3 of 0·5 N) is taken in one beaker and an equal volume of NaOH of the same concentration (i.e. 100 cm^3 of 0·5 N) is taken in another beaker.

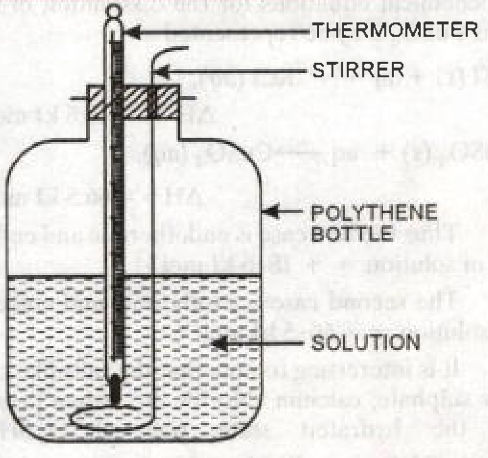

FIGURE 5.13. Measurement of heat of neutralisation.

(*ii*) Both the beakers are kept in water bath till the solutions attain the same temperature.

(*iii*) HCl solution kept in the first beaker is transferred into the polythene bottle. Immediately NaOH solution kept in the second beaker is added into the polythene bottle. Stirring is done to mix HCl and NaOH. The highest temperature attained is noted.

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*Instead of polythene bottle, a foamed polystyrene cup with a cover is also sometimes used. It is called **coffee-cup calorimeter.**

Calculations. Assuming that the density of the solution is same as that of water (i.e. $1 g/cm^3$) and the specific heat of the solution is nearly equal to that of water (i.e. $4{\cdot}184\ JK^{-1}\ g^{-1} = 4{\cdot}2\ JK^{-1}\ g^{-1}$) and neglecting the heat capacity of the polythene bottle, the result is calculated as follows –

Suppose the initial temperature of the acid and the base = $t°_1$C

Final tempearature of the solution after mixing = $t°_2$C

$\therefore$ Rise in temperature = $(t_2 - t_1)$°C

Total mass of the solution = 100 + 100 = 200 g

$\therefore$ Heat produced = Mass × Specific heat × Rise in temp.

$$= 200 \times 4{\cdot}184 \times (t_2 - t_1)\ J = x\ J \text{ (say)}.$$

This is the heat produced by neutralisation of 100 cc of 0·5 N HCl.

$\therefore$ Heat produced by neutralisation of 1000 cc of 1 N HCl (containing one gram equivalent of HCl)

$$= \frac{x}{100} \times 1000 \times \frac{1}{0{\cdot}5} \text{ joules}$$

5.15.3. Measurement of heat of reaction at constant pressure (q_p or ΔH). For any reaction occurring in solution, the heat change accompanying the reaction at constant pressure, q_p (generally under atmospheric pressure) *i.e.* the enthalpy change (ΔH) can be measured by using the calorimeter shown in Fig. 5.13. The reaction is allowed to take place in the polythene bottle. If the reaction is exothermic, temperature will rise and if reaction is endothermic, temperature will fall. The result is calculated as above. For exothermic reactions, ΔH is negative whereas for endothermic reactions. ΔH is positive, as already explained.

Alternatively, for the measurement of q_p or ΔH, the reaction may be carried out in a vessel with conducting walls. This vessel may be placed in an insulated outer vessel containing water and filled with a stirrer and a thermometer. The rise or fall in temperature may be recorded and the result calculated.

PROBLEMS ON CALCULATION OF ENTHALPY OF COMBUSTION AND ENTHALPY OF NEUTRALISATION

• **EXAMPLE 1.** *A 1·250 g sample of octane (C_8H_{18}) is burned in excess of oxygen in a bomb calorimeter. The temperature of the calorimeter rises from 294·05 K to 300·78 K. If heat capacity of the calorimeter is 8·93 kJ/K, find the heat transferred to the calorimeter. Also calculte the enthalpy combustion of the sample of octane.* **(N.C.E.R.T.)**

Solution. Rise in temperature

$$= 300{\cdot}78 - 294{\cdot}05\ K = 6{\cdot}73\ K$$

Heat transferred to the calorimeter = Heat capacity of the calorimeter × Rise in temp.

$$= (8{\cdot}93\ kJ\ K^{-1})\ (6{\cdot}73\ K) = \mathbf{60{\cdot}1\ kJ}$$

Molar mass of $C_8H_{18} = 8 \times 12 + 18$

$$= 114\ g\ mol^{-1}$$

$\therefore$ Enthalpy of combustion

$$= \frac{60{\cdot}1}{1{\cdot}250} \times 114\ kJ\ mol^{-1}$$

$$= \mathbf{5481{\cdot}1\ kJ\ mol^{-1}}$$

• **EXAMPLE 2.** *Calculate the amount of heat evolved when*

(i) 500 cm³ of 0.1 M hydrochloric acid is mixed with 200 cm³ of 0·2 M sodium hydroxide solution

(ii) 200 cm³ of 0·2M sulphuric acid is mixed with 400 cm³ of 0.5 M potassium hydroxide solution.

Assuming that the specific heat of water is 4·18J K⁻¹ g⁻¹ and ignoring the heat absorbed by the container, thermometer, stirrer etc., what would be the rise is temperature in each of the above cases ?

Solution. (*i*) 500 cm³ of 0·1 M HCl

$$= \frac{0{\cdot}1}{1000} \times 500 \text{ mole of HCl}$$

$$= 0{\cdot}05 \text{ mole of HCl}$$

$$= 0{\cdot}05 \text{ mole of } H^+ \text{ ions}$$

200 cm³ of 0·2 M NaOH

$$= \frac{0{\cdot}2}{1000} \times 200 \text{ mole of NaOH}$$

$$= 0{\cdot}04 \text{ mole of NaOH}$$

$$= 0{\cdot}04 \text{ mole of } OH^- \text{ ions}$$

Thus 0·04 mole of H^+ ions will combine with 0·04 mole of OH^- ions to form 0·04 mole of H_2O and 0·01 mole of H^+ ions will remain unreacted. Heat evolved when 1 mole of H^+ ions combine with 1 mole of OH^- ions = 57.1 kJ.

$\therefore$ Heat evolved when $0\cdot04$ mole of H^+ ions combine with $0\cdot04$ mole of OH^- ions

$$= 57.1 \times 0\cdot04 = \mathbf{2.284\ kJ}$$

(*ii*) 200 cm³ of $0\cdot2$ M H_2SO_4

$$= \frac{0\cdot2}{1000} \times 200 \text{ mole of } H_2SO_4$$

$$= 0\cdot04 \text{ mole of } H_2SO_4$$

$$= 0\cdot08 \text{ mole of } H^+ \text{ ions}$$

400 cm³ of $0\cdot5$ M KOH

$$= \frac{0\cdot5}{1000} \times 400 \text{ mole of KOH}$$

$$= 0\cdot2 \text{ mole of KOH}$$

$$= 0\cdot2 \text{ mole of } OH^- \text{ ions}$$

Thus $0\cdot08$ mole of H^+ ions will neutralize $0\cdot08$ mole of OH^- ions. (out of $0\cdot2$ mole of OH^- ions) to form $0\cdot08$ mole of H_2O.

Hence heat evolved $= 57\cdot1 \times 0\cdot08$

$$= \mathbf{4\cdot568\ kJ}$$

In case (i), heat produced $= 2\cdot284$ kJ

$$= 2284 \text{J}$$

Total mass of the solution $= 500 + 200 = 700$ g

Specific heat $= 4\cdot18\ \text{J K}^{-1} g^{-1}$

$$Q = m \times s \times \Delta t$$

$$\therefore \quad \Delta t = \frac{Q}{m \times s}$$

$$= \frac{2284}{700 \times 4\cdot18} = \mathbf{0\cdot78^\circ}$$

In case (ii), heat produced $= 4\cdot568$ kJ

$$= 4568 \text{ J}$$

Total mass of the solution $= 200 + 400$

$$= 600\text{g}$$

$$\therefore \quad \Delta t = \frac{Q}{m \times s} = \frac{4568}{600 \times 4\cdot18} = \mathbf{1\cdot82^\circ}$$

PROBLEMS FOR PRACTICE

1. $0\cdot562$ g of a sample of graphite was taken in a bomb calorimeter in presence of excess of oxygen at 298 K and 1 atm pressure. When it was completely burnt, the temperature rose to $298\cdot89$ K. If the heat capacity of the calorimeter and its contents is $20\cdot7\ \text{kJ K}^{-1}$, calculate the standard enthalpy of combustion of graphite. [Ans. $\mathbf{-393\cdot4\ kJ\ mol^{-1}}$]

2. $20\cdot0$ *g* of ammonium nitrate (NH_4NO_3) is dissolved in 125 *g* of water in a coffee-cup calorimeter, the temperature falls from $296\cdot5$ K to $286\cdot4$ K. Find the value of *q* for the calorimeter. (**Hint.** Treat heat capacity of water as the heat capacity of the calorimeter and its content).

(N.C.E.R.T.) [Ans. $\mathbf{-5\cdot28\ kJ}$]

HINTS FOR DIFFICULT PROBLEMS

1. $$\Delta H_{\text{combustion}} = -\frac{(20\cdot7\ \text{kJ K}^{-1}) \times (0\cdot89\ \text{K})}{0\cdot562\ g} \times 12\ g\ \text{mol}^{-1}$$

$$= -393\cdot4\ \text{kJ mol}^{-1}.$$

2. As heat capacity of water = heat capacity of calorimeter, the heat gained by water = heat lost by the calorimeter

$$= 125 \times (296\cdot5 - 286\cdot4) \times 4\cdot184\ \text{J}$$

$$= 52\cdot82\ \text{J} = 5\cdot282\ \text{kJ}.$$

5.16. Enthalpy Changes During Phase Transitions

1. Heat of Fusion.

Heat of fusion is the heat change accompanying the transformation of one mole of a solid substance into its liquid state at its melting point.

For example, the heat of fusion (ΔH_{fus}) of ice (m.p. = 273 K) is $6\cdot0$ kJ mol⁻¹. It may be represented as :

$$\underset{\text{Ice}}{H_2O\,(s)} \longrightarrow \underset{\text{Water}}{H_2O\,(l)}, \Delta H = +\,6\cdot0\ \text{kJ mol}^{-1}$$

2. Heat of Vaporisation.

It is the heat change accompanying the conversion of one mole of a liquid into its gaseous state at its boiling point.

For example, the heat of vaporisation ($\Delta H_{vap.}$) of water into its gaseous state (steam) at the boiling point of water (373 K) is $40\cdot7$ kJ. It may be represented as

$$\underset{\text{Water}}{H_2O\,(l)} \longrightarrow \underset{\text{Steam}}{H_2O\,(g)},\ \Delta H = +40{\cdot}7\ \text{kJ mol}^{-1}$$

3. Heat of Sublimation.

Sublimation is a process in which a solid on heating changes directly into gaseous state below its melting point.

Heat of sublimation of a substance is the heat change accompanying the conversion of 1 mole of a solid directly into vapour phase at a given temperature below its melting point.

For example, the heat of sublimation of iodine is 62·39 kJ mol^{-1}.

$$I_2\,(s) \longrightarrow I_2\,(g),\ \Delta H = +62{\cdot}39\ \text{kJ mol}^{-1}$$

Most solids that sublime readily are molecular solids, *e.g.*, iodine, naphthalene etc.

It may be pointed out that sublimation is nothing but fusion and vaporisation carried out in one step, *i.e.*,

$$\Delta H_{\text{sublimation}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vaporisation}}$$

Otherwise also, this equation is true because enthalpy is a state property.

The magnitude of enthalpy change for a phase transition depends upon the strength of intermolecular forces *e.g.* ΔH_{vap} for H_2O is much larger than that for acetone because the former has intermolecular hydrogen bonding.

IUPAC symbols used in representing different types of enthalpy changes. According to the latest IUPAC recommendations, the entualpy change accompanying any physical change or a chemical reaction is represented by putting symbol for the type of change or reaction as subscript with the symbol Δ followed by H, *e.g.* heat of combustion by Δ_c H, heat of formation by Δ_f H, heat of reaction by Δ_r H, heat of vaporisation by Δ_v H (or Δ_{vap} H), heat of fusion by $\Delta_{\text{fus}}\,\Delta$, heat of sublimation by Δ_{sub} H, heat of neutralization by Δ_{neut} H etc. For the standard state conditions, superscript $\ominus$ is used with H, *i.e.* we write,

$\Delta_r H^{\ominus}$, $\Delta_c H^{\ominus}$, $\Delta_f H^{\ominus}$ etc. However, more common way of representation is ΔH_c, ΔH_f etc. or ΔH_c°, ΔH_f° etc.

5.17. Hess's Law of Constant Heat Summation

G.H. Hess, a Russian chemist, in 1840, gave a law about the heats of reactions on the basis of experimental observations. This law is known after his name as Hess's law. It states as follows :—

The total amount of heat evolved or absorbed in a reaction is the same whether the reaction takes place in one step or in a number of steps. In other words, the total amount of heat change in a reaction depends only upon the nature of the initial reactants and the nature of the final products and is independent of the path or the manner by which this change is brought about.

Basis of Hess's Law. Hess'a law follows from the fact that enthalpy is a state function *i.e.* enthalpy change depends only on the initial state (*i.e.* enthalpy of the reactants) and the final state (*i.e.* enthalpy of the products) and does not depend upon the path followed.

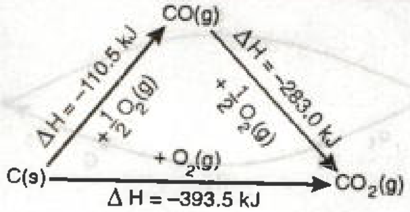
Examples. (1) When carbon (graphite) burns to form carbon dioxide directly in one step, 393·5 kJ mol^{-1} of heat is produced *i.e.*

$$C(s) + O_2(g) \longrightarrow CO_2\,(g),\ \Delta H = -393{\cdot}5\ \text{kJ mol}^{-1}$$

If carbon burns to form carbon monoxide first which then burns to form carbon dioxide, the heats evolved in the two steps are as follows :—

$$(i)\ C\,(s) + \tfrac{1}{2}O_2\,(g) \longrightarrow CO\,(g),$$
$$\Delta H = -110{\cdot}5\ \text{kJ mol}^{-1}$$

$$(ii)\ CO(g) + \tfrac{1}{2}O_2\,(g) \longrightarrow CO_2\,(g),$$
$$\Delta H = -283{\cdot}0\ \text{kJ mol}^{-1}$$



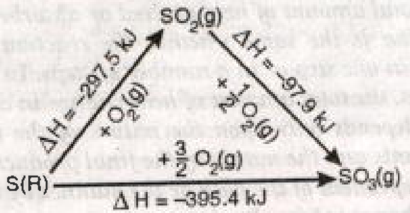
Thus the total heat evolved in the two steps will be ΔH = (− 110.5) + (−283·0) = − 393·5 kJ mol^{-1} which is the same when the reaction takes place directly in one step.

(2) Sulphur (Rhombic) burns to form SO_3 directly in one step as

$$S\,(R) + \tfrac{3}{2}O_2\,(g) \longrightarrow SO_3\,(g),$$
$$\Delta H = -395{\cdot}4\ \text{kJ mol}^{-1}$$

Sulphur may change to SO_3 in two steps as

$$(i)\ S\,(R) + O_2\,(g) \longrightarrow SO_2\,(g),$$
$$\Delta H = -297{\cdot}5\ \text{kJ mol}^{-1}$$



(*ii*) $SO_2\,(g) + \frac{1}{2}\,O_2\,(g) \longrightarrow SO_3\,(g)$,

$$\Delta H = -97 \cdot 9 \text{ kJ mol}^{-1}$$

Total heat evolved in the two steps is

$$\Delta H = -297 \cdot 5 + (-97 \cdot 9) = -395 \cdot 4 \text{ kJ mol}^{-1}$$

This is the same as for the direct reaction in one step.

Theoretical Proof of Hess's Law. Consider the general reaction $A \longrightarrow D$

Suppose the heat evolved in this reaction directly is Q joules.

Now suppose the same reaction takes place in three steps as follows :–

$$A \longrightarrow B \longrightarrow C \longrightarrow D$$

Suppose the heats evolved in these three steps are q_1, q_2, q_3 joules respectively.

Thus the total heat evolved $= q_1 + q_2 + q_3$

$= Q'$ joules (say)

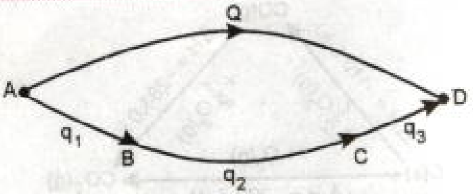


FIGURE 5.14. Theoretical Proof of Hess's Law.

According to Hess's law, we must have $Q = Q'$

If Hess's law were not correct, then either $Q' < Q$ or $Q' > Q$.

Suppose $Q' > Q$. This means that if we go from A to D in a number of steps, the heat evolved is more than the heat absorbed when we return from D to A directly in one step. (Remember that for the direct process $A \longrightarrow D$, Q joules of heat is evolved. So for the reverse process viz. $D \longrightarrow A$, Q' joules of heat will be absorbed). Thus when the cyclic process is completed, $Q - Q'$ joules of heat is produced. Thus by repeating the cyclic process a number of times, a large amount of heat can be created. This is, however, against the law of conservation of energy. Hence Q must be equal to Q′ *i.e.* Hess's law must be correct.

Applications of Hess's Law. The most important application of Hess's law is in the calculation of heat changes for those reactions for which experimental determintion is not possible. The calculations are based upon the following consequence of Hess's law :–

The thermochemical equations can be treated as algebraic equations which can be added, substracted, multiplied or divided.

A few important applications of Hess's law are given below :–

1. Calculation of enthalpy of formation. The enthalpies of formation of many compounds cannot be determined experimentally. These are calculated by the application of Hess's law. The following examples illustrate the method :–

EXAMPLE 1. *Calculate the enthalpy of formation of methane (CH_4) from the following data :*

(*i*) $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$,

$$\Delta H = -393 \cdot 7 \text{ kJ mol}^{-1}$$

(*ii*) $H_2\,(g) + \frac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(l)$,

$$\Delta H = -285 \cdot 8 \text{ kJ mol}^{-1}$$

(*iii*) $CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(l)$,

$$\Delta H = -890 \cdot 4 \text{ kJ mol}^{-1}$$

Solution. We aim at

$$C\,(s) + 2H_2\,(g) \longrightarrow CH_4\,(g)\,; \quad \Delta H = ?$$

Multiplying equation (*ii*) with 2, adding to (*i*) and then subtracting equation (*iii*) from the sum *i.e.* operating (*i*) + 2 × (*ii*) – (*iii*), we get

$$C(s) + 2H_2\,(g) - CH_4\,(g) \longrightarrow 0,$$

$$\Delta H = -393 \cdot 7 + 2\,(-285 \cdot 8) - (-890 \cdot 4)$$

$$= -74 \cdot 9 \text{ kJ mol}^{-1}$$

or $C\,(s) + 2H_2\,(g) \longrightarrow CH_4\,(g)\,;$

$$\Delta H = -74 \cdot 9 \text{ kJ mol}^{-1}$$

Hence heat of formation of methane is

$$\Delta H_f = -74 \cdot 9 \text{ kJ mol}^{-1}$$

EXAMPLE 2. *Calculate the enthalpy of formation of carbon monoxide (CO) from the following data :*

$$(i)\quad C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -393\cdot3 \text{ kJ mol}^{-1}$$

$$(ii)\quad CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -282\cdot8 \text{ kJ mol}^{-1}$$

Solution. We aim at

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g);\ \Delta H = ?$$

Subtracting equation (*ii*) from (*i*), we get

$$C(s) + \frac{1}{2}O_2(g) - CO(g) \longrightarrow 0;$$

$$\Delta H = -393\cdot3-(-282\cdot8) = -110\cdot5 \text{ kJ mol}^{-1}$$

$$\text{or}\quad C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g);$$

$$\Delta H = -110\cdot5 \text{ kJ.}$$

∴ Heat of formation of CO is

$$\mathbf{\Delta H_f = 110\cdot5 \text{ kJ mol}^{-1}}$$

2. Calculation of enthalpy of allotropic transformation. Elements like carbon and sulphur exist in different allotropic forms. The change of one form to the other involves a very small amount of heat and is a very slow process. Hence the experimental determination of heat changes for such transformations is very difficult. These are calculated by the application of Hess's law as illustrated by the example given below :–

EXAMPLE. *Calculate the enthalpy change accompanying the transformation of C (graphite) to C(diamond). Given that the enthalpies of combustion of graphite and diamond are 393·5 and 395·4 kJ mol^{-1} respectively.*

Solution. We are given

$$(i)\quad C\text{(graphite)} + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -393\cdot5 \text{ kJ mol}^{-1}$$

$$(ii)\quad C\text{(diamond)} + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -395\cdot4 \text{ kJ mol}^{-1}$$

We aim at

$$C\text{(graphite)} \longrightarrow C\text{(diamond)},\ \Delta H = ?$$

Subtracting equation (*ii*) from (*i*), we get

$$C\text{(graphite)} - C\text{(diamond)} \longrightarrow 0;$$

$$\Delta H = -393\cdot5 - (-395.4) = +1\cdot9 \text{ kJ}$$

$$\text{or}\quad C\text{(graphite)} \longrightarrow C\text{(diamond)};$$

$$\mathbf{\Delta H = +1\cdot9 \text{ kJ}}$$

3. Calculation of the enthalpy of hydration. The experimental determination of the enthalpy of hydration is almost impossible. However, it can be easily calculated using Hess's law as illustrated by the following example :

EXAMPLE. *Calculate the enthalpy of hydration of anhydrous copper sulphate ($CuSO_4$) into hydrated copper sulphate ($CuSO_4.5H_2O$). Given that the enthalpies of solutions of anhydrous copper sulphate and hydrated copper sulphate are – 66·5 and + 11·7 kJ mol^{-1} respectively*

Solution. We are given

$$(i)\quad CuSO_4(s) + aq \longrightarrow CuSO_4(aq); \quad \Delta H = -66\cdot5 \text{ kJ mol}^{-1}$$

$$(ii)\quad CuSO_4.5H_2O(s) + aq \longrightarrow CuSO_4(aq); \quad \Delta H = +11\cdot7 \text{ kJ mol}^{-1}$$

We aim at

$$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4.5H_2O(s);\ \Delta H = ?$$

Equation (*i*) can be written in two steps as

$$(iii)\quad CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4.5H_2O(s);\ \Delta H = q_1 \text{ kJ mol}^{-1}$$

$$(iv)\quad CuSO_4.5H_2O(s) + aq \longrightarrow CuSO_4(aq);\ \Delta H = q_2 \text{ kJ mol}^{-1}$$

According to Hess's law $q_1 + q_2 = -66\cdot5$ kJ mol^{-1}

Further, equations (*ii*) and (*iv*) are same.

$$\therefore\quad \mathbf{q_2 = +11\cdot7 \text{ kJ mol}^{-1}}$$

Putting this value above, we get

$$q_1 + 11\cdot7 = -66\cdot5$$

$$\text{or}\quad q_1 = -66\cdot5 - 11\cdot7 \text{ kJ}$$

$$= -78\cdot2 \text{ kJ mol}^{-1}$$

Thus equation (*iii*) may be written as

$$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4.5H_2O(s);\ \Delta H - 78\cdot2 \text{ kJ mol}^{-1}$$

This is what we aimed at. Hence the required value of the enthalpy of hydration is ΔH = **– 78·2 kJ mol^{-1}.**

***If may be noted that the heat change for the same reaction is sometimes slightly different in different problems as these are the values reported by different workers and depend upon the conditions of temperature etc.**

4. Predicting the enthalpy change for any reaction. Hess's law can be applied to predict the enthalpy change for any reaction from the enthalpy changes of certain other reactions. The numerical problems given below will illustrate the application of Hess's law.

SOME ADDITIONAL NUMERICAL PROBLEMS ON HESS'S LAW

TYPE I. On the calculation of heats of formation

EXAMPLE 1. *The enthalpy of combustion of ethyl alcohol (C_2H_5OH) is 1380.7 kJ mol^{-1}. If the enthalpies of formation of CO_2 and H_2O are 394·5 and 286·6 kJ mol^{-1} respectively, calculate the enthalpy of formation of ethyl alcohol.*

Solution. We are given :

(*i*) $C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O,\quad \Delta H = -1380\cdot7\ \text{kJ mol}^{-1}$

(*ii*) $C + O_2 \longrightarrow CO_2,\ \Delta H = -394\cdot5\ \text{kJ mol}^{-1}$

(*iii*) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O,\ \Delta H = -286\cdot6\ \text{kJ mol}^{-1}$

We aim at

$$2C + 3H_2 + \frac{1}{2}O_2 \longrightarrow C_2H_5OH$$

In order to get this thermochemical equation, multiply Eq. (*ii*) by 2 and Eq. (*iii*) by 3 and substract Eq. (*i*) from their sum, *i.e.* operating 2 × Eqn. (*ii*) + 3 × Eqn (*iii*) – Eqn (*i*), we get

$$2C + 3H_2 + \frac{1}{2}O_2 \longrightarrow C_2H_5OH\ ;$$

$$\Delta H = 2(-394\cdot5) + 3(-286\cdot6) - (-1380.7)$$
$$= -268\cdot1\ \text{kJ mol}^{-1}$$

Thus the heat of formation of ethyl alcohol is

$$\Delta H_f = \mathbf{-268\cdot1\ kJ\ mol^{-1}}$$

EXAMPLE 2. *Calculate the enthalpy of formation of methane, given that the enthalpies of combustion of methane, graphite and hydrogen are 890·2 kJ, 393·4 kJ and 285·7 kJ mol^{-1} respectively.*

Solution. We are given :

(*i*) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O,\quad \Delta H = -890\cdot2\ \text{kJ mol}^{-1}$

(*ii*) $C + O_2 \longrightarrow CO_2,\quad \Delta H = -393\cdot4\ \text{kJ mol}^{-1}$

(*iii*) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O,\quad \Delta H = -285\cdot7\ \text{kJ mol}^{-1}$

We aim at :

$$C + 2H_2 \longrightarrow CH_4,\ \Delta H = ?$$

In order to get this thermochemical equation, multiply Eq. (*iii*) by 2 and add it to Eq. (*ii*) and then subtract Eq. (*i*) from their sum. We get :

$$C + 2H_2 \longrightarrow CH_4,$$

$$\Delta H = -393\cdot4 + 2(-285\cdot7) - (-890\cdot2)\ \text{kJ mol}^{-1}$$
$$= -74\cdot6\ \text{kJ mol}^{-1}$$

Hence the heat of formation of methane is

$$\Delta H_f = \mathbf{-74\cdot6\ kJ\ mol^{-1}}$$

EXAMPLE 3. *Calculate the heat of formation of KCl from the following data :*

(*i*) $KOH\ (aq) + HCl\ (aq) \longrightarrow KCl\ (aq) + H_2O\ (l),\quad \Delta H = -57\cdot3\ kJ\ mol^{-1}$

(*ii*) $H_2\ (g) + \frac{1}{2}O_2\ (g) \longrightarrow H_2O\ (l),\quad \Delta H = -286\cdot2\ kJ\ mol^{-1}$

(*iii*) $\frac{1}{2}H_2\ (g) + \frac{1}{2}Cl_2\ (g) + aq \longrightarrow HCl\ (aq),\quad \Delta H = -164\cdot4\ kJ\ mol^{-1}$

(*iv*) $K(s) + \frac{1}{2}O_2\ (g) + \frac{1}{2}H_2(g) + aq \longrightarrow KOH(aq),\quad \Delta H = -487\cdot4\ kJ\ mol^{-1}$

(*v*) $KCl\ (s) + aq \longrightarrow KCl\ (aq),\quad \Delta H = +18\cdot4\ kJ\ mol^{-1}$

Solution. We aim at

$$K\ (s) + \frac{1}{2}Cl_2\ (g) \longrightarrow KCl\ (s),\ \Delta H = ?\ ...(vi)$$

In order to get this thermochemical equation, we follow the following two steps :

Step I. Adding Eqns. (*iii*) and (*iv*) and subtracting Eq. (*v*), we have

$$K\ (s) + \frac{1}{2}Cl_2\ (g) + H_2\ (g) + \frac{1}{2}O_2\ (g) \longrightarrow KCl\ (s) + HCl\ (aq) + KOH\ (aq) - KCl\ (aq)$$

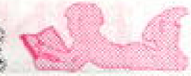
$$\Delta H = -487\cdot4 + (-164\cdot4) - (18\cdot4)$$
$$= -670\cdot2\ \text{kJ mol}^{-1} \quad ...(vii)$$

Step 2. To cancel out the terms of this equation which do not appear in the required equation (*vi*), add Eq. (*i*) to Eq. (*vii*) and subtract Eq. (*ii*) from their sum. This gives

$$K\ (s) + \frac{1}{2}Cl_2\ (g) \longrightarrow KCl\ (s)\ ;$$

$$\Delta H = -670\cdot2 + 57\cdot3 - (-286\cdot2)$$
$$= \mathbf{-441\cdot3\ kJ\ mol^{-1}}$$

PROBLEMS FOR PRACTICE



1. Ethylene on combustion gives carbon dioxide and water. Its enthalpy of combustion is 1410.0 kJ/mol. If the enthalpy of formation of CO_2 and H_2O are 393.3 kJ and 286.2 kJ respectively. Calculate the enthalpy of formation of ethylene.

   [Ans. +51.0 kJ mol^{-1}]

2. Calculate the enthalpy of formation of carbon disulphide given that the enthalpy of combustion of carbon disulphide is 110.2 kJ mol^{-1} and those of sulphur and carbon are 297.4 kJ and 394.5 kJ/g atom respectively. [Ans. – 879.1 kJ mol^{-1}]

3. Calculate the enthalpy of formation of acetic acid from the following data :

   (i) $C(s) + O_2(g) \longrightarrow CO_2(g)$, $\Delta H = -393.7$ kJ

   (ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$, $\Delta H = -285.8$ kJ

   (iii) $CH_3COOH(l) + 2O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$, $\Delta H = -873.2$ kJ

   [Ans. – 485.8 kJ mol^{-1}]

4. Calculate the enthalpy of formation of sucrose ($C_{12}H_{22}O_{11}$) from the following data :—

   (i) $C_{12}H_{22}O_{11} + 12O_2 \longrightarrow 12CO_2 + 11H_2O$, $\Delta H = -5200.7$ kJ mol^{-1}

   (ii) $C + O_2 \longrightarrow CO_2$, $\Delta H = -394.5$ kJ mol^{-1}

   (iii) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$, $\Delta H = -285.8$ kJ mol^{-1}

   [Ans. – 2677.1 kJ mol^{-1}]

5. Calculate the enthalpy of formation of benzene, given that enthalpies of combustion of benzene, carbon and hydrogen are –3281.5 kJ, –394.9 kJ and –286.1 kJ/mol, respectively.

   [Ans. +53.8 kJ mol^{-1}]

6. Calculate the standard enthalpy of formation of SO_3 at 298 K using the following reactions and enthalpies.

   $S_8(s) + 8O_2(g) \longrightarrow 8SO_2(g)$, $\Delta H^\circ = -2775$ kJ mol^{-1}

   $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$, $\Delta H^\circ = -198$ kJ mol^{-1}

   [Ans. – 445.9 kJ mol^{-1}]

7. Calculate the enthalpy of formation of anhydrous Al_2Cl_6 from the following data :

   (i) $2Al(s) + 6HCl(aq) \longrightarrow Al_2Cl_6(aq) + 3H_2(g)$ + 1004.2 kJ. kJ mol^{-1}

   (ii) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ + 184.1 kJ mol^{-1}

   (iii) $HCl(g) + aq \longrightarrow HCl(aq)$ + 73.2 kJ mol^{-1}

   (iv) $Al_2Cl_6(s) + aq \longrightarrow Al_2Cl_6(aq)$ + 643.1 kJ mol^{-1}

   [Ans. – 1352.6 kJ mol^{-1}]

8. From the following thermochemical equations, calculate the standard enthalpy of formation of HCl (g).

   (A) $H_2(g) \longrightarrow 2H(g)$, $\Delta H = +436.0$ kJ mol^{-1}

   (B) $Cl_2(g) \longrightarrow 2Cl(g)$, $\Delta H = +242.7$ kJ mol^{-1}

   (C) $HCl(g) \longrightarrow H(g) + Cl(g)$, $\Delta H = +431.8$ kJ mol^{-1}

   [Ans. –92.45 kJ mol^{-1}]

9. Calculate the enthalpy of formation of *n*-butane from the following data :

   (i) $2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(l)$, $\Delta H = -5757.2$ kJ mol^{-1}

   (ii) $C(s) + O_2(g) \longrightarrow CO_2(g)$, $\Delta H = -405.4$ kJ mol^{-1}

   (iii) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$, $\Delta H = -572.4$ kJ mol^{-1}

   On what law are your calculations based ?

   [Ans. –174 kJ mol^{-1}]

10. Calculate the enthalpy of formation of acetic acid if the enthalpy of combustion to $CO_2(g)$ and $H_2O(l)$ is –867.0 kJ mol^{-1} and enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are respectively –393.5 and –285.9 kJ mol^{-1}.

    [Ans. –491.8 kJ mol^{-1}]

HINTS FOR DIFFICULT PROBLEMS

1. Given

(*i*) $C_2H_4\,(g) + \frac{5}{2}O_2\,(g) \longrightarrow 2\,CO_2\,(g) + 2\,H_2O\,(l)$, $\Delta H = -1410{\cdot}0\ \text{kJ mol}^{-1}$

(*ii*) $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$, $\Delta H = -393{\cdot}3\ \text{kJ mol}^{-1}$

(*iii*) $H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l)$, $\Delta H = -286{\cdot}2\ \text{kJ mol}^{-1}$

Aim : $2\,C\,(s) + 2\,H_2\,(g) \longrightarrow C_2H_4\,(g)$ $\Delta H = ?$

2 × Eqn. (*ii*) + 2 × Eqn. (*iii*) —Eqn. (*i*) gives the required result.

2. Aim : $C\,(s) + 2\,S\,(s) \longrightarrow CS_2\,(l)$, $\Delta H = ?$

Given :

(*i*) $CS_2\,(l) + 3\,O_2\,(g) \longrightarrow CO_2\,(g) + 2\,SO_2\,(g)$, $\Delta H = -110{\cdot}2\ \text{kJ mol}^{-1}$

(*ii*) $S\,(s) + O_2\,(g) \longrightarrow SO_2\,(g)$, $\Delta H = -297{\cdot}4\ \text{kJ mol}^{-1}$

(*iii*) $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$, $\Delta H = -394{\cdot}5\ \text{kJ mol}^{-1}$

Eq. (*iii*) + 2 × Eqn. (*ii*)—Eqn. (*i*) gives the required result.

3. Aim : $2\,C\,(s) + 2\,H_2\,(g) + O_2\,(g) \longrightarrow CH_3COOH$, $\Delta H = ?$

2 × Eqn. (*i*) + 2 × Eqn. (*ii*) —Eqn. (*iii*) gives the required result.

4. Aim : $12\,C\,(s) + 11\,H_2\,(g) + \frac{11}{2}O_2\,(g) \longrightarrow C_{12}H_{12}O_{11}\,(s)$, $\Delta H = ?$

5. Aim : $6\,C\,(s) + 3\,H_2\,(g) \longrightarrow C_6H_6\,(l)$, $\Delta H = ?$

Given : (*i*) $C_6H_6\,(l) + \frac{15}{2}O_2\,(g) \longrightarrow 6\,CO_2\,(g) + 3\,H_2O$, $\Delta H = -3281{\cdot}5\ \text{kJ mol}^{-1}$

(*ii*) $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$, $\Delta H = -394{\cdot}9\ \text{kJ mol}^{-1}$

(*iii*) $H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l)$, $\Delta H = -286{\cdot}1\ \text{kJ mol}^{-1}$

6 × Eqn. (*ii*) + 3 × Eqn. (*iii*) —Eqn. (*i*) gives the required result.

6. Aim : $\frac{1}{8}S_8\,(s) + \frac{3}{2}O_2\,(g) \longrightarrow SO_3\,(g)$, $\Delta H = ?$

7. Aim : $2\,Al\,(s) + 3\,Cl_2\,(g) \longrightarrow Al_2Cl_6\,(s)$, $\Delta H = ?$

Eqn. (*i*) + 3 × Eqn. (*ii*)—Eqn. (*iv*) + 6 × Eqn. (*iii*) gives the required result.

8. Aim : $\frac{1}{2}H_2\,(g) + \frac{1}{2}Cl_2\,(g) \longrightarrow HCl\,(g)$

9. Aim : $4\,C\,(s) + 5\,H_2\,(g) \longrightarrow C_4H_{10}\,(g)$, $\Delta H = ?$

4 × Eqn. (*ii*) + $\frac{5}{2}$ × Eqn. (*iii*) $-\frac{1}{2}$ × Eqn. (*i*) gives the required result.

10. Similar to problem 3.

TYPE II. On the calculation of enthalpies of combustion

EXAMPLE. *Calculate the enthalpy of combustion of ethylene (gas) to form CO_2 (gas) and H_2O (gas) at 298 K and 1 atmospheric pressure. The enthalpies of formation of CO_2, H_2O and C_2H_4 are -393.7, -241.8 + 52.3 kJ per mole respectively.*

Solution. We are given :

(*i*) $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$, $\Delta H = -393{\cdot}7\ \text{kJ mol}^{-1}$

(*ii*) $H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(g)$, $\Delta H = -241{\cdot}8\ \text{kJ mol}^{-1}$

(*iii*) $2C\,(s) + 2H_2\,(g) \longrightarrow C_2H_4\,(g)$, $\Delta H = +52{\cdot}3\ \text{kJ mol}^{-1}$

We aim at :

$C_2H_4\,(g) + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 2H_2O\,(g)$, $\Delta H = ?$

2 × Equation (*i*) + 2 × Equation (*ii*) – Equation (*iii*) gives

$$\begin{array}{lcl} 2C\,(s) + 2O_2\,(g) & \longrightarrow & 2CO_2\,(g) \\ \quad + O_2\,(g) + 2H_2\,(g) & & + 2H_2O\,(g) \\ -2C\,(s) \quad - 2H_2\,(g) & & - C_2H_4\,(g) \end{array}$$

$$3O_2\,(g) \longrightarrow 2CO_2\,(g) + 2H_2O\,(g) - C_2H_4\,(g)$$

or $C_2H_4\,(g) + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 2H_2O\,(g)$

$$\Delta H = 2(-393\cdot7) + 2(-241\cdot8) - (52\cdot3)$$

$$= \mathbf{-1323\cdot3\ kJ\ mol^{-1}}$$

Alternative Method :

We aim at :

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

We are given : $\Delta H_{f(CO_2)} = -393\cdot7$ kJ mol^{-1}

$$\Delta H_{f(H_2O)} = -\ 241\cdot8\ \text{kJ mol}^{-1}$$

$$\Delta H_{f(C_2H_4)} = +52\cdot3\ \text{kJ mol}^{-1}$$

$\Delta H_{Reaction}$ = (Sum of $\Delta H_f°$ values of Products) − (Sum of $\Delta H_f°$ values of Reactants)

$$= [2\times\Delta H°_{f(CO_2)} + 2\times\Delta H°_{f(H_2O)}] - [\Delta H°_{f(C_2H_4)} + 3\times\Delta H°_{f(O_2)}]$$

$$= [2\times(-393\cdot7)+2\times(-241\cdot8)]-[(52\cdot3)+0]$$

($\because$ $\Delta H_f°$ for elementary substance$=0$)

$$= [-787\cdot4-483\cdot6]-52\cdot3 = \mathbf{-1323\cdot3\ kJ\ mol^{-1}}$$

PROBLEMS FOR PRACTICE

1. Calculate the enthalpy of combustion of benzene from the following data :—

(*i*) $6C\,(s) + 3H_2\,(g) \longrightarrow C_6H_6\,(l)$,

$\Delta H = 49.0$ kJ mol^{-1}

(*ii*) $H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l)$,

$\Delta H = -285.8$ kJ mol^{-1}

(*iii*) $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$,

$\Delta H = -389.3$ kJ mol^{-1}

[Ans. —3242.2 kJ mol^{-1}]

2. The enthalpies of formation of methane, carbon dioxide and water (liquid) are —74.8, —393.5 and —286.2 kJ respectively. Calculate the enthalpy of combustion of methane at ordinary temperature.

[Ans. —891.1 kJ mol^{-1}]

3. Calculate the enthalpy of reaction for

$$CO\,(g) + \tfrac{1}{2}O_2\,(g) \longrightarrow CO_2\,(g)$$

Given $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$,

$\Delta H = -393.5$ kJ mol^{-1}

$C\,(s) + \frac{1}{2}O_2\,(g) \longrightarrow CO\,(g)$ $\Delta H = -110.5$ kJ mol^{-1}

[Ans. —283 kJ mol^{-1}]

4. Find the enthalpy of combustion of carbon (graphite) to produce carbon monoxide (*g*) on the basis of data given below :—

C(graphite) + $O_2\,(g) \longrightarrow$

$CO_2\,(g) + 393.4$ kJ mol^{-1}

$CO\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow CO_2\,(g) + 283\cdot0$ kJ mol^{-1}

[Ans. ΔH = —110.4 kJ mol^{-1}]

HINTS FOR DIFFICULT PROBLEMS

1. Aim : $C_6H_6\,(l) + \frac{15}{2}O_2\,(g)$

$\longrightarrow 6\,CO_2\,(g) + 3\,H_2O\,(l)$, $\Delta H = ?$

6 × Eqn. (*iii*) + 3 × Eqn. (*ii*)

—Eqn. (*i*) gives the required result.

2. Aim : $CH_4\,(g) + 2\,O_2\,(g) \longrightarrow CO_2\,(g) + 2\,H_2O\,(l)$

$\Delta H_{Reaction} = [\Delta H°_f(CO_2) + 2\,\Delta H°_f(H_2O)]$

$- [\Delta H°_f(CH_4) + 2\,\Delta H°_f(O_2)]$

4. Aim : $C\,(s) + \frac{1}{2}O_2\,(g) \longrightarrow CO\,(g)$, $\Delta H = ?$

Eqn. (*i*)—Eqn. (*ii*) gives the required result.

TYPE III. On the calculation of enthalpies of transitions

EXAMPLE. *Given the following thermochemical equations*

(*i*) *S (rhombic)* + $O_2\,(g) \longrightarrow SO_2\,(g)$,

$\Delta H = -297\cdot5$ *kJ mol*$^{-1}$

(*ii*) *S(monoclinic)* + $O_2 \longrightarrow SO_2\,(g)$,

$\Delta H = -300\cdot0$ *kJ mol*$^{-1}$

Calculate ΔH *for the transformation of one gram atom of rhombic sulphur into monoclinic sulphur.* **(Bihar CEE 1998)**

Solution. We aim at :

$$S(\text{rhombic}) \longrightarrow S(\text{monoclinic}),\ \Delta H = ?$$

Equation (*i*) – Equation (*ii*) gives

$$S(\text{rhombic}) - S(\text{monoclinic}) \longrightarrow 0,$$

$$\Delta H = 297{\cdot}5 - (-300{\cdot}0) = 2{\cdot}5 \text{ kJ mol}^{-1}$$

or

$$S(\text{rhombic}) \longrightarrow S(\text{monoclinic}),\quad \Delta H = +2{\cdot}5 \text{ kJ mol}^{-1}$$

Thus for the transformation of one gram atom of rhombic sulphur into monoclinic sulphur, 2 · 5 kJ mol^{-1} of heat is absorbed.

PROBLEMS FOR PRACTICE

1. The enthalpies of combustion of graphite and diamond are 393.5 kJ and 395.4 kJ respectively. Calculate the enthalpy change accompanying the transformation of 1 mole of graphite into diamond. **[Ans. 1.9 kJ mol^{-1}]**

2. There are two crystalline forms of PbO ; one is yellow and the other is red. The standard enthalpies of formation of these two forms are —217.3 and —219.0 kJ per mole respectively. Calculate the enthalpy change for the solid-solid phase transition.

$$PbO\ (\text{yellow}) \longrightarrow PbO(\text{red})$$

[Ans. —1.7 kJ mol^{-1}]

HINTS FOR DIFFICULT PROBLEMS

1. Given : (*i*) $C\,(gr) + O_2\,(g) \longrightarrow CO_2\,(g),\quad \Delta H = -393{\cdot}5 \text{ kJ mol}^{-1}$

(*ii*) $C\,(dia) + O_2\,(g) \longrightarrow CO_2\,(g),\quad \Delta H = -395{\cdot}4 \text{ kJ mol}^{-1}$

Aim : $C\,(gr) \longrightarrow C\,(dia),\ \Delta H = ?$

Eqn. (*i*)—Eqn. (*ii*) gives the required result.

2. Given : (*i*) $Pb\,(s) + \frac{1}{2}O_2\,(g) \longrightarrow PbO$ (yellow), $\Delta H = -217{\cdot}3 \text{ kJ mol}^{-1}$

(*ii*) $Pb\,(s) + \frac{1}{2}O_2\,(g) \longrightarrow PbO$ (Red), $\Delta H = -219{\cdot}0 \text{ kJ mol}^{-1}$

Eqn. (*ii*)—Eqn. (*i*) gives the required result.

TYPE IV. On the calculation of enthalpies of hydration

EXAMPLE. *Enthalpy of solution (ΔH) for $BaCl_2 . 2H_2O$ and $BaCl_2$ are 8·8 and – 20·6 kJ mol^{-1} respectively. Calculate the heat of hydration of $BaCl_2$ to $BaCl_2 . 2H_2O$.*

Solution. We are given

(*i*) $BaCl_2 . 2H_2O\,(s) + aq \longrightarrow BaCl_2\,(aq),\quad \Delta H = 8{\cdot}8 \text{ kJ mol}^{-1}$

(*ii*) $BaCl_2\,(s) + aq \longrightarrow BaCl_2\,(aq),\quad \Delta H = -20{\cdot}6 \text{ kJ mol}^{-1}$

We aim at

$$BaCl_2\,(s) + 2H_2O \longrightarrow BaCl_2 . 2H_2O\,(s),\quad \Delta H = ?\quad ...(iii)$$

Equation (*ii*) may be written in two steps as

$$BaCl_2\,(s) + 2H_2O \longrightarrow BaCl_2 . 2H_2O\,(s),\quad \Delta H = \Delta H_1 \text{ (say)}\quad ...(iv)$$

$$BaCl_2 . 2H_2O\,(s) + aq \longrightarrow BaCl_2\,(aq),\quad \Delta H = \Delta H_2 \text{ (say)}\quad ...(v)$$

Then according to Hess's law

$$\Delta H_1 + \Delta H_2 = -20{\cdot}6 \text{ kJ}$$

But $\Delta H_2 = 8{\cdot}8 \text{ kJ mol}^{-1}$

[∵ Equation (*i*) = Equation (*v*)]

$$\therefore \Delta H_1 = -20{\cdot}6 - 8{\cdot}8 = -29{\cdot}4 \text{ kJ mol}^{-1}$$

But Equation (*iii*) = Equation (*iv*)

Hence the heat of hydration of $BaCl_2$

$$= -29{\cdot}4 \text{ kJ mol}^{-1}$$

PROBLEMS FOR PRACTICE

The enthalpy of solution of anhydrous copper sulphate ($CuSO_4$) and hydrated copper sulphate ($CuSO_4 . 5H_2O$) are —66·5 and +11·7 kJ mol^{-1} respectively. Calculate the enthalpy of hydration of anhydrous copper sulphate to pentahydrate. **[—78·2 kJ mol^{-1}]**

HINTS FOR DIFFICULT PROBLEMS

Given : (*i*) $CuSO_4\,(s) + aq. \longrightarrow CuSO_4\,(aq)$, $\Delta H = -66{\cdot}5\ kJ\ mol^{-1}$

(*ii*) $CuSO_4 \,.\, 5\,H_2O\,(s) + aq. \longrightarrow CuSO_4\,(aq)$, $\Delta H = +11{\cdot}7\ kJ\ mol^{-1}$

Aim : $CuSO_4\,(s) + 5\,H_2O\,(l) \longrightarrow CuSO_4 \,.\, 5\,H_2O\,(s)$, $\Delta H = ?$

See solution on page 5/31.

TYPE V. On the calculation of enthalpy change for any reaction

EXAMPLE 1. *Calculate the enthalpy of hydrogenation of ehtylene, given that the enthalpy of combustion of ethylene, hydrogen and ethane are − 1410·0, − 286·2 and − 1560·6 kJ mol⁻¹ respectively at 298 K.* **(N.C.E.R.T.)**

Solution. We are given

(*i*) $C_2H_4\,(g) + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 2H_2O\,(l)$, $\Delta H = -1410\ kJ\ mol^{-1}$

(*ii*) $H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l)$, $\Delta H = -286{\cdot}2\ kJ\ mol^{-1}$

(*iii*) $C_2H_6\,(g) + 3\frac{1}{2}O\,(g) \longrightarrow 2CO_2\,(g) + 3H_2O\,(l)$, $\Delta H = -1560.6\ kJ\ mol^{-1}$

We aim at $C_2H_4 + H_2\,(g) \longrightarrow C_2H_6\,(g)$, $\Delta H = ?$

Equation (*i*) + Equation (*ii*) − Equation (*iii*) gives

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g),$$

$$\Delta H = -1410{\cdot}0 + (-286{\cdot}2) - (1560{\cdot}6)$$

$$= -\ \mathbf{135{\cdot}6\ kJ\ mol^{-1}}$$

EXAMPLE 2. *The thermite reaction used for welding of metals involves the reaction*

$$2Al\,(s) + Fe_2O_3\,(s) \longrightarrow Al_2O_3\,(s) + 2Fe\,(s)$$

What is ΔH° at 25°C for this reaction ? Given that the standard heats of formation of Al_2O_3 and Fe_2O_3 are −1675·7 kJ and −828·4 kJ mol⁻¹ respectively.

Solution. We are given

(*i*) $2\,Al\,(s) + \frac{3}{2}O_2(g) \longrightarrow Al_2O_3(s)$, $\Delta H = -1675{\cdot}7\ kJ\ mol^{-1}$

(*ii*) $2Fe\,(s) + \frac{3}{2}O_2\,(g) \longrightarrow Fe_2O_3\,(s)$, $\Delta H = -828{\cdot}4\ kJ\ mol^{-1}$

We aim at

$2Al\,(s) + Fe_2O_3\,(s) \longrightarrow Al_2O_3\,(s) + 2Fe\,(s)$, $\Delta H = ?$

Equation (*i*) − Equation (*ii*) gives

$2Al\,(s) + Fe_2O_3\,(s) \longrightarrow Al_2O_3\,(s) + 2Fe\,(s)$,

$\Delta H = -1675{\cdot}7 - (-828{\cdot}4) = -\ \mathbf{847{\cdot}3\ kJ\ mol^{-1}}$.

Alternative Method

We aim at

$2Al\,(s) + Fe_2O_3\,(s) \longrightarrow Al_2O_3\,(s) + 2Fe\,(s)$, $\Delta H = ?$

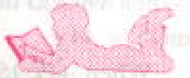
$$\Delta H_{Reaction} = \text{Sum of } \Delta H^\circ_f \text{ of products} - \text{Sum of } \Delta H^\circ_f \text{ of reactants}$$

$$= [\Delta H^\circ_f(Al_2O_3) + 2 \times \Delta H^\circ_f(Fe)] - [2 \times \Delta H^\circ_f(Al) + \Delta H^\circ_f(Fe_2O_3)]$$

$$= [-1675{\cdot}7 + 0] - [0 + (-828{\cdot}4)]$$

$$= -\ \mathbf{847{\cdot}3\ kJ\ mol^{-1}}$$

PROBLEMS FOR PRACTICE



1. The enthalpies of formation of carbon monoxide and steam are —110·5 and —243·0 kJ mol⁻¹ respectively. Calculate the enthalpy of the reaction when steam is passed over coke *i.e.* for the reaction

$$C + H_2O \longrightarrow CO + H_2$$

[Ans. +132.5 kJ mol⁻¹]

2. Chloroform is prepared from methane according to the reaction

$$CH_4\,(g) + 3Cl_2\,(g) \longrightarrow CHCl_3\,(l) + 3HCl\,(g)$$

Calculate ΔH for the reaction given that enthalpies of formation of HCl (g), CH_4 (g) and $CHCl_3$ (l) are —92.0, —74.9 and —134.3 kJ per mole respectively. **[Ans. —335.4 kJ mol^{-1}]**

3. Calculate the enthalpy of reaction (ΔH°) when ammonia is oxidized :

$$4NH_3\,(g) + 5O_2\,(g) \longrightarrow 6H_2O\,(g) + 4NO\,(g)$$

Standard enthalpies of formation (ΔH_f°) at 25° C for NH_3 (g), H_2O (g) and NO (g) are —46.2, —241.8 and +90.4 kJ/mole respectively. **[Ans. —904·4 kJ mol^{-1}]**

4. The standard enthalpy of formation of Fe_2O_3 (s) is – 824·2 kJ mol^{-1}. Calculate the enthalpy change for the reaction

$$4\,Fe\,(s) + 3\,O_2\,(g) \longrightarrow 2\,Fe_2O_3\,(s)$$

[Ans. – 1648·4 kJ]

HINTS FOR DIFFICULT PROBLEMS

1. $\Delta H_{\text{Reaction}} = [\Delta H^\circ_f(CO) + \Delta H^\circ_f(H_2)] - [\Delta H^\circ_f(C) + \Delta H^\circ_f(H_2O)]$

$= [-110{\cdot}5 + 0] - [0 + (-243{\cdot}0)]$

$= +132{\cdot}5 \text{ kJ mol}^{-1}$

2. $\Delta H_{\text{Reaction}} = [\Delta H^\circ_f(CHCl_3) + 3\,\Delta H^\circ_f(HCl)] - [\Delta H^\circ_f(CH_4) + 3\,\Delta H^\circ_f(Cl_2)]$

$= [(-134{\cdot}3) + 3\,(-92{\cdot}0)] - [(-74{\cdot}9) + 0]$

$= -335{\cdot}4 \text{ kJ mol}^{-1}$

4. $\Delta H_r^\circ = [2 \times \Delta H_f^\circ(Fe_2O_3)] - [\Delta H_f^\circ(Fe) + 3\,H_f^\circ(O_2)]$

$= [2\,(-824{\cdot}2)] - [0 + 0] = -1648{\cdot}4$ kJ.

MISCELLANEOUS PROBLEMS ON THERMOCHEMISTRY

EXAMPLE 1. *The heat evolved in the combustion of methane is given by the following equation :*

$$CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(l), \quad \Delta H = -890{\cdot}3 \text{ kJ mol}^{-1}$$

(a) How many grams of methane would be required to produce 445·15 kJ of heat of combustion ?

(b) How many grams of carbon dioxide would be formed when 445·15 kJ of heat is evolved ?

(c) What volume of oxygen at STP would be used in the combustion process (a) or (b) ?

Solution. (a) From the given equation,

890·3 kJ of heat is produced from 1 mole of CH_4 *i.e.*, 12 + 4 = 16 g of CH_4

∴ 445.15 kJ of heat is produced from 8 g of CH_4

(b) From the given equation,

When 890.3 kJ of heat is evolved, CO_2 formed = 1 mole = 44 g

∴ When 445·15 kJ of heat is evolved, CO_2 formed = **22 g**

(c) From the equation, O_2 used in the production of 890·3 kJ of heat = 2 moles = 2 × 22·4 litres at STP = 44·8 litres at STP

Hence O_2 used in the production of 445·15 kJ of heat = **22·4 litres at STP.**

EXAMPLE 2. *The heat evolved in the combustion of glucose is shown in the following equation :—*

$$C_6H_{12}O_6\,(s) + 6O_2\,(g) \longrightarrow 6CO_2\,(g) + 6H_2O\,(g), \quad \Delta H = -2840 \text{ kJ mol}^{-1}$$

What is the energy requirement for production of 0·36 g of glucose by the reverse reaction ?

Solution. The given equation is

$$C_6H_{12}O_6 + 6O_2\,(g) \longrightarrow 6CO_2\,(g) + 6H_2O\,(g)\,; \quad \Delta H = -2840 \text{ kJ mol}^{-1}$$

Writing the reverse reaction, we have

$$6CO_2\,(g) + 6H_2O\,(g) \longrightarrow C_6H_{12}O_6\,(s) + 6O_2\,(g)\,; \quad \Delta H = +2840 \text{ kJ mol}^{-1}$$

Thus for production of 1 mole of $C_6H_{12}O_6$ (= 72 + 12 + 96 = 180 g) heat required (absorbed) = 2840 kJ.

$\therefore$ For production of 0·36 g of glucose, heat absorbed $= \frac{2840}{180} \times 0{\cdot}36 = \mathbf{5{\cdot}68\ kJ}$

EXAMPLE 3. *From the thermochemical equation*

$$C_6H_6\,(l) + 7\frac{1}{2}O_2\,(g) \longrightarrow 3H_2O\,(l) + 6CO_2\,(g),$$

$$\Delta H = -3264{\cdot}64\ kJ\ mol^{-1}$$

calculate the energy evolved when 39 g of C_6H_6 are burnt in an open container.

Solution. From the given equation,

When 1 mole of C_6H_6 (78 g of C_6H_6) is burnt, heat evolved = 3264·64 kJ

$\therefore$ When 39 g of C_6H_6 is burnt, heat evolved

$$= \frac{3264{\cdot}64}{78} \times 39 = \mathbf{1632{\cdot}32\ kJ}$$

EXAMPLE 4. *The thermochemical equation for solid and liquid rocket fuel are given below :–*

$$2Al\,(s) + 1\frac{1}{2}O_2\,(g) \longrightarrow Al_2O_3\,(s);$$

$$\Delta H = -1667{\cdot}8\ kJ\ mol^{-1}$$

$$H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l);$$

$$\Delta H = -285.9\ kJ\ mol^{-1}$$

(a) If equal masses of aluminium and hydrogen are used, which is a better rocket fuel ?

(b) Determine ΔH for the reaction

$$Al_2O_3\,(s) \longrightarrow 2Al\,(s) + 1\frac{1}{2}O_2\,(g)$$

Solution. (*a*) From the first given equation

2 moles of Al (*i.e.* 2 × 27 g = 54 g) on combustion give heat = 1667·8 kJ

$\therefore$ 1 g of Al on combustion gives heat

$$= \frac{1667{\cdot}8}{54} = 30{\cdot}9\ kJ$$

From the second given equation

1 mole of H_2 (= 2 g) on combustion gives heat = 285·9 kJ

$\therefore$ 1 g of H_2 on combustion gives heat

$$= \frac{285{\cdot}9}{2} = 142{\cdot}95\ kJ$$

Thus, H_2 *is a better rocket fuel.*

(*b*) Writing the reverse of the first reaction, we have $Al_2O_3(s) \longrightarrow 2Al\,(s) + 1\frac{1}{2}O_2\,(g)$;

$$\Delta H = +\,1667{\cdot}8\ kJ\ mol^{-1}$$

Thus for the reaction given in part (*b*) of the problem, $\Delta H = +\,\mathbf{1667{\cdot}8\ kJ\ mol^{-1}}$

EXAMPLE 5. *When 1 g liquid naphthalene ($C_{10}H_8$) solidifies, 149 joules of heat is evolved. Calculate the enthalpy of fusion of naphthalene.*

Solution. Molecular mass of naphthalene ($C_{10}H_8$) = 128

When 1 g of liquid naphthalene solidified, heat evolved = 149 joules.

When 1 mole *i.e.* 128 g of naphthalene solidifies, heat evolved = 149 × 128 joules = 19072 Joules

Since fusion is reverse of solidification, therefore heat absorbed for fusion of one mole of naphthalene = 19072 joules

i.e. Enthalpy of fusion (ΔH_f)

$$= \mathbf{+\,19072\ joules/mole}$$

EXAMPLE 6. *If a man takes a diet which gives him energy equal to 9500 kJ per day and he expends energy in all forms to a total of 12000 kJ per day, what is the change in internal energy per day ? If the energy lost was stored as sucrose (1632 kJ per 100 g), how many days should it take to lose 1 kg ? Ignore the water loss.*

Solution. Loss of energy per day

$$= 12000 - 9500 = 2500\ kJ$$

Since the man can be considerded as a system with constant volume, hence loss of energy can be taken as equal to the loss of internal energy. As internal energy decreases, ΔE is negative. Thus change in internal energy,

$$\Delta E = -2500\ kJ.$$

For a loss of 1632 kJ of energy, sucrose ($C_{12}H_{22}O_{11}$) lost = 100 g (given)

For a loss of 2500 kJ of energy, sucrose lost

$$= \frac{100}{1632} \times 2500\ g = 153{\cdot}2g$$

Thus 153·2 g of loss of weight takes place in 1 day

$\therefore$ 1 kg (1000 g) of loss of weight will take place

$$= \frac{1}{153{\cdot}2} \times 1000\ days = \mathbf{6{\cdot}5\ days}$$

EXAMPLE 7. *Standard vaporisation enthalpy of benzene at its boiling point is 30·8 kJ mol^{-1}. For how long would a 100 W electric heater have to operate in order to vaporize a 100 g sample of benzene at its boiling temperature ?*

(power = energy/time, 1 W = 1 Js^{-1})

(N.C.E.R.T.)

Solution. 1 mole of benzene, C_6H_6 (78 g) requires energy for vaporization = 30·8 kJ

∴ 100 g benzene will require energy

$$= \frac{30 \cdot 8}{78} \times 100 \text{ kJ} = 39 \cdot 5 \text{ kJ}$$

100 W heater gives energy of 100 J per second.

∴ Time required for getting 39·5 kJ of energy

$$= \frac{39500 \text{ J}}{100 \text{ J}} = 395\ s$$

= 6 min. 35 sec.

PROBLEMS FOR PRACTICE

1. Given that

(*i*) C(graphite) + $O_2(g) \longrightarrow CO_2(g)$;

$$\Delta H = -\ 393.7 \text{ kJ mol}^{-1}$$

(*ii*) C(diamond) ⟶ C(graphite) ;

$$\Delta H = -2.1 \text{ kJ mol}^{-1}$$

(*a*) Calculate ΔH for burning of diamond to CO_2

(*b*) Calculate the quantity of graphite that must be burnt to evolve 5000 kJ of heat

[Ans. (*a*) —395·8 kJ (I) 152.4 g]

2. Compare the quantity of heat produced by the combustion of 1.0 g glucose ($C_6H_{12}O_6$) with that produced by 1.0 g sucrose ($C_{12}H_{22}O_{11}$). Given that the standard heats of formation of CO_2, H_2O, glucose and sucrose are —393.5, —285.9, —1260 and —2221 kJ mol^{-1} respectively.

[Ans. ΔH for glucose = —15.6 kJ g^{-1}
ΔH for the sucrose = —9.6 kJ g^{-1}]

3. Calculate the enthalpy change for the reaction between CO_2 and H_2O to produce one mole of glucose ($C_6H_{12}O_6$). What would be enthalpy change for the production of 18 g of glucose ? The enthalpy of combustion of glucose is 2840 kJ mol^{-1}

[Ans. ΔH = + 2840 kJ, ΔH = + 284 kJ]

4. (*a*) A cylinder of gas is assumed to contain 11.2 kg of butane. If a normal family needs 20,000 kJ of energy per day for cooking, how long will the cylinder last ? Given that the heat of combustion of butane is 2658 kJ mol^{-1}.

(*b*) If the air supply of the burner is insufficient (*i.e.* you have a yellow instead of a blue flame), a portion of the gas escapes without combustion. Assuming that 33% of the gas is wasted due to this inefficiency, how long would the cylinder last ?

[Ans. 26 days approx., 17 days approx.]

5. An average person needs about 10,000 kJ per day. How much carbohydrates (in mass) will he have to consume, assuming that all his energy needs are met only by carbohydrates in the form of glucose? Given that the heat of combustion of glucose is 2900 kJ mol^{-1} **[Ans. 620.7 g]**

6. Reaction between red phosphorus and liquid bromine is an exothermic reaction represented as follows :

$$2\text{ P }(s) + 3\text{ Br}_2\ (l) \longrightarrow 2\text{ P Br}_3\ (g),$$

$$\Delta H^\circ = -\ 243 \text{ kJ mol}^{-1}.$$

What will be the enthalpy change when 2·63 g of phosphorus reacts according to the above reaction. Take atomic mass of phosphorus as 31·0.

[Ans. 10·3 kJ]

7. A swimmer when comes out of the swimming pool weighs 80 g extra due to water sticking on his body. How much heat he should absorb from the sun so that all the water evaporates off from his body. Given that the latent heat of vaporisation of water is 40·79 kJ mol^{-1}. **[Ans. 181·3 kJ]**

8. Calculate the enthalpy change when 2·38 *g* of carbon monoxide (CO) vaporize at its normal boiling point. Given that the enthalpy of vaporisation of carbon monoxide is 6·04 kJ mol^{-1} at its normal boiling point of 82·0 K. *(N.C.E.R.T.)* **[Ans. 513 J]**

HINTS FOR DIFFICULT PROBLEMS

1. (*a*) Eqn. (*ii*)—Eqn. (*i*) gives the required result.

(*b*) $393\cdot7$ kJ of heat is produced from graphite

$= 12\,g$

∴ 5000 kJ of heat will be produced from graphite

$$= \frac{12}{393\cdot7} \times 5000\,g = 152\cdot4\,g$$

2. $C_6H_{12}O_6 + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O$

$$\Delta H_{\text{Reaction}} = [6\,\Delta H^\circ_f(CO_2) + 6\,\Delta H^\circ_f(H_2O)] - [\Delta H^\circ_f(C_6H_{12}O_6) + 6\,\Delta H^\circ_f(O_2)]$$

$$= [6\,(-393\cdot5) + 6\,(-285\cdot9)] - [(-1260) + 6\,(0)]$$

$$= -2816\cdot4 \text{ kJ mol}^{-1}$$

∴ Heat produced from 1 g glucose

$$= \frac{2816\cdot4}{180} = 15\cdot6 \text{ kJ}$$

$C_{12}H_{22}O_{11} + 6\,O_2 \longrightarrow 6\,CO_2 + 11\,H_2O$

$$\Delta H_{\text{Reaction}} = [6\,(-393\cdot5) + 11\,(-285\cdot9)] - [-2221 + 0]$$

$$= -3284\cdot9 \text{ kJ mol}^{-1}$$

∴ Heat produced from 1 g sucrose

$$= \frac{3284\cdot9}{342} \text{ kJ} = 9\cdot6 \text{ kJ}$$

3. Given : $C_6H_{12}O_6\,(s) + 6\,O_2\,(g) \longrightarrow 6\,CO_2\,(g) + 6\,H_2O\,(l),$

$\Delta H = -2840 \text{ kJ mol}^{-1}$

Aim : Reverse Reaction for which

$\Delta H = +2840 \text{ kJ mol}^{-1}$

This is the enthalpy change for production of 1 mole (180 g) of glucose. Hence for 18 g glucose, $\Delta H = +284$ kJ

4. (*a*) 1 Mole $C_4H_{10} = 58\,g$,

∴ Heat produced from $11200\,g$

$$= \frac{2658}{58} \times 11200 = 513268\cdot9 \text{ kJ}.$$

No. of days for which it will last

$= 513268\cdot9/20{,}000 = 25\cdot7$ days ≈ 26 days

(*b*) After wastage, heat available

$$= \frac{67}{100} \times 513268\cdot9 = 343890 \text{ kJ}$$

No. of days for which it will last

$= 343890/20000 = 17$ days

5. Mol mass of glucose $(C_6H_{12}O_6) = 180.$

Glucose required per day

$= (180 / 2900) \times 10{,}000$g.

6. Required $\Delta H = \dfrac{243}{62} \times 2\cdot63 \text{ J} = 10\cdot3 \text{ kJ}.$

7. For evaporation of 1 mol of H_2O *i.e.* 18 g, heat required $= 40\cdot79$ kJ

∴ For evaporation of 80 g of H_2O, heat required

$$= \frac{40\cdot79}{18} \times 80 = 181\cdot3 \text{ kJ}.$$

8. ΔH_{vap} for CO $= 6\cdot04 \text{ kJ mol}^{-1}$

i.e. $6\cdot04$ kJ for $28\,g$

∴ Enthalpy change for vaporisation of $2\cdot38\,g$

$$= \frac{6\cdot04}{28} \times 2\cdot38 \text{ kJ} = 0\cdot5134 \text{ kJ} = 513\cdot4 \text{ J}.$$

5.18. Bond Enthalpy Or Bond Energy

We know that energy is evolved when a bond is formed and energy is required for the dissociation of a bond. Hence bond energy is defined as follows : –

Bond energy is the amount of energy released when one mole of bonds are formed from the isolated atoms in the gaseous state or the amount of energy required to dissociate one mole of bonds present between the atoms in the gaseous molecules.

For diatomic molecules like H_2, O_2, N_2, Cl_2, HCl, HF etc., the bond energies are equal to their dissociation energies.

For polyatomic molecules, the bond energy of a particular bond is not the same when present in different types of compounds (*e.g.* bond energy of C – Cl is not same in CH_3Cl, CH_2Cl_2 $CHCl_3$ CCl_4). In fact, the bond energy of a particular type of bond is not same even in the same compound (*e.g.* in CH_4, the bond energy for first, second, third and fourth C – H bonds are not equal – their values being + 427, + 439, + 452 and + 347 kJ mol^{-1} respectively). Hence in such cases, an *average* value is taken.

Thus average C – H bond energy

$$= \frac{427 + 439 + 452 + 347}{4} = \frac{1665}{4}$$

$$= 416 \text{ kJ mol}^{-1}$$

The most accepted values of the bond energies of some common bonds are given in Table 5.1.

REMEMBER

Bond energy usually means bond dissociation energy.Hence it is always taken as positive because it is the energy required and not the energy released. Further, it is the energy for one mole of a particular type of bonds and not for 1 mole of the substance.

Difference between bond energy and bond enthalpy. Strictly speaking, bond energies should be $\Delta E°$ (or $\Delta U°$) values. However, the normally reported values are bond enthalpies *i.e.* $\Delta H°$ values. Bond dissociation energies are obtained at 0K by spectroscopic methods whereas bond enthalpies ($\Delta H°$ or ΔH at any other temperature) are calculated by considering contributions from heat capacities and $p\ \Delta V$ terms. For example, bond enthalpy of H_2 at 298 K is 435 kJ mol^{-1}

i.e. $H_2\ (g) \longrightarrow 2\ H\ (g),\ \Delta H° = 435\ kJ\ mol^{-1}$

The corresponding bond energy ($\Delta U°$) for this reaction is 430·8 kJ mol^{-1}. Thus, there is very small difference and the two are used interchangeably.

An important use of the bond enthalpy is that it helps to calculate the enthalpy of formation of atoms. For example, from the above reaction.

Enthalpy of formation of H-atom $= \frac{435}{2}$

$= 217{\cdot}5\ kJ\ mol^{-1}$

Calculation of bond enthalpy. For polyatomic molecules, the bond enthalpy of a particular bond is found from the values of the enthalpies of formation (which is turn may be obtained from the enthalpies of combustion, enthalpies of sublimation, enthalpies of dissociation etc.). Similarly, the bond enthalpies of heteronuclear diatomic molecules like HCl, HF etc. can be obtained directly from experiments or may be calculated from the bond enthalpies of homonuclear diatomic molecules. These calculations are illustrated in the examples given on page 5/43 and 5/44.

TABLE 5.1. Bond energies of some common bonds

BOND	BOND ENTHALPY* (kJ mol^{-1})	BOND	BOND ENTHALPY** (kJ mol^{-1})
H — H	436	C — H	414
H — F	565	O — H	463
H — Cl	431	N — H	389
H — Br	364	C — C	347
H — I	297	C = C	619
F — F	155	C ≡ C	812
Cl — Cl	242	C — Cl	326
Br — Br	190	C — O	335
I — I	149	C = O	707
O = O	494	C — N	293
N ≡ N	941	C = N	616
		C ≡ N	879

FORMULAS AND UNITS

(*i*) $\Delta H_{reaction} = \Sigma\ \Delta H_f\ (Products) - \Sigma\ \Delta H_f\ (Reactants)$

(*ii*) $\Delta H_{reaction}$ = Σ Bond Energies or Enthalpies of Reactants
—Σ Bond Energies or Enthalpies of Products
= Σ B.E. (Reactants) − Σ B. E. (Products)

(*iii*) Hess's law treats thermochemical equations as algebraic equations.

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*These are exact values because they involve dissociation of diatomic molecules, which contain only one bond.

**These are average values becuase they are obtained from molecules which contain more than one bond.

• **EXAMPLE 1.** *Calculate the bond enthalpy of HCl. Given that the bond enthalpies of H_2 and Cl_2 are 430 kJ mol^{-1} and 242 kJ mol^{-1} respectively and ΔH_f° for HCl is -91 kJ mol^{-1}.*

Solution. First Method. *By using the relation*

$$\Delta H_{Reaction} = \Sigma\, \Delta H^\circ_f\, (Products) - \Sigma\, \Delta H^\circ_f\, (Reactants)$$

Here we are given

$$H_2\,(g) \longrightarrow 2H\,(g), \Delta H = +430 \text{ kJ mol}^{-1} \quad ...(i)$$

$$Cl_2\,(g) \longrightarrow 2Cl\,(g), \Delta H = +242 \text{ kJ mol}^{-1} \quad ...(ii)$$

We aim at

$$HCl\,(g) \longrightarrow H\,(g) + Cl\,(g), \Delta H = ? \quad ...(iii)$$

Evidently, for reaction (*iii*)

$$\Delta H = \Sigma\, \Delta H_f^\circ \text{ (Products)} - \Sigma\, \Delta H_f^\circ \text{ (Reactants)}$$

$$= [\Delta H_f^\circ (H) + \Delta H_f^\circ (Cl)] - [\Delta H_f^\circ (HCl)] \quad ...(iv)$$

From equations (*i*) and (*ii*),

$$\Delta H_f^\circ (H) = \frac{1}{2}(+430 \text{ kJ}) = 215 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ (Cl) = \frac{1}{2}(+242 \text{ kJ}) = +121 \text{ kJ mol}^{-1}$$

Also we are given ΔH_f° (HCl) $= -91$ kJ mol^{-1}

Putting these values in eqn. (*iv*), we get

$$\Delta H = [+215 + 121] - [-91]$$

$$= \mathbf{427 \text{ kJ mol}^{-1}}$$

Second method. *By using Hess's law*

We are given

$$(i)\ H_2(g) \longrightarrow 2H(g), \Delta H = +430 \text{ kJ mol}^{-1}$$

$$(ii)\ Cl_2(g) \longrightarrow 2Cl(g), \Delta H = +242 \text{ kJ mol}^{-1}$$

$$(iii)\ \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g), \quad \Delta H = -91 \text{ kJ mol}^{-1}$$

We aim at

$$HCl(g) \longrightarrow H(g) + Cl\,(g), \Delta H = ?$$

$\frac{1}{2} \times (i) + \frac{1}{2} \times (ii) - (iii)$ gives the required result.

Third Method. *By applying the relation*

$$\Delta H_{Reaction} = \Sigma \text{ Bond Enthalpies of Reactants} - \Sigma \text{ Bond Enthalpies of Products}$$

For the formation of HCl

$$\frac{1}{2}H_2\,(g) + \frac{1}{2}Cl_2\,(g) \longrightarrow HCl\,(g), \Delta H = \Delta H_f$$

$$\therefore \Delta H = \Sigma \text{ B.E. (Reactants)} - \Sigma \text{ B.E. (Products)}$$

$$= \frac{1}{2}\text{B.E.}\,(H_2) + \frac{1}{2}\text{B.E.}\,(Cl_2) - \text{B.E. (HCl)}$$

$$-91 = \frac{1}{2} \times 430 + \frac{1}{2} \times 242 - \text{B.E. (HCl)}$$

$$\therefore \text{B.E. (HCl)} = 215 + 121 + 91$$

$$= \mathbf{427 \text{ kJ mol}^{-1}}$$

EXAMPLE 2. *Calculate the bond energy of C—H bond, given that the heat of formation of CH_4, heat of sublimation of carbon and heat of dissociation of H_2 are $-74 \cdot 8$, $+719 \cdot 6$ and $435 \cdot 4$ kJ mol^{-1} respectively.*

Solution. Here we are given

$$C(s) + 2H_2\,(g) \longrightarrow CH_4\,(g), \quad \Delta H = -74 \cdot 8 \text{ kJ} \quad ...(i)$$

$$C\,(s) \longrightarrow C\,(g), \Delta H = +719 \cdot 6 \text{ kJ} \quad ...(ii)$$

$$H_2\,(g) \longrightarrow 2H\,(g), \Delta H = +435 \cdot 4 \text{ kJ} \quad ...(iii)$$

We aim at

$$CH_4\,(g) \longrightarrow C\,(g) + 4H(g) \quad ...(iv)$$

Eqn. (*ii*) + 2 × Eqn (*iii*) − Eqn (*i*) gives

$$C(s) + 2H_2\,(g) \longrightarrow C\,(g) + 4H(g) - C\,(s) - 2H_2\,(g) - CH_4\,(g)$$

$$0 = C(g) + 4H(g) - CH_4\,(g),$$

$$\Delta H = 719 \cdot 6 + 2(435 \cdot 4) - (-74 \cdot 8)$$

or

$$CH_4\,(g) \longrightarrow C(g) + 4H(g), \quad \Delta H = +1665 \cdot 2 \text{ kJ}$$

This gives the enthalpy of dissociation of four moles of C—H bonds

Hence bond energy for C—H bond

$$= \frac{1665 \cdot 2}{4} = 416 \cdot 3 \text{ kJ mol}^{-1}$$

Use of bond energy data. When a chemical reaction takes place, some bonds of the reacting molecules are broken whereas some new bonds of the product molecules are formed. Knowing the bond energies of the various bonds involved, the enthalpy change of the reaction can be calculated as illustrated in the problem below.

EXAMPLE 1. *Calculate the enthalpy change for the reaction*

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

Given that the bond enthalpies of H–H, Br–Br and H–Br are 435, 192 and 364 kJ mol^{-1} respectively.

Solution. Energy absorbed for dissociation of 1 mole of H – H bonds = 435 kJ

Energy absorbed for dissociation of 1 mole of Br – Br bonds = 192 kJ

Total energy absorbed = 435 + 192 = 627 kJ

Energy released in the formation of 1 mole of H – Br bonds = 364 kJ

∴ Energy released in the formation of 2 moles of H – Br bonds = 2 × 364 kJ = 728 kJ.

Energy released > Energy absorbed

Hence net result is the release of energy.

Energy released = 728 kJ – 627 kJ = 101 kJ

i.e. for the given reaction, ΔH = **–101 kJ**

Alternatively, the problem may be solved by applying Hess's law or by applying the following relation directly

$$\Delta H_{\text{Reaction}} = \Sigma \text{ B.E. (Reactants)} - \Sigma \text{ B.E. (Products)}$$

$$= [\text{B.E.}(H_2) + \text{B.E.}(Br_2)] - 2\text{ B.E.}(HBr)$$

$$= 435 + 192 - 2 \times 364 = \mathbf{-101\ kJ}$$

EXAMPLE 2. *Propane has the structure $H_3C-CH_2-CH_3$. Calculate the change in enthalpy for the following reaction :*

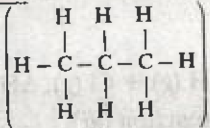
$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(g)$$

Given that average bond enthalpies are :

C–C	C–H	C = O	O = O	O–H
347	414	741	498	464 kJ mol^{-1}

(N.C.E.R.T.)

Solution. $\Delta H_{\text{reaction}}$



$$= \left[\text{B.E.}\left(H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H\right) + 5 \times \text{B.E.}(O = O)\right]$$

$$- [3 \times \text{B.E.}(O = C = O) + 4\text{ B.E.}(H-O-H)]$$

$$= [2\text{ B.E.}(C - C) + 8\text{ B.E.}(C-H) + 5\text{ B.E.}(O = O)]$$

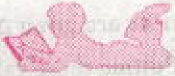
$$- [6 \times \text{B.E.}(C = O) + 8\text{ B.E.}(O-H)]$$

$$= [2(347) + 8(414) + 5(498)] - [6(741) + 8(464)]\text{ kJ mol}^{-1}$$

$$= [694 + 3312 + 2490] - [4446 + 3712]$$

$$= \mathbf{-1662\ kJ\ mol^{-1}}$$

PROBLEMS FOR PRACTICE



1. Find the enthalpy of formation of Hydrogen fluoride on the basis of following data :

   Bond energy of H—H bond = 434 kJ mol^{-1}

   Bond energy of F—F bond = 158 kJ mol^{-1}

   Bond energy of H—F bond = 565 kJ mol^{-1}

   [Ans. –269 kJ mol^{-1}]

2. Calculate the enthalpy change for the reaction

   $$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

   Given that the bond energies of H—H, I—I and H—I are 433, 151 and 299 kJ mol^{-1} respectively.

   [Ans. –14 kJ]

3. Calculate the enthalpy of formation of water, given that the bond energies of H—H, O = O and O—H bond are 433 kJ mol^{-1}, 492 kJ mol^{-1} and 464 kJ mol^{-1} respectively. [Ans. –249 kJ mol^{-1}]

4. From the following data at 25° C, calculate the bond energy of O—H bond :

   (*i*) $H_2(g) \longrightarrow 2H(g),\ \Delta H_1 = 104.2$ kcal

   (*ii*) $O_2(g) \longrightarrow 2O(g),\ \Delta H_2 = 118.4$ kcal

   (*iii*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$

   $\Delta H_3 = -57.8$ kcal

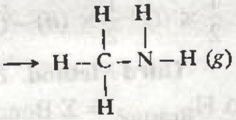
   [Ans. 110.6 kcal]

5. Calculate the enthalpy of hydrogenation of $C_2H_2(g)$ to $C_2H_4(g)$.

   (Given bond energies : C—H = 414·0 kJ mol^{-1}, C ≡ C = 827·6 kJ mol^{-1} C = C = 606·0 kJ mol^{-1}, H—H = 430·5 kJ mol^{-1})

   (*A.I.S.B. 1997*) [Ans. –175·9 kJ mol^{-1}]

6. ΔH for the reaction

   $$H{-}C \equiv N(g) + 2H_2(g) \longrightarrow H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{N}-H(g)$$

   is —150 kJ. Calculate the bond energy of C ≡ N bond.

PRACTICE PROBLEMS CONTD.

[Given bond energies of C—H = 414 kJ mol^{-1}; H—H = 435 kJ mol^{-1}; C—N = 293 kJ mol^{-1}, N—H = 396 kJ mol^{-1}] *(D.S.B. 1998)*

[Ans. 839 kJ mol^{-1}]

7. Calculate the enthalpy change for the following reaction $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

Given that the bond dissociation energies of H—H, Cl—Cl and H—Cl are 437 kJ, 244 kJ and 433 kJ mol^{-1} respectively. **[Ans. —185 kJ]**

8. Calculate the C—C bond energy from the following data : (*i*) $2C(\text{graphite}) + 3H_2(g) \longrightarrow C_2H_6(g)$, $\Delta H = —84.67$ kJ

(*ii*) $C(\text{graphite}) \longrightarrow C(g)$, $\Delta H = 716.7$ kJ

(*iii*) $H_2(g) \longrightarrow 2H(g)$, $\Delta H = 435.9$ kJ

Assume the C—H bond energy as 416 kJ

[Ans. 329.77 kJ]

9. Calculate ΔH° for the reaction $CH_2=CH_2 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

Given that the average bond energies of the different bonds are

Bond	C–H	O=O	C=O	O–H	C=C
Bond energy (kJ mol^{-1})	414	499	724	460	619

[Ans. —964 kJ mol^{-1}]

HINTS FOR DIFFICULT PROBLEMS

1. Aim : $\frac{1}{2}H_2 + \frac{1}{2}F_2 \longrightarrow HF, \Delta H = ?$

$$\Delta H = \Sigma \text{ B.E. (Reactants)} — \Sigma \text{ B.E. (Products)}$$

$$= \frac{1}{2}\text{ B.E. }(H_2) + \frac{1}{2}\text{ B.E. }(F_2) - \text{B.E. (HF)}$$

$$= \frac{1}{2} \times 434 + \frac{1}{2} \times 158 - 565 = -269 \text{ kJ mol}^{-1}.$$

3. Aim : $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O, \Delta H = ?$

or $H-H + \frac{1}{2}O=O \longrightarrow H-O-H, \Delta H = ?$

$$\underbrace{\begin{matrix}433 + \frac{1}{2} \times 492 \\ = 679 \text{ kJ}\end{matrix}}_{\text{Energy absorbed}} \qquad \underbrace{\begin{matrix}2 \times 464 \\ = 928 \text{ kJ}\end{matrix}}_{\text{Energy released}}$$

∴ Net energy released = 928 — 679

= 249 kJ mol^{-1}

i.e. $\Delta H = -249$ kJ mol^{-1}

Alternatively, $\Delta H = \text{B.E. }(H_2) + \frac{1}{2}\text{ B.E. }(O_2) - 2\text{ B.E. (O–H)}$

$$= 433 + \frac{1}{2} \times 492 - 2 \times 464 = -249 \text{ kJ mol}^{-1}.$$

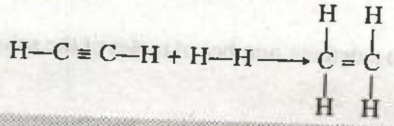
4. For reaction (*iii*)

$$\Delta H = \text{B.E. }(H_2) + \frac{1}{2}\text{ B.E. }(O_2) - 2\text{ B.E. (O–H)}$$

$$-57 \cdot 8 = 104 \cdot 2 + \frac{1}{2} \times 118 \cdot 4 - 2 \times \text{B.E. (O–H)}$$

or $2 \times$ B.E. (O—H) = 221·2 kcal

or B.E. (O—H) = 110·6 kcal.

5. 

$$H—C \equiv C—H + H—H \longrightarrow \begin{matrix} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{matrix}$$

$$\Delta H = \text{B.E. (Reactants)} — \text{B.E. (Products)}$$

$$= [\text{B.E. }(C \equiv C) + 2 \times \text{B.E. (C—H)} + \text{B.E. (H—H)}] — [\text{B.E. }(C = C) + 4\text{ B.E. (C—H)}]$$

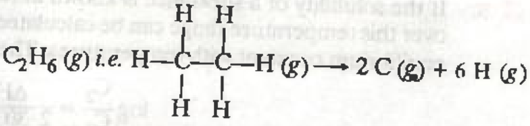
$$= [827 \cdot 6 + 2 \times 414 \cdot 0 + 430 \cdot 5] — [606 \cdot 0 + 4 \times 414 \cdot 0]$$

$$= 175 \cdot 9 \text{ kJ mol}^{-1}$$

6. $\Delta H_{reaction} = \Sigma$ B.E. (Reactants) —Σ B.E. (Products)

$$—150 = [\text{B.E. (C—H)} + \text{B.E. }(C \equiv N) + 2\text{ B.E. (H—H)}] - [3 \times \text{B.E. (C – H)} + \text{B.E. (C – N)} + 2 \times \text{B.E. (N – H)}]$$

8. Let us calculate ΔH for the reaction



$$C_2H_6(g) \text{ i.e. } H—\begin{matrix} H \\ | \\ C \\ | \\ H \end{matrix}—\begin{matrix} H \\ | \\ C \\ | \\ H \end{matrix}—H(g) \longrightarrow 2C(g) + 6H(g)$$

2 × Eqn. (*ii*) + 3 × Eqn. (*iii*)—Eqn. (*i*) gives

$\Delta H_{Reaction} = 2825 \cdot 77$ kJ

If x is the bond energy of C—C bond, then

$$x + 6 \text{ B.E. (C—H)} = 2825 \cdot 77$$

$$x + 6(416) = 2825 \cdot 77$$

or $x = 329 \cdot 77$ kJ

9. $\Delta H_{reaction} = [\text{B.E. }(C = C) + 4\text{ B.E. (C—H)} + 3\text{ B.E. }(O = O)] - [2 \times 2 \times \text{B.E. }(C = O) + 2 \times 2 \times \text{B.E. (O—H)}]$

$$= [619 + 4(414) + 3(499)] - [4(724) + 4(460)] \text{ kJ}$$

$$= -964 \text{ kJ}$$

ADD TO YOUR KNOWLEDGE

1. The compounds which have negative enthalpies of formation are called **exothermic compounds** while those with positive enthalpies of formation are called **endothermic compounds.**
2. Variation of heat of reaction with temperature is given by Kirchoff's equation viz.

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \Delta C_p \quad \text{or} \quad \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$$

or

$$\left(\frac{\partial(\Delta E)}{\partial T}\right)_V = \Delta C_v \quad \text{or} \quad \frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_v$$

where ΔH_1 and ΔH_2 are enthalpy changes at temperatures T_1 and T_2 and ΔE_1 and ΔE_2 are internal energy changes at temperatures T_1 and T_2 respectively.

$$\Delta C_p = \Sigma\, C_p \text{ of products} - \Sigma\, C_p \text{ of reactants}$$
$$\Delta C_v = \Sigma\, C_v \text{ or products} - \Sigma\, C_v \text{ of reactants}$$

C_p and C_v represent heat capacities at constant pressure and at constant volume respectively.

3. Enthalpy of formation of H^+ ion in dilute aqueous solution is taken as zero (*i.e.* $\frac{1}{2}H_2(g) + aq \longrightarrow H^+(aq) + e^-, \Delta H° = 0$). Using this value, the enthalpy of formation of any other ion can be calculated.

e.g. $HCl(g) \xrightarrow{\text{water}} H^+(aq) + Cl^-(aq), \quad \Delta H = -75{\cdot}14 \text{ kJ}$

i.e. $\Delta H°_f(H^+(aq)) + \Delta H°_f(Cl^-(aq)) - \Delta H°_f(HCl(g)) = -75{\cdot}14 \text{ kJ}$

But $\Delta H°_f(HCl(g)) = -92{\cdot}30$ kJ. Putting the values, we get

$$0 + \Delta H°_f(Cl^-(aq)) - (-92{\cdot}30) = -75{\cdot}14 \text{ kJ}$$

or $$\Delta H°_f(Cl^-(aq)) = -167{\cdot}44 \text{ kJ}$$

4. Enthalpy of formation of an atom is nearly half of the bond dissociation energy of its gaseous diatomic molecule *e.g.* $H_2(g) \longrightarrow 2H(g), \Delta H° = 435 \text{ kJ mol}^{-1}$

$\therefore$ Enthalpy of formation of H-atom = $435/2 = 217{\cdot}5 \text{ kJ mol}^{-1}$.

5. If the solubility of a substance is known at two different temperatures, the mean molar enthalpy of solution over this temperature range can be calculated by applying an equation similar to van't Hoff equation (relating equilibrium constant with temperature). The equation is

$$\log\frac{C_2}{C_1} = \frac{\Delta H}{2{\cdot}303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where C_1 and C_2 are solubilities at temperatures T_1 and T_2 respectively.

6. An adult requires about 2500 to 3000 kcal per day.
7. When an element exhibits allotropy, the standard enthalpy of formation is taken as zero for the allotropic form which is most stable under standard conditions *i.e.* 298 K and 1 bar pressure. For example, in case of carbon, $\Delta H_f° = 0$ for graphite and not for diamond. Similarly in case of sulphur, $\Delta H_f° = 0$ for rhombic form and not for monoclinic.
8. During hydration, the physical state of the solid does not change [*e.g.* $CuSO_4(s) + 5H_2O \longrightarrow CuSO_4.5H_2O(s)$]. However during dissolution, it changes.
9. The enthalpy change when one mole of the solute is dissolved in a definite number of moles of the solvent is called **integral** heat of solution.

ADD TO YOUR KNOWLEDGE (CONTD)

10. Enthalpy of ionization of a weak acid can be calculated by subtracting enthalpy of neutralisation of that acid with a strong base from 57·1 kJ *e.g.* heat of ionization of $CH_3COOH = 57{\cdot}1 - 55{\cdot}2 = 1{\cdot}9$ kJ

Likewise enthalpy of ionization of a weak base can be calculated.

11. Enthalpy of neutralisation of HF is about 68 kJ *i.e.* more than that of a strong acid with a strong base viz 57·1 kJ. This is due to very high hydration energy of fluoride ions.

12. $\Delta H_{combustion}$ is always negative. However, there are some reactions which involve combination with oxygen leading to partial combustion but ΔH is positive *e.g.* $N_2 + O_2 \longrightarrow 2\,NO, \Delta H = +ve$

Further when F_2 combines with O_2 to form OF_2, F_2 is reduced and not oxidized and ΔH for the reaction is positive

i.e.
$$F_2 + \frac{1}{2}O_2 \longrightarrow OF_2, \Delta H = +ve.$$

13. The neutralisation reaction of a strong acid with a strong base is

$$H^+ (aq) + OH^- (aq) \longrightarrow H_2O\,(l), \qquad \Delta H = -57{\cdot}1 \text{ kJ mol}^{-1}$$

From this, it may be concluded that enthalpy of dissociation of water is $+57{\cdot}1$ kJ mol^{-1}.

14. **Enthalpy of atomisation** is the heat required to break one mole of the substance into isolated atoms in the gaseous phase *e.g.* $Na\,(s) \longrightarrow Na\,(g)$.

SECTION—V

SOURCES OF ENERGY

5.19. Different Sources of Energy

We need energy almost in every sphere of life *e.g.* for lighting, cooking, transportation, communication etc. Further every industry is dependent upon energy. In fact, the progress of a country is determined on the basis of the electrical energy it consumes as it is an indication of the industrial progress and the progress of living standards of that country.

In this respect, India is still backward as the electrical energy consumption per person is quite low as compared to the developed countries. A few sources of energy are briefly explained below : –

1. Fossil fuels. Coal and petroleum which are believed to have been formed from animals and plants that remained buried under the surface of the earth for millions of years where they were subjected to high temperature and pressure are called fossil fuels. These are the most common fuels at the disposal of man and hence are called *conventional fuels.* In India, nearly 90% of the total energy requirement is met by these fuels. The various fractions obtained by fractional distillation of crude petroleum (e.g gasoline, diesel oil, kerosene oil etc.) provide the best source for means of transportation (i.e. scorters, cars, buses, trucks etc). Condensed Natural Gas (CNG) has been another substitute for petroleum products. Similarly, the heat energy produced by burning of coal may be used 'directly wherever required or may be used for the production of steam which may then run the turbine and produce electricity. This is the principle of a thermal plant.

The sudden sharp rise in prices of crude petroleum by oil producing countries in the mid 2000 and threat from global warming, rising sea levels and climatic changes due to green house gas emissions from fossil fuels forced the countries across the world to think of **alternative sources** of energy *i.e. non- conventional* and *renewable.* A few of these are given below.

2. Dung and wood. This is another very cheap and easily available source of energy. Gobar gas plants are becoming more and more popular in the rural areas which make use of cow-dung and decayed plants.

3. Water. Falling water has high kinetic energy which can be used to run the turbine and produce electricity. This is the principle of *hydro-electric power stations* set up at Nangal and Shivasamudram.

4. Radioactive elements. A small amount of a radioactive element such as uranium when undergoes nuclear fission produces a tremendous amount of energy which is equivalent to the energy produced by the burning of thousands of quintals of coal. Hence every country of the world has been trying to harness energy from this source. The plants which work on this principle are called *Nuclear power stations*. In India, we have nuclear power stations at Tarapur (Maharashtra), Kota (Rajasthan) and Kalpakkam (Tamil Nadu).

5. Wind. This is a gift of nature. The use of wind mills has been quite common but this source has not been exploited fully yet.

6. Geothermal sources. The interior of the earth is very hot. Hence, at a number of places, we find hot gases and hot steam rushing out of the earth's interior in the form of hot springs. The heat of these springs can be utilized as a source of energy. There are some places where people cook their dishes in the hot water springs.

7. Tidal waves and ocean currents which possess high kinetic energy can also be exploited as a source of energy.

In India, coal has been the main source of energy. It is only during the last few years that Oil and Natural Gas Commission has made a breakthrough in the field of petroleum. After independence, considerable development has also taken place in the field of hydroelectric power as a source of energy.

The different sources of energy consumption in India and in the world, as they existed in 1998, are shown in Fig. 5.15 below :

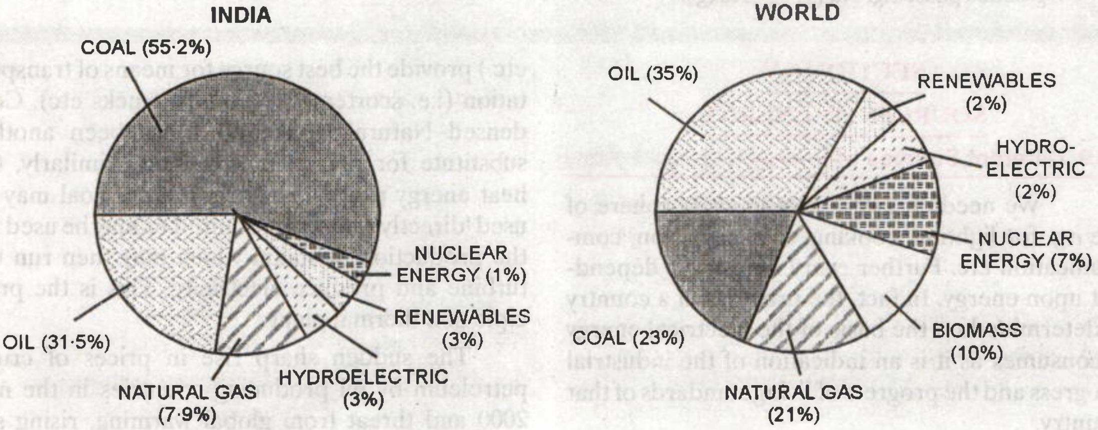


FIGURE 5.15. Sources of energy consumption in India and World (1998).

5.20. The Sun as the Primary or Ultimate Source of Energy

The various sources of energy such as fossil fuels, wood, hydroelectric power, wind power, nuclear power etc. are ultimately dependent upon the sun, *e.g.*

(*i*) Plants grow by synthesising their food in the presence of sunlight (photosynthesis).

(*ii*) The plants (forests) are then fossilized to form coal or they are food for the animals which in turn are a source of gobar gas or are fossilized to form petroleum.

(*iii*) The heat of the sun causes rain and hence we have water-falls acting as a source of hydroelectric power.

(*iv*) The heat of the sun causes winds, tides and ocean waves.

(*v*) It is believed that all elements including radioactive elements like uranium are synthesised from hydrogen by the process of nuclear fusion taking place in sun or other stars.

Efforts have also been made to explore the solar energy for generating electricity. However, these efforts have not met with any appreciable success so far.

The various processes are shown diagrammatically in Fig. 5.16.

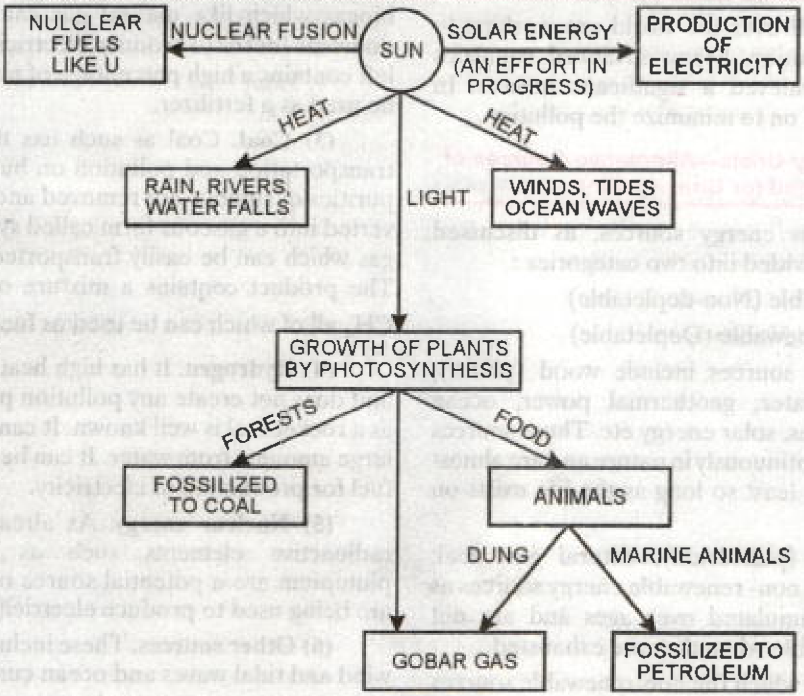


FIGURE 5.16. The Sun as the ultimate source of energy.

5.21. Pollution Associated with Consumption of Fuels

For the production of electricity by the thermal power plants and to meet the ever increasing needs of transport in the cities and towns, the consumption of fossil fuels (*i.e.* coal and petroleum products) is on the increase. The combustion of these fuels produces carbon dioxide, carbon monoxide, oxides of nitrogen and sulphur (by oxidation of compounds of sulphur and nitrogen or elemental sulphur present as impurity in the fossil fuels) and some unburnt hydrocarbons. All of these are the pollutants of the atmosphere as explained below :

(i) Carbon dioxide. This is the main product of combustion of the fossil fuels. If its percentage in the atmosphere increases beyond a particular level, the climate of that place may change *e.g.* the average temperature may increase*.

(ii) Carbon monoxide. It combines with the haemoglobin of the blood forming carboxyhaemoglobin thereby making it incapable of transporting oxygen to the different parts of the body.

(iii) Oxides of nitrogen and sulphur. They are corrosive and poisonous. They dissolve in the rain water thereby making it acidic. This is called 'acid rain'. It damages the stone buildings and forests and also the metals.

(iv) Unburnt hydrocarbons. Some of these hydrocarbons are a great health hazard and may even cause cancer.

Besides fossil fuels, another very important source of energy is the 'nuclear fuel' being used in the nuclear power stations. This sometimes causes even greater problems. Although the release of radioactivity into the atmosphere is strictly controlled, yet disasters do occur sometimes. For example in 1986, such a disaster took place in Russia (in Chernobyl). A very large number of people are affected when such a disaster occurs. The storage of radioactive waste (produced by the nuclear

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*This effect is called 'greenhouse effect', (discussed in Unit 18).

power stations) which has still a very high radioactive level poses a very serious problem.

Scientists all over the world are working to control the pollution. Many advanced countries have already achieved a significant success. In India, efforts are on to minimize the pollution.

5.22. Why Energy Crisis—Alternative Sources of Energy : Need for Conservation

The various energy sources, as discussed above, may be divided into two categories :

(1) Renewable (Non-depletable)

(2) Non-renewable (Depletable)

Renewable sources include wood (plants), wind, falling water, geothermal power, ocean waves, tidal waves, solar energy etc. These sources are produced continuously in nature and are almost inexhaustible, at least so long as the life exists on this earth.

Crude oil (petroleum), natural gas, coal, uranium etc. are non- renewable energy sources as these have accumulated over ages and are not quickly replaceable when they are exhausted.

The rate at which the non-renewable sources of energy are being consumed, it is expected that their stocks are likely to exhaust by the middle of the 21st century. Hence there is a likelihood of energy crisis.

It may be pointed out that the law of conservation of energy does not fail here. The only problem is that the combustion of fuels is a one way process *i.e.* either the products of combustion are not converted back into the original substances at all or they are converted back at a rate much slower than the rate of their consumption. For example, coal burns to form CO_2 but CO_2 is converted back into carbon by nature through photosynthesis at a much slower rate.

Foreseeing the problem of energy crisis, scientists all over the world are trying to find ways and means of getting all types of energy from **alternative sources*** *i.e.* renewable and non-conventional sources. A few of these are given below :

(1) Solar energy *e.g.* in the form of solar cookers, solar water pumps, solar photovoltaic cells, solar water heating systems etc.

(2) Biomass. It is the waste material obtained from animals and plants *e.g.* cattle dung and dead parts of plants and animals. When allowed to rotten in the absence of air, it decomposes to produce biogas which like natural gas can be used as a domestic fuel or to produce electricity. The residue left contains a high percentage of nitrogen and can be used as a fertilizer.

(3) Coal. Coal as such has the problem of transportation and pollution on burning. The impurities of sulphur are removed and then it is converted into a gaseous form called synthetic natural gas which can be easily transported in pipe lines. The product contains a mixture of CO, H_2 and CH_4 all of which can be used as fuels.

(4) Hydrogen. It has high heat of combustion and does not create any pollution problem. Its use as a rocket fuel is well known. It can be obtained in large amounts from water. It can be used as a good fuel for production of electricity.

(5) Nuclear energy. As already mentioned, radioactive elements such as uranium and plutonium are a potential source of energy which are being used to produce electricity.

(6) Other sources. These include geothermal, wind and tidal waves and ocean currents.

However, we should also try to conserve energy as far as possible. A few practical **suggestions for the conservation of energy** are listed below :

(1) Use the fuel that is renewable.

(2) Use high efficiency oil or gas stoves which burn the fuel with a blue flame and not with a yellow flame (which is an incomplete combustion producing less heat).

(3) Keep ready the next item to be heated, otherwise, put off the stove.

(4) Use the vessels with flat bottom for heating and not the vessels with round bottoms.

(5) Use energy-saving devices for cooking like pressure cookers etc.

(6) Switch off the lights, fans etc. when not required.

(7) In winter, better sit in the sun to warm yourself instead of using heaters inside the rooms.

(8) Use casseroles for keeping the eatables hot instead of heating them again.

(9) Take bath with fresh running water instead of using geysers.

(10) Plant trees if you have surplus land.

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*To tap alternative sources, India has set up Ministry for Non-Conventional Energy Sources (MNES). It has tapped nearly all sources like solar, wind, biomass, hydro projects etc.

Conceptual Questions

Q. 1. Classify the following into open, closed or isolated systems :

(*i*) Animals and plants (*ii*) A referigerator or a fridge (*iii*) A solar cooker.

Ans. (*i*) Open system (*ii*) Isolated system (*iii*) Closed system.

Q. 2. To what type of system the following belong ?

(*i*) Tree (*ii*) Tea placed in a kettle.

Ans. (*i*) Open system (*ii*) closed system.

• **Q. 3. Which of the following are open, closed or nearly isolated systems ?**

(*i*) Human beings (*ii*) the earth (*iii*) can of tomato soup (*iv*) Ice-cube tray filled with water (*v*) A satellite in an orbit (*vi*) Coffee in a thermos flask and (*vii*) Helium filled balloon. *(N.C.E.R.T.)*

Ans. **Open :** Human beings, Earth, Ice cube tray

Close : Can of tomato soup, A satellite in an orbit

Isolated : Coffee in thermos flask, Helium filled balloon.

• **Q. 4. Separate out the following into extensive and intensive:**

Volume, Temperature, Pressure, Boiling point, Free energy

Ans. Volume and free energy are extensive, others are intensive.

Q. 5. What is the most important condition for a process to be reversible in Thermodynamics ?

Ans. The process should be carried out infinitesimally slowly or the driving force should be infinitesimally greater or smaller than the opposing force.

Q. 6. Which of the following are state functions ?

(*i*) Height of a hill (*ii*) Distance travelled in climbing the hill (*iii*) Energy change in climbing the hill. *(N.C.E.R.T.)*

Ans. (*i*) and (*iii*).

• **Q. 7. Why 'Kelvin scale of temperature' is called 'Absolute scale of temperature' ? What are the reference points on this cale.**

Ans. On the Kelvin scale of temperature, zero point is the lowest possible temperature whereas on the celsius scale, zero point is only with reference to ice point. Hence the former is called absolute scale. The reference points are absolute zero of temperature and the triple point of water (0·01°C or 273·16 K).

Q. 8. Can the absolute value of internal energy be determined ? Why or why not ?

Ans. No, because it is the sum of different types of energies some of which cannot be determined.

Q. 9. One mole of CO_2 at 300 K and 1 atm pressure is heated in a closed vessel so that temp. is 500 K and pressure is 5 atm. Then it is cooled so that temp. is 300 K and pressure is 1 atm. What is the change in internal energy of the gas ?

Ans. No change because internal energy is a state function.

Q. 10. Water decomposes by absorbing 286·2 kJ of electrical energy per mole. When H_2 and O_2 conbine to form one mole of H_2O, 286·2 kJ of heat is produced. Which law is proved ? What statement of the law follows from it ?

Ans. Law of conservation of energy or 1st law of thermodynamics. **Def.** Energy can neither be created or destroyed, although it may be converted from one form to another.

Q. 11. Neither q nor w is a state function, yet $q + w$ is a state function. Explain why.

Ans. $q + w = \Delta E$ and ΔE is a state function.

Q. 12. Why heat is not a state function ?

Ans. According to first law of thermodynamics, $\Delta E = q + w$ or $q = \Delta E - w$. As ΔE is a state function but w is not a state function, therefore q is also not a state function.

Q. 13. Why absolute value of enthalpy cannot be determined ?

Ans. As $H = E + PV$ and absolute value of internal energy, E cannot be determined, therefore absolute value of H cannot be determined.

Q. 14. What is the relation between ΔH and ΔU ? Under what condition, the two are equal ?

Ans. $\Delta H = \Delta U + P\Delta V = \Delta U + \Delta n_g RT$. For conditions see page 5/14.

Q. 15. Explain why heat capacity is not a state function.

Ans. Heat capacity (C) = $\frac{q}{\Delta T}$. As 'q' is not a state function, therefore C is also not a state function.

Q. 16. Derive that for an ideal gas, $C_v = dE / dT$ and $C_p = dH / dT$.

Ans. See page 5/17.

Q. 17. Specific heat of Li (*s*), Na (*s*), K (*s*), Rb (*s*) and Cs (*s*) at 398 K are 3·57, 1·23, 0·756, 0·363 and 0·242 $J\,g^{-1}\,K^{-1}$ respectively. Compute the molar heat capacities of these elements and identify any periodic trend. If there is a trend, use it to predict the molar heat capacity of Fr. *(N.C.E.R.T.)*

Ans. Molar heat capacity = Specific heat × Molar mass

Hence for Li, Na, K, Rb and Cs, their values ($JK^{-1}\,mol^{-1}$) will be respectively
$3{\cdot}57 \times 7 = 25{\cdot}0$, $1{\cdot}23 \times 23 = 28{\cdot}3$, $0{\cdot}756 \times 39 = 29{\cdot}5$, $0{\cdot}363 \times 85 = 30{\cdot}86$,

$0{\cdot}242 \times 133 = 32{\cdot}2\ JK^{-1}\,mol^{-1}$.

Plotting and extrapotation gives $33{\cdot}5\ JK^{-1}\,mol^{-1}$ for Fr^{223}.

Q. 18. Is q_p always greater than q_v ? Explain why or why not.

Ans. q_p is not greater than q_v always. It depends upon whether Δn_g is +ve or —ve *i.e.* $n_p > n_r$ or $n_p < n_r$ ($q_p = q_v + \Delta n_g RT$)

Q. 19. In what form the energy is produced when petrol is burnt in the engine of a car or a scooter ?

Ans. Partly as mechanical work and partly as heat.

Q. 20. What is the most important reaction that takes place in our body that maintains body temperature ?

Ans. Slow oxidation of carbohydrates.

Q. 21. Why some reactions are exothermic while some others are endothermic ?

Ans. If the total internal energy of the reactants (E_R) is greater than that of the products (E_P), the energy is released and the reaction is exothermic. However if $E_R < E_P$, then energy is absorbed and the reaction is endothermic.

Q. 22. The reaction
$N_2(g) + O_2(g) \longrightarrow 2\,NO(g)$ —180·7 kJ is........ thermic and ΔH = ...kJ

Ans. Endothermic and $\Delta H = +180{\cdot}7$ kJ

Q. 23. Will the heat evolved be same in the following two cases ?

(*a*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$ (*b*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$
If not, in which case it will be greater and why ?

Ans. No. It will be greater in case (*b*) because when $H_2O(g)$ condenses to form $H_2O(l)$, heat is released.

Q. 24. Which of the following is/are exothermic and which is/are endothermic ?

(*i*) $Ca(g) \longrightarrow Ca^{2+}(g) + 2e^-$ (*ii*) $O(g) + e^- \longrightarrow O^-(g)$
(*iii*) $N^{2-}(g) + e^- \longrightarrow N^{3-}(g)$

Ans. (*i*) Endothermic (ionization energy is required)
(*ii*) Exothermic (first electron affinity is energy released)
(*iii*) Endothermic (higher electron affinities are energies required).

Q. 25. The products of combustion of 6 g cabron contained 50% CO_2 and 50% CO. The heat evolved was 126 kJ. Calculate the enthalpy of combustion of carbon. Given that the enthalpy of formation of CO is —110·5 kJ mol^{-1}.

Ans. Heat evolved from the combustion of *one mole* of C to form 50% CO_2 and 50% CO = 2 × 126 = 252 kJ

Suppose heat evolved from combustion of 1 mole of C to CO_2 = x kJ

$\therefore$ Heat of evolved from $\frac{1}{2}$ mole $= \frac{x}{2}$ kJ

Heat evolved from combustion of 1 mole of C to CO = 110·5 kJ

$\therefore$ Heat evolved from $\frac{1}{2}$ mole $= \frac{110 \cdot 5}{2} = 55 \cdot 25$ kJ

$$\frac{x}{2} + 55 \cdot 25 = 252 \quad \text{or} \quad x = 393 \cdot 5 \text{ kJ mol}^{-1}.$$

Q. 26. The enthalpy of combustion of glucose ($C_6H_{12}O_6$) is 2840 kJ mol^{-1}. What is its calorific value ?

Ans. Molar mass of glucose ($C_6H_{12}O_6$) = 180 g mol^{-1}

$$\therefore \text{Calorific value} = \frac{2840 \text{ kJ mol}^{-1}}{180 \text{ g mol}^{-1}} = 15 \cdot 78 \text{ kJ g}^{-1}$$

Q. 27. Heat of dissociation of acetic acid is 1·9 kJ mol^{-1}. How much heat will be evolved when one mole of acetic acid is neutralized by NaOH solution ?

Ans. 57·1 — 1·9 = 55·2 kJ

Q. 28. Fill in the blanks.

***(i)* The dissolution of $CuSO_4$ is .... thermic while dissolution of $CuSO_4 . 5H_2O$ is ....thermic.**

***(ii)* $\Delta H_{sublimation} = \Delta H_{fusion}$ + ...**

***(iii)* The enthalpy of solution of $BaCl_2$ (s) and $BaCl_2 . 2H_2O$ (s) are x and y kJ mol^{-1} respectively. Then enthalpy of hydration of $BaCl_2$ will be........**

Ans. (*i*) exothermic, endothermic (*ii*) $\Delta H_{vaporisation}$ (*iii*) $(x - y)$ kJ mol^{-1}.

Q. 29. Why bond energy is taken as an average value ? Explain with a suitable example.

Ans. The bond energy of the same bond in different polyatomic molecules is not same *e.g.* bond energy of C—Cl bond in CH_3Cl, CH_3CH_2Cl etc. is not same. Even in the same polyatomic molecule like CH_4, the bond energy of all the four C—H bonds is not same. Hence an average value is taken.

Q. 30. Give appropriate reasons for the following :

***(i)* It is preferable to determine a change in enthalpy than change in internal energy.**

***(ii)* It is necessary to define the 'Standard state'.**

***(iii)* It is necessary to specify the phases of the reactants and products in a thermochemical equation.** *(N.C.E.R.T)*

Ans. (*i*) Change in enthalpy is the heat evolved or absorbed at constant pressure. As most of the reactions are carried out in open vessels *i.e.* at constant pressure of one atmosphere, hence change in enthalpy is preferred.

(*ii*) This is because the enthalpy of a reaction depends upon the conditions under which the reaction is carried out.

(*iii*) The enthalpy change of a reaction depends upon the physical state of the reactants and products *e.g.* standard enthalpy of formation of water is not same for H_2O (g) and H_2O (l).

Q. 31. The enthalpy of neutralisation of acetic acid by KOH is —55·8 kJ mol^{-1} while that of hydrochloric acid by KOH is —57·3 kJ mol^{-1}. Why are they different and what does the difference represent ? *(N.C.E.R.T.)*

Ans. Heat of neutralisation of acetic acid is less than that of HCl because acetic acid is a weak acid and does not ionize completely. Some heat is used up for the ionization of acetic acid. The difference represents the enthalpy of ionization of acetic acid.

Q. 32. What is the basic difference between enthalpy of formation and enthalpy of reaction ? Illustrate with suitable examples. *(N.C.E.R.T.)*

Ans. (*i*) Enthalpy of formation is enthalpy change for the formation of **1 mole of the substance** from its elements. For example, let us consider the following two thermochemical equations :

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l), \quad \Delta H^\circ = -285 \cdot 8 \text{ kJ mol}^{-1}$$

$$\text{and } 2H_2(g) + O_2(g) \longrightarrow 2H_2O(l), \quad \Delta H^\circ = -571 \cdot 6 \text{ kJ mol}^{-1}$$

In the first case, $\Delta H°$ is enthalpy of formation of H_2O (*l*), while in the second case, it is enthalpy of reaction.

(*ii*) Enthalpy of formation is for the formation of 1 mole of the substance **from its elements only.** For example, we have

$$CaO\,(s) + CO_2\,(g) \longrightarrow CaCO_3\,(s), \quad \Delta H° = -178{\cdot}3 \text{ kJ mol}^{-1}$$

As 1 mole of $CaCO_3$ (*s*) has been formed from CaO (*s*) and CO_2 (*g*) and not from its elements, $\Delta H°$ is not enthalpy of formation. It is simply enthalpy of reaction.

Q. 33. Why in a reaction enthalpy change is always written per mole even if two or more moles of a reactant or product are present in the balanced equation ?

Ans. This is because if the units are multiplied by a number, the units do not change.

Q. 34. One kg of graphite is burnt in a closed vessel. The same amount of the same sample is brunt in an open vessel. Will the heat evolved in the two cases be same ? If not, in which case it would be greater ?

Ans. Same in both cases because $\Delta n_g = 0$.

Q. 35. Why standard heat of formation of diamond is not zero though it is an element ? ***(H.S.B. 1997)***

Ans. The standard state chosen for carbon is graphite and not diamond because graphite is more common and stabler form of carbon in the standard state.

Q. 36. Is the bond energy of all the four C—H bonds in CH_4 molecule equal ? If not then why ? How is the C—H bond energy then reported ?

Ans. No because after breaking of C—H bonds one by one, the electronic environments change. The reported value is the average value of the bond dissociation energies of the four C—H bonds.

Q. 37. The enthalpy change for the reaction $N_2\,(g) + 3\,H_2\,(g) \longrightarrow 2\,NH_3\,(g)$ is $-92{\cdot}2$ kJ. What is the enthalpy of formation of ammonia ?

Ans. Aim : $\frac{1}{2} N_2\,(g) + \frac{3}{2} H_2\,(g) \longrightarrow NH_3\,(g), \Delta H_f° = ?$

Given : $N_2\,(g) + 3\,H_2\,(g) \longrightarrow 2\,NH_3\,(g), \Delta H_r° = -92{\cdot}2$ kJ

$$\therefore \Delta H_f° (NH_3) = -\frac{92{\cdot}2}{2} = -46{\cdot}1 \text{ kJ.}$$

Q. 38. What is the basis of Hess's Law ?

Ans. Hess's law is based upon the fact that enthalpy is a state function *i.e.* enthalpy change depends only upon the initial state (*i.e.* enthalpy of the reactants) and the final state (*i.e.* enthalpy of the products) and does not depend upon the path followed.

Q. 39. Write the standard state for each of the following in which $\Delta H_f°$ is taken as zero : Carbon, Sulphur and Bromine.

Ans. C (graphite), S_8 (Rhombic) and Br_2 (*l*).

Q. 40. Given that :

$$O\,(g) + e^- \longrightarrow O^-\,(g), \Delta H = -142 \text{ kJ mol}^{-1} \text{ and } O\,(g) + 2\,e^- \longrightarrow O^{2-}\,(g), \Delta H = +712 \text{ kJ mol}^{-1}$$

What will be ΔH for $O^-\,(g) + e^- \longrightarrow O^{2-}\,(g)$?

Ans. The second reaction takes place in two steps as :

$$O\,(g) + e^- \longrightarrow O^-\,(g), \Delta H = \Delta H_1, \quad O^-\,(g) + e^- \longrightarrow O^{2-}\,(g), \Delta H = \Delta H_2$$

Hence $\Delta H_1 + \Delta H_2 = +712$

But $\Delta H_1 = -142$ kJ mol^{-1} (*Given*)

$\therefore -142 + \Delta H_2 = +712$ or $\Delta H_2 = \mathbf{854 \text{ kJ mol}^{-1}}$

Alternatively, subtract Ist eqn. from 2nd eqn.

Q. 41. Calculate the enthalpy of vaporisation of water at 25°C and 1 atm pressure. Given that the standard enthalpies of formation of H_2O (*l*) and H_2O (*g*) are $-285{\cdot}8$ and $-241{\cdot}8$ kJ mol^{-1} respectively.

Ans. Aim : $H_2O\,(l) \longrightarrow H_2O\,(g), \Delta H^\circ = ?$

$$\Delta H^\circ = \Delta H_f^\circ\,(H_2O\,(g)) - \Delta H_f^\circ\,(H_2O\,(l)) = -241 \cdot 8 - (-285 \cdot 8)\text{ kJ mol}^{-1} = \mathbf{44\text{ kJ mol}^{-1}}.$$

Q. 42. ΔH_f° for freon, $CHClF_3$ is $-480 \cdot 0$ kJ mol^{-1}. Represent it by thermochemical equation.

Ans. $C\,(s) + \frac{1}{2} H_2\,(g) + \frac{1}{2} Cl_2\,(g) + F_2\,(g) \longrightarrow CHClF_2, \Delta H_f^\circ = -480 \cdot 0\text{ kJ mol}^{-1}.$

Q. 43. Why is $\Delta U = 0$ for isothermal expansion of an ideal gas ?

Ans. For an ideal gas, the internal energy is a function of temperature only. During isothermal expansion, as temperature remains constant, there is no change in internal energy *i.e.* $\Delta U = 0$.

Q. 44. Why standard enthalpy of formation of elementary substances is taken as zero ?

Ans. Enthalpy of formation is the heat change involved in the formation of one mole of the substance from its elements. An element formed from itself means no heat change *i.e.* $\Delta H_f^\circ = 0$.

Q. 45. The specific heat of a gas is found to be 0·075 calorie at constant volume and its formula weight is 40. What is the atomicity of the gas ?

Ans. Molar heat capacity, $C_v = 0 \cdot 075 \times 40$ calorie $= 3$ cal mol^{-1}

$$C_p = C_v + R = 3 + 2\text{ cal mol}^{-1} = 5\text{ cal mol}^{-1}$$

$\therefore \gamma = C_p / C_v = 5/3 = 1 \cdot 66$. Hence the gas is monoatomic.

Very Short Answer Questions CARRYING 1 MARK

Q. 1. Under what condition, the heat evolved or absorbed is equal to the internal energy change ?

Ans. When the volume remains contant

Q. 2. Under what condition, an extensive property can become intensive ?

Ans. An extensive property becomes intensive when unit amount of the substance is taken e.g. mass and volume are extensive but density (mass per unit volume) and specific volume (volume per unit mass) are intensive.

Q. 3. Why we usually study enthalpy change and not internal energy change ?

Ans. Because most of the processes (reactions) are carried out in open vessels *i.e* at constant pressure (= 1 atm)

Q. 4. What are the conditions for expressing standard enthalpy change ?

Ans. 25° C(298 K) and one atmospheric pressure.

Q. 5. What is the sign of ΔH for endothermic reactions and why ?

Ans. ΔH is positive because $\Delta H = H_p - H_R$ and $H_R < H_P$

Q. 6. What is the relationship between standard enthalpy of formation and the enthalpy of a compound ?

Ans. They are equal.

Q. 7. What is the value of enthalpy of neutralization of a strong acid by a strong base ?

Ans. −57.1 kJ

Q. 8. Why enthalpy of neutralisation is less if either the acid or the base or both are weak ?

Ans. A part of the heat is used up for the dissociation of the weak acid or the weak base or for both if they are weak.

Q. 9. Why enthalpy of neutralisation of HF is greater than 57·1 kJ mol^{-1} ?

Ans. This is due to high hydration energy of fluoride ions.

Q. 10. What are specific heat capacity and molar heat capacity for water ?

Ans. Specific heat capacity for $H_2O = 4 \cdot 18\text{ JK}^{-1}\text{ mol}^{-1}$

Molar heat capacity for $H_2O = 4 \cdot 18 \times 18 = 75 \cdot 24\text{ JK}^{-1}\text{ mol}^{-1}$.

Q. 11. What is the law called which states that the total enthalpy change in a chemical reaction is always same at the same temperature ?

Ans. Hess's law of constant heat summation

Q. 12. What are renewable sources of energy ?

Ans. Those which are produced continuously in nature and are inexhaustible *e.g.* wood, solar energy etc.

Q. 13. What is SI definition of one Kelvin ?

Ans. One Kelvin is 1/273·16 of the triple point temperature of water (viz 273·16 K).

Short Answer Questions CARRYING 2 or 3 MARKS

Sec. 5.1. to 5.2. **1.** What do you understand by open, closed and isolated systems ? Illustrate with suitable examples.

2. What are extensive and intensive properties ? Give two examples of each.

3. Classify, giving reason, the following into intensive and extensive properties :

(*i*) Entropy (*ii*) Viscosity (*iii*) Heat capacity (*iv*) Surface tension (*v*) Vapour pressure (*vi*) Refractive index

4. How will you distinguish between the two

(*i*) open and closed system

(*ii*) extensive and intensive properties ?

Sec. 5.3. to 5.4. **5.** Define Zeroth Law of Thermodynamics. How has it been useful in the measurement of temperature ?

Sec. 5.5. to 5.6. **6.** Explain, giving reasons, which of the quantities out of internal energy, heat and work are state functions and which are not.

7. Derive an expression for the work of expansion of a gas ($w = — P\,\Delta V$).

8. (*a*) Show that the pressure volume work, $W = —P\Delta V$.

(*b*) List the important sign conventions for heat and work.

9. What do you mean by law of conservation of energy ? Write a mathematical relationship between heat, internal energy and work done by the system.

10. State the law of conservation of energy and give a mathematical expression for it. Mention also two examples to support the law.

11. How can you justify that though q and w are not state functions, yet $(q + w)$ is a state function ?

12. Discuss the significance of the mathematical expression in which the heat absorbed by a system is related to interal energy and work done by the system.

13. Describe the 1st law of Thermodynamics.

14. State the first law of thermodynamics and derive a mathematical expression for it.

Sec. 5.7. **15.** What do you understand by 'Enthalpy' and 'Enthalpy change' ?

16. Starting with the thermodynamic relationships $\Delta E = q - P\Delta V$ and $H = E + PV$, derive relationship $\Delta H = q_p$

Sec. 5.8. **17.** Starting with the thermodynamic relationsip $H = E + PV$, derive the following relationship :

$\Delta H = \Delta E + (\Delta n)\,RT$

18. Derive the relationship between heat of reaction at constant pressure, q_p and heat of reaction at constant volume, q_v. or Derive the following equation $\Delta H = \Delta E + (\Delta n)\,RT$.

Sec 5.9. **19.** What is meant by C_p and C_v ? Derive the reaction $C_p - C_v = R$.

Sec. 5.10. **20.** What is the origin of enthalpy change in a chemical reaction ?

21. Give some examples to show that different types of energies are evolved or absorbed in different reactions.

Sec. 5.11. **22.** What are exothermic and endothermic reactions ? Explain with suitable examples.

23. Why enthalpy change is negative for exothermic reactions while it is positive for endothermic reactions?

Sec. 5.12. **24.** What do you understand by a thermochemical equation ? Can we use fractional coefficients in such an equation ?

Sec. 5.13. **25.** Define 'Enthalpy of reaction'. On what factors does it depend ? What happens to the value of the heat of reaction if the reaction is reversed ?

Sec. 5.14. **26.** Define the following :

(*i*) Enthalpy of combustion, (*ii*) Enthalpy of formation, (*iii*) Enthalpy of neutralization, (*iv*) Enthalpy of vaporisation.

27. Fill in the blanks :—

(*i*) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) + 185\ kJ$

This reaction is ..... thermic (exo or endo), ΔH = ... kJ

(*ii*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$, $\Delta H = -286$ kJ

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ .... kJ (± ?)

(*iii*) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$, $\Delta H = -809$ kJ

The calorific value of 1 kg of $CH_4(g)$ is .... kJ/kg.

(*iv*) $C(s) \longrightarrow C(g)$, $\Delta H = 716.7$ kJ, ΔH is the heat of .... of graphite

(*v*) $H_2O(g) \longrightarrow H_2O(l)$, $\Delta H = -40.7$ kJ, ΔH is the heat of .... of steam.

(*vi*) Enthalpy of neutralization of H_2SO_4 with NaOH is the amount of heat evolved when 1 mole of NaOH is neutralized by .... mole of H_2SO_4.

28. Explain why the enthalpy of neutralization of a strong acid with a strong base is always same while it is less if either the acid is weak or the base is weak.

Sec. 5.16. **29.** How is enthalpy of sublimation related to enthalpy of fusion and enthalpy of vaporisation ?

Sec. 5.17. **30.** State and explain Hess's Law of constant heat summation.

Sec. 5.18. **31.** Define 'bond energy'. What is the origin of enthalpy change in a chemical reaction ?

Sec. 5.19. to 5.21. **32.** Briefly explain the various sources of energy.

33. What are fossil fuels ?

34. Justify the statement that 'Sun is the ultimate source of energy.

Sec. 5.22. **35.** What are renewable and non-renewable sources of energy ? Why is there a likelihood of energy crisis ?

36. List some practical suggestions for the conservation of energy.

Long Answer Questions CARRYING 5 or more MARKS

Sec. 5.1. **1.** Define 'thermodynamics'. Briefly describe the importance and limitiations of thermodynamics.

Sec. 5.2. **2.** Define the following terms :

(*i*) System (*ii*) State variables (*iii*) State function (*iv*) Extensive and intensive properties (*v*) Isothermal process (*vi*) Adiabatic process (*vii*) Reversible process (*viii*) Internal energy.

Sec 5.3 to 5.4. **3.** State and explain Zeroth Law of Thermodynamics.

Sec 5.5 to 5.6 **4.** Briefly explain the terms internal energy, work and heat. How are they interrelated ? Justify that internal energy is a state function but work and heat are not.

5. State and explain the 'First law of thermodynamics'.

Sec 5.7. to 5.8. **6.** Briefly explain the terms Enthalpy and Enthalpy change. How is it related to the internal energy change ? Derive the relationship.

7. Derive the relationship between heat of reaction at constant pressure and that at constant volume. Under what conditions are the two equal to each other ?

Sec. 5.9. **8.** Define the terms 'specific heat' and 'molar heat capacity'. Name the two types of molar heat capacities. Derive the relationship between them.

Sec. 5.10. **9.** Define 'Energetics'. Explain with suitable examples. What are the different modes of transference of energy between the system and the surroundings ?

Sec 5.11. **10.** What are Exothermic and Endothermic reactions ? Give three examples of each type. Explain the sign of ΔH for these reactions.

Sec. 5.13. **11.** Explain the term 'Enthalpy of Reaction.' What are the factors on which the heat of reaction depends ?

Sec. 5.14. **12.** Define and explain the following terms :

(*i*) Enthalpy of combustion (*ii*) Enthalpy of formation (*iii*) Enthalpy of neutralisation

(*iv*) Enthalpy of solution (*v*) Enthalpy of hydration

Sec 5.15. **13.** Briefly explain how the following heats of reaction are measured experimentally :

(*a*) Heat of reaction at constant volume (or internal energy change) (*b*) Heat of neutralisation.

Sec. 5.16. **14.** Explain the following terms :

(*i*) Enthalpy of fusion (*ii*) Enthalpy of vaporisation (*iii*) Enthalpy of sublimation.

Sec. 5.17. **15.** State 'Hess's law of constant heat summation'. How does it help in the calculation of

(*i*) heat of allotropic transformation ? (*ii*) heat of hydration ?

Sec. 5.18. **16.** Define 'Bond energy'. How does it help in the calculation of enthalpy of reaction ?

Sec.5.19. to 5.21. **17.** List the various sources of energy. Briefly explain each one of them. Explain that sun is the ultimate source of energy. How pollution is caused by the consumption of fuels ?

Sec. 5.22. **18.** Why there is energy crisis if energy is conserved in nature ? Give some practical suggestions for the conservation of energy.

COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

1. Entropy (S) and Gibbs Free Energy (G). *Entropy (S) is a measure of randomness of a system.* The change in entropy during a process is equal to the heat absorbed isothermally and reversibly during a process divided by the absolute temperature at which heat is absorbed *i.e.* $\Delta S = q_{iso,\ rev.} / T$. Its units are $JK^{-1}\ mol^{-1}$.

Gibbs free energy (G) is another thermodynamic quantity related to the enthalpy and entropy of the system according to the equation $G = H - TS$. The change in its value during an isothermal process is given by $\Delta G = \Delta H - T\Delta S$.

2. Spontaneous process. A process which can take place by itself or by initiation independent of rate is called a spontaneous process or a feasible process. For a process to be spontaneous, ΔG is —ve.

3. Application of First law of Thermodynamics to different types of processes

(*i*) *For an isochoric process.* As volume is kept constant, $\Delta V = 0$. Hence $\Delta E = q - P\Delta V$ becomes $\Delta E = q_v$

(*ii*) *For an isobaric process.* As pressure is kept constant, $\Delta E = q_p - P\Delta V$ *i.e.* $q_p = \Delta E + P\Delta V = \Delta H$

(*iii*) *For an isothermal process.* At constant temperature, for ideal gas, $\Delta E = 0$. As already derived in the text under this condition. $w_{exp} = -2{\cdot}303\, n\, RT \log \frac{V_2}{V_1} = -2{\cdot}303\, n\, RT \log \frac{P_1}{P_2}$

(*iv*) *For an adiabatic process.* As $\delta q = 0$,

$\therefore\ dE = \delta q + \delta w$ gives $dE = \delta w$.

But $\frac{dE}{dT} = C_v$ or $dE = C_v\, dT$.

Hence $\delta w = C_v\, dT$ for 1 mole or $\delta w = nC_v\, dT$ for n moles.

$$\therefore \text{ Total work done, } \quad w = \int_{T_1}^{T_2} n\, C_v\, dT = nC_v (T_2 - T_1)$$

Further $C_p - C_v = R$. Dividing by C_v, $\frac{C_p}{C_v} - 1 = \frac{R}{C_v}$ or $\gamma - 1 = \frac{R}{C_v}$ or $C_v = \frac{R}{\gamma - 1}$.

Substituting this value, we get $w = \frac{nR\,(T_2 - T_1)}{\gamma - 1}$

Thus if $T_2 > T_1$, $w = +ve$ *i.e.* work is done on the system

If $T_2 < T_1$, $w = -ve$ *i.e.* work is done by the system.

ADDITIONAL USEFUL INFORMATION contd.

2. The ratio C_p / C_v represented by γ is as follows:

Nature of the gas :	*Monatomic* (He, Ar etc.)	*Diatomic* (H_2, O_2, CO etc.)	*Triatomic* (CO_2, H_2S etc.)
$\gamma = C_p / C_v$:	1·66	1·40	1·30

4. Relationships between P, V and T for adiabatic expansion of an ideal gas

$$PV^{\gamma} = \text{constant}$$

or $$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

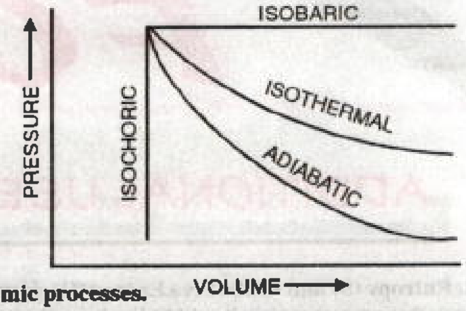
$$T\,P^{(1-\gamma)/\gamma} = \text{constant}$$

or $$T_1\,P_1^{(1-\gamma)/\gamma} = T_2\,P_2^{(1-\gamma)/\gamma}$$

$$TV^{\gamma-1} = \text{constant}$$

or $$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

5. Graphical representation of four basic thermodynamic processes.



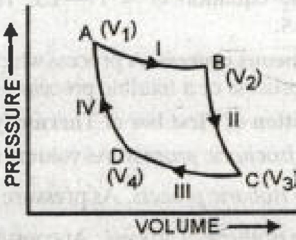
6. Lavoisier and Laplace law. This is another law of thermochemistry which was put foward before Hess's law. It states as follows :

The enthalpy of decomposition of a compound into its elements is equal to its enthalpy of formation but with opposite sign e.g.,

$$C(s) + O_2(g) \longrightarrow CO_2(g),\ \Delta H = -\,393{\cdot}5\ kJ$$

$$CO_2(g) \longrightarrow C(s) + O_2(g),\ \Delta H = +\,393{\cdot}5\ kJ$$

7. Cyclic process. If a system returns to its original state after undergoing a number of successive changes, it is said to be a cyclic process. The most common example of such a process is that of Carnot cycle which consists of the following four stages :



I. Isothermal expansion
II. Adiabatic expansion
III. Isothermal compression
IV. Adiabatic compression.

i.e. $A(P_1, V_1, T_1) \longrightarrow B(P_2, V_2, T_1) \longrightarrow C(P_3, V_3, T_2) \longrightarrow D(P_4, V_4, T_2) \longrightarrow A(P_1, V_1, T_1)$

It may be noted that the internal energy change or enthalpy change or entropy change in a cyclic process is zero.

8. Conversion of heat into work—Carnot heat engine. The fraction of the heat absorbed by a machine that is converted into work is called the efficiency of the machine. It is given by

$$\eta = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2}$$

where Q_2 = heat absorbed from the *source* at temp. T_2

Q_1 = heat rejected to the *sink* at temp. T_1

C.B.S.E.-P.M.T. (MAINS) SPECIAL

A. SUBJECTIVE QUESTIONS

Q. 1. How can you justify that the work done in the reversible expansion of a gas is the maximum work obtained from the system ?

Ans. Work done in the reversible expansion of a gas is given by

$$W = - P_{ext} \Delta V$$

For the expansion of the gas, the external pressure (P_{ext}) has to be less than the internal pressure of the gas. However, for reversible expansion, P_{ext} should be infinitesimally smaller than the internal pressure. In other words, for reversible expansion, P_{ext} is the maximum value of external pressure. Hence for a given change of volume (ΔV), $P_{ext} \Delta V$ is the maximum value. Thus,

$$W_{rev} = W_{max}.$$

Q. 2. A system is changed from state I to state II by two different paths. In the first path $\Delta H = q$. Comment on the value of ΔH and q by the second path. Give reasons for your answer.

Ans. ΔH by second path will be same as in the first path because ΔH is a state function. However, q will not be same by second path because it is not a state function.

Q. 3. What is the difference between bond energy and bond enthalpy ? Explain taking example of H_2 (g).

Ans. Refer to page 5/42.

Q. 4. What is difference between heat and work ? For what type of processes the two become equal ?

Ans. Difference between heat and work. Refer to page 5/9.

Condition under which $q = w$. From first law of thermodynamics $\Delta E = q + w$. Thus $q = w$ in magnitude when $\Delta E = 0$. This happens during the isothermal expansion of an ideal gas.

Q. 5. Why temperature falls during adiabatic expansion of a real gas but remains constant during adiabatic expansion of an ideal gas ?

Ans. In the adiabatic expansion of a real gas, some work is done in overcoming the intermolecular forces of attraction. This work is done at the expense of internal energy which therefore falls. As internal energy of a gas is a function of temperature, hence the temperature falls. In case of ideal gases, the forces of attraction between the molecules are negligible. Hence no work is done to overcome the intermolecular forces of attraction. As a result, internal energy remains constant and so is the temperature.

Q. 6. Show that in the isothermal expansion of the ideal gas, $\Delta E = 0$ and $\Delta H = 0$.

Ans. (*i*) For one mole of an ideal gas, $C_v = \frac{dE}{dT}$

or $dE = C_v \, dT$

For a finite change, $\Delta E = C_v \Delta T$

For isothermal process, T = constant so that $\Delta T = 0$. Hence $\Delta E = 0$.

(*ii*) $H = E + PV \quad \therefore \quad \Delta H = \Delta E + \Delta (PV) = \Delta E + \Delta (RT) = \Delta E + R\Delta T$. But $\Delta E = 0$ (proved above) and $\Delta T = 0$ (for isothermal process). $\therefore \ \Delta H = 0$.

Q. 7. In what way internal energy is different from enthalpy ? Explain both the terms with suitable examples. *(N.C.E.R.T.)*

Ans. Internal energy (U) is the energy stored in a substance the change in whose value during a process is equal to the heat evolved or absorbed if the process is carried out at constant volume or is not accompanied by any change in volume *i.e.* $\Delta U = q_v$. Enthalpy (H) is the energy stored in a subtance in the form of heat. That is why it is also called heat content of the substance or system. The change in its value during a process is equal to the heat evolved or absorbed if the process is carried out at constant pressure *i.e.* $\Delta H = q_p$.

The two are related as $H = U + PV$ or $\Delta H = \Delta U + \Delta n_g RT$.

Thus if $\Delta n_g = 0$, $\Delta H = \Delta U$.

If Δn_g is +ve (*i.e.* $n_p > n_r$)$_{gaseous}$ $\Delta H > \Delta U$.

If Δn_g = −ve (*i.e.* $n_p < n_r$)$_{gaseous}$, $\Delta H < \Delta U$.

For example, for the reaction

$$N_2 (g) + O_2 (g) \longrightarrow 2 NO (g),$$

$\Delta n_g = 0$, therefore, $\Delta H = \Delta U$. For the reaction

$$CH_4 (g) + 2 O_2 (g) \longrightarrow CO_2 (g) + 2 H_2O (l)$$

$\Delta n_g = 1 - 3 = -2$ *i.e.* therefore, $\Delta H < \Delta U$.

For the reaction,

$$CaCO_3 (s) \longrightarrow CaO (s) + CO_2 (g)$$

$\Delta n_g = 1 - 0 = 1$ *i.e.* it is +ve. Hence $\Delta H > \Delta U$.

Q. 8. Why should there be energy crisis when law of conservation of energy holds good ?

Ans. No doubt, the law of conservation of energy holds good but the only problem is that the combustion of fuels is a one way process *i.e.* either the products of combustion are not converted back into the original substances at all or they are converted back at a rate much slower than the rate of their consumption. For example, coal burns to from CO_2 but CO_2 is converted back into carbon by nature through photosynthesis at a much slower rate.

B. PROBLEMS

Problem 1. **How long will a 2 kW heater take to boil 2 L of water taken at 25°C ? Given that the average specific heat of water in the range 25°C – 100°C is $4 \cdot 184 \text{ JK}^{-1} g^{-1}$.**

Solution. 2 L of water $= 2000 \text{ cm}^3 = 2000 g$ $(d_{H_2O} = 1 g \text{ cm}^{-3})$

$\therefore$ Heat required by 2 L of water to raise its temperature from 25°C to 100°C

$= m \times C \times \Delta T$

$= (2000 g) \times (4 \cdot 184 \text{ JK}^{-1} g^{-1}) \times (100 - 25) \text{ K}$

$= 627600 \text{ J}$

Heat supplied by 2 kW heater $= 2000 \text{ Js}^{-1}$

$(\because 1 \text{ W} = 1 \text{ Js}^{-1})$

$\therefore$ Time required to supply the required heat

$= \dfrac{627600 \text{ J}}{2000 \text{ Js}^{-1}} \simeq 314 s$

$= \mathbf{5 \text{ min } 14 s}$.

Problem 2. **Given that the enthalpy of formation of H_2O (*l*) is $-68 \text{ kcal mol}^{-1}$. Calculate the enthalpy of formation of OH^- (*aq*) ions.**

Solution. For neutralization reaction, we know that

$$H^+ + OH^- \longrightarrow H_2O, \Delta H = -13 \cdot 7 \text{ kcal}$$

Thus $\Delta H_{\text{Reaction}} = [\Delta H_f^\circ (H_2O)]$

$- [\Delta H_f^\circ (H^+) + \Delta H_f^\circ (OH^-)]$

But $\Delta H_f^\circ (H^+) = 0$ (by convention)

$\therefore -13 \cdot 7 \text{ kcal} = [-68 \text{ kcal}] - [0 + \Delta H_f^\circ (OH^-)]$

or $\Delta H_f^\circ (OH^-) = -68 + 13 \cdot 7 \text{ kcal}$

$= \mathbf{-54 \cdot 3 \text{ kcal mol}^{-1}}$.

Problem 3. **Calculate the standard internal energy change for the reaction $OF_2 (g) + H_2O (g) \longrightarrow O_2 (g) + 2 HF (g)$ at 298 K, given that the enthalpies of formation of $OF_2 (g)$, $H_2O (g)$ and HF (*g*) are +20, –250 and –270 kJ mol^{-1} respectively.**

Solution. **Step I.** *Calculation of standard enthalpy of reaction*

$\Delta H_f^\circ = \Sigma \Delta H_f^\circ (\text{Products}) - \Sigma \Delta H_f^\circ (\text{Reactants})$

$= [\Delta H_f^\circ (O_2) + 2 \Delta H_f^\circ (HF)]$

$- [\Delta H_f^\circ (OF_2) + \Delta H_f^\circ (H_2O)]$

$= [0 + 2(-270)] - [+20 + (-250)] \text{ kJ mol}^{-1}$

$= -310 \text{ kJ mol}^{-1}$

Step II. *Calculation of standard internal energy change*

For the given reaction,

$\Delta n_g = (1 + 2) - (1 + 1) = 1$

$\Delta H^\circ = \Delta E^\circ + \Delta n_g RT$

or $\Delta E^\circ = \Delta H^\circ - \Delta n_g RT$

$= (-310 \text{ kJ mol}^{-1}) - (1)$

$(8 \cdot 314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) (298 \text{ K})$

$= \mathbf{-312 \cdot 48 \text{ kJ mol}^{-1}}$.

Problem 4. **Calculate the work done when 11·2 *g* of iron dissolves in hydrochloric acid in (*i*) a closed vessel (*ii*) an open beaker at 25°C (Atomic mass of Fe = 56 *u*).**

Solution. Iron reacts with HCl acid to produce H_2 gas as

$$Fe (s) + 2 HCl (aq) \longrightarrow FeCl_2 (aq) + H_2 (g)$$

Thus 1 mole of Fe *i.e.* 56 *g* Fe produce H_2 gas = 1 mole

$\therefore$ 11·2 *g* Fe will produce H_2 gas

$= \dfrac{1}{56} \times 11 \cdot 2 = 0 \cdot 2$ mole.

(*i*) If the reaction is carried out in a closed vessel, $\Delta V = 0$

$\therefore \quad w = -P_{ext} \Delta V = 0$

(*ii*) If the reaction is carried out in open beaker (external pressure being 1 atm)

Initial volume = 0 (because no gas is present)

Final volume occupied by 0·2 mole of H_2 at 25°C and 1 atm pressure can be calculated as follows :

$PV = nRT \quad \therefore \quad V = \dfrac{nRT}{P}$

$= \dfrac{0 \cdot 2 \text{ mol} \times 0 \cdot 0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{1 \text{ atm}}$

$= \mathbf{4 \cdot 89 \text{ L}}$

$$\therefore \Delta V = V_{\text{final}} - V_{\text{initial}} = 4{\cdot}89 \text{ L}$$

$$w = -P_{\text{ext}}\,\Delta V = -1 \text{ atm} \times 4{\cdot}89 \text{ L atm}$$

$$= -4{\cdot}89 \text{ L atm}$$

$$= -4{\cdot}89 \times 101{\cdot}3 \text{ J} = -495{\cdot}4 \text{ J}$$

Problem 5. **Calculate ΔU and ΔH in calories if one mole of a monoatomic ideal gas is heated at constant pressure of 1 atm from 25°C to 50°C.**

Solution. For monoatomic ideal gas, $C_v = \frac{3}{2}R$

$$C_p = \frac{\Delta H}{\Delta T}$$

$$\therefore \Delta H = C_p\,\Delta T \text{ mol}^{-1} \text{ (or } n\,C_p\,\Delta T \text{ for } n \text{ moles)}$$

$$= \frac{5}{2} \times 1{\cdot}987 \times 25 = \mathbf{124{\cdot}2 \text{ cal}}$$

Work done,

$$w = -P\,\Delta V = -P(V_2 - V_1)$$

$$= -(PV_2 - PV_1) = -(n\,RT_2 - n\,RT_1)$$

$$= -n\,R\,(T_2 - T_1)$$

$$= -1 \times 1{\cdot}987\,(323 - 298) \text{ cal}$$

$$= -49{\cdot}7 \text{ cal}$$

$$\Delta E = q + w$$

$$= 124{\cdot}2 - 49{\cdot}7 \text{ cal} = \mathbf{74{\cdot}5 \text{ cal.}}$$

Problem 6. **10 moles of an ideal gas expand isothermally and reversibly from a pressure of 5 atm to 1 atm at 300 K. What is the largest mass that can be lifted through a height of 1 metre by this expansion ?**

Solution. $w_{\text{exp}} = -2{\cdot}303\,n\,RT \log \frac{P_1}{P_2}$

$$= -2{\cdot}303 \text{ (10 mol)} \times (8{\cdot}314 \text{ JK}^{-1} \text{ mol}^{-1} \text{ (300 K)} \log \frac{5}{1}$$

$$= -40{\cdot}15 \times 10^3 \text{ J}$$

If M is the mass that can be lifted by this work, through a height of 1 metre, then

work done = M*gh*

$$40{\cdot}15 \times 10^3 \text{ J} = M \times 9{\cdot}81 \text{ ms}^{-2} \times 1\,m$$

$$\text{or } M = \frac{40{\cdot}15 \times 10^3 \text{ kg}\,m^2\,s^{-2}}{9{\cdot}18 \text{ ms}^{-2} \times 1\,m} \quad (J = \text{kg}\,m^2\,s^{-2})$$

$$= \mathbf{4092{\cdot}76 \text{ kg.}}$$

Problem 7. **The enthalpy change for the reaction**

$$Zn\,(s) + 2\,H^+\,(aq) \longrightarrow Zn^{2+}\,(aq) + H_2\,(g)$$

is $-154{\cdot}40$ kJ mol^{-1}. The formation of 2 g of hydrogen expands the system by 22·4 litres at 1 atm pressure. What is the internal energy change of the reaction ?

Solution. Taking the initial volume as negligible, change in volume during expansion (ΔV) = 22·4 L. External pressure (P_{ext}) = 1 atm

$$\Delta H = \Delta E + P\Delta V$$

$$\text{or} \quad \Delta E = \Delta H - P\Delta V$$

$$P\Delta V = 1 \text{ atm} \times 22{\cdot}4 \text{ L} = 22{\cdot}4 \text{ L atm}$$

$$= 22{\cdot}4 \times 101{\cdot}3 \text{ J} = 2307 \text{ J} = 2{\cdot}31 \text{ kJ}$$

$$\therefore \quad \Delta E = -154{\cdot}4 - 2{\cdot}31 = \mathbf{-156{\cdot}71 \text{ kJ.}}$$

Problem 8. **The heat of formation of**

(*i*) $CO_2\,(g)$ from its elements is +94·4 kcal

(*ii*) CuO (*s*) from its elements is 151·8 kcal, and

(*iii*) The heat of reaction between CuO (*s*) and $CO_2\,(g)$ is +42·25 kcal. Calculate the heat of formation of $CuCO_3\,(s)$. ***(I.S.M. Dhanbad 1987)***

Solution. We are given

(*i*) $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$, $\Delta H = -94{\cdot}4$ kcal

(*ii*) $Cu\,(s) + \frac{1}{2}O_2\,(g) \longrightarrow CuO\,(s)$, $\Delta H = -151{\cdot}8$ kcal

(*iii*) $CuO(s) + CO_2\,(g) \longrightarrow CuCO_3\,(s)$, $\Delta H = -42{\cdot}25$ kcal

We aim at

$$Cu\,(s) + C\,(s) + \frac{3}{2}O_2\,(g) \longrightarrow CuCO_3\,(s), \quad \Delta H = ?$$

Eqn. (*i*) + Eqn. (*ii*) + Eqn. (*iii*) gives the required result. **(ΔH = —288·45 kcal)**

Problem 9. **The molar heat of formation of NH_4NO_3 is —367·54 kJ and those of $N_2O(g)$ and $H_2O(l)$ are 81·46 kJ and —285·78 kJ respectively at 25°C and 1 atm pressure. Calculate ΔH for the reaction**

$$NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(l)$$

(Bihar C.E.E. 1997)

Solution. $\Delta H^\circ_{\text{reaction}} = \Sigma\,\Delta H^\circ_f\text{(Products)} - \Delta H^\circ_f\text{(Reactants)}$

$= [\Delta H^\circ_f(N_2O) + 2 \times \Delta H^\circ_f(H_2O)] - \Delta H^\circ_f(NH_4NO_3)$

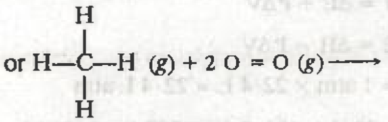
$= 81{\cdot}46 + 2 \times (-285{\cdot}78) - (-367{\cdot}54)$

$= -122{\cdot}56$ **kJ mol^{-1}**

Problem 10. **Calculate the heat of combustion of methane at 25°C. The mean bond energies for the C—H, O=O, C = O and O—H are respectively 415, 498, 803 and 463 kJ mol^{-1}.** *(C.E.E. Bihar 1998)*

Solution. We aim at

$$CH_4\,(g) + 2\,O_2\,(g) \longrightarrow CO_2\,(g) + 2\,H_2O\,(l),\ \Delta H = ?$$



$$\text{or } H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}{-}H\,(g) + 2\,O=O\,(g) \longrightarrow$$

$$O=C=O\,(g) + 2\,H-O-H\,(l),\ \Delta H = ?$$

$$\Delta H_{\text{Reaction}} = \Sigma\,\text{B.E. (Reactants)} - \Sigma\,\text{B.E. (Products)}$$

$$= [4 \times \text{B.E.}\,(C-H) + 2 \times \text{B.E.}\,(O=O)]$$

$$- [2 \times \text{B.E.}\,(C=O) + 4 \times \text{B.E.}\,(O-H)]$$

$$= (4 \times 415 + 2 \times 498) - (2 \times 803 + 4 \times 463)$$

$$= 2656 - 3458 = \mathbf{-802\ kJ}$$

Problem 11. **A chemist while studying the properties of gaseous CCl_2F_2, a chlorofluorocarbon refrigerant cooled a 1·25 g sample at constant atmospheric pressure of 1·0 atm from 320 K to 293 K. During cooling, the sample volume decreased from 274 to 248 mL. Calculate ΔH and ΔU for the chlorofluorocarbon for this process. For CCl_2F_2, $C_p = 80{\cdot}7$ J/(mol K).** *(N.C.E.R.T.)*

Solution. $\Delta H = q_p$ and C_p is heat evolved or absorbed per mole for 1° fall or rise in temperature. Here, fall in temperature = 320—293 = 27 K.

Molar mass of $CCl_2F_2 = 12 + 2 \times 35{\cdot}5 + 2 \times 19$

$= 121$ g mol^{-1}

$\therefore$ Heat evolved from 1·25 g of the sample on being cooled from 320 K to 293 K at constant pressure

$$= \frac{80{\cdot}7}{121} \times 1{\cdot}25 \times 27\ J = \mathbf{22{\cdot}51\ J}$$

Further $\Delta H = \Delta U + P\Delta V = -22{\cdot}51$ J

$$P\Delta V = 1\ \text{atm} \times \frac{(248 - 274)}{1000}\ L = -0{\cdot}026\ L\ \text{atm}$$

$$= -0{\cdot}026 \times 101{\cdot}325\ J = -2{\cdot}63\ J$$

$$\therefore\quad -22{\cdot}51 = \Delta U - 2{\cdot}63\ J$$

$$\text{or}\quad \Delta U = -22{\cdot}51 + 2{\cdot}63\ J = \mathbf{-19{\cdot}88\ J}$$

Problem 12. **When 10 g of anhydrous $CaCl_2$ is dissolved in 200 g of water, the temperature of the solution rises by 7·7°C. Calculate the heat of hydration of $CaCl_2$ to $CaCl_2 \cdot 6\,H_2O$. Given that the heat of dissolution of $CaCl_2 \cdot 6\,H_2O$ is 19·08 kJ mol^{-1}. Assume specific heat of the solution to be same as that of water i.e. 4·184 J g^{-1} K^{-1}.**

Solution. **Step I.** *Calculation of heat of dissolution of anhydrous $CaCl_2$*

Molar mass of $CaCl_2$

$= 40 + 2 \times 35{\cdot}5 = 111$ g mol^{-1}

Heat evolved in dissolution of 10 g $CaCl_2$ in 200 g water $= m \times c \times \Delta t$

$= 200 \times 4{\cdot}184 \times 7{\cdot}7$ J

$\therefore$ Heat of dissolution per mole

$$= \frac{200 \times 4{\cdot}184 \times 7{\cdot}7}{10} \times 111\ J$$

$$= 71{\cdot}52\ kJ$$

i.e. $\Delta H_{\text{disso.}}\,(CaCl_2) = -71{\cdot}52$ kJ mol^{-1}

Step II. *Calculation of heat of hydration.*

Aim : $CaCl_2\,(s) + 6\,H_2O\,(l) \longrightarrow CaCl_2 \cdot 6\,H_2O\,(s)$

We have :

$\Delta H_{\text{disso.}}\,(CaCl_2) = -71{\cdot}52$ kJ mol^{-1} (Calculated above)

$\Delta H_{\text{disso.}}\,(CaCl_2 \cdot 6\,H_2O) = 19{\cdot}08$ kJ mol^{-1} *(Given)*

i.e. (*i*) $CaCl_2\,(s) + aq \longrightarrow CaCl_2\,(aq)$, $\Delta H_1 = -71{\cdot}52$ kJ mol^{-1}

(*ii*) $CaCl_2 \cdot 6\,H_2O\,(s) + aq \longrightarrow CaCl_2\,(aq)$, $\Delta H_2 = 19{\cdot}08$ kJ mol^{-1}

Reaction : (*i*) can be written in two steps as

$CaCl_2\,(s) + 6\,H_2O\,(l) \longrightarrow CaCl_2 \cdot 6\,H_2O\,(s)$, $\Delta H = \Delta H_3$

$CaCl_2 \cdot 6\,H_2O\,(s) + aq \longrightarrow CaCl_2\,(aq)$, $\Delta H = \Delta H_4$

$\therefore \Delta H_3 + \Delta H_4 = \Delta H_1 = -71{\cdot}52$ kJ mol^{-1}

But $\Delta H_4 = \Delta H_2 = 19{\cdot}08$ kJ mol^{-1}

$\therefore\quad \Delta H_3 + 19{\cdot}08 = -71{\cdot}52$ kJ mol^{-1}

or $\quad \Delta H_3 = -90{\cdot}6$ **kJ mol^{-1}**.

I.I.T. (MAINS) SPECIAL

Problem 1. **In a gobar gas plant, gobar gas is obtained by bacterial fermentation of animal refuse. The main combustible gas present in the gobar gas is found to be methane (80% by weight) whose heat of combustion is 809 kJ mol^{-1}. How much gobar gas would have to produced per day for a village of 100 families if the average consumption of a family is 20,000 kJ per day to meet all its energy requirements.**

Solution. Total energy requirement for 100 families per day = 20,000 × 100 kJ = 2×10^6 kJ

Methane (CH_4) undergoes combustion as follows :

$$CH_4\,(g) + 2\,O_2\,(g) \longrightarrow CO_2\,(g) + 2\,H_2O\,(l), \quad \Delta H = -809 \text{ kJ mol}^{-1}$$

For 809 kJ of energy, CH_4 required = 16 *g*

(Molar mass of $CH_4 = 16\,g\,mol^{-1}$)

For 2×10^6 kJ of energy, CH_4 required

$$= \frac{16}{809} \times 2 \times 10^6\,g = 39 \cdot 56 \text{ kg}$$

As gobar gas contains 80% by weight of methane, therefore gobar gas required $= \frac{100}{80} \times 39 \cdot 56$ kg

= **49·45 kg.**

Problem 2. **In an oven, due to insufficient supply of oxygen, 60% of the carbon is converted to carbon-dioxide whereas the remaining 40% is converted into carbon monoxide. If the heat of combustion of carbon to CO_2 is 394 kJ mol^{-1} while that of its oxidation to CO is 111 kJ mol^{-1}, calculate the total heat produced in the oven by burning 10 kg of coal containing 80% carbon by weight. Also calculate the efficiency of the oven.**

Solution. The reactions taking place in the oven are

$$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g) + 394 \text{ kJ mol}^{-1}$$

$$C\,(s) + \frac{1}{2}O_2\,(g) \longrightarrow CO\,(g) + 111 \text{ kJ mol}^{-1}$$

Carbon present in 10 kg coal

$$= \frac{80}{100} \times 10 \text{ kg} = 8 \text{ kg}$$

Carbon converted to CO_2

$$= \frac{60}{100} \times 80 \text{ kg} = 4 \cdot 8 \text{ kg}$$

Carbon converted to CO $= \frac{40}{100} \times 8 \text{ kg} = 3 \cdot 2 \text{ kg}$

12 *g i.e.* 0·012 kg of carbon on combustion to CO_2 produce heat = 394 kJ

∴ 4·8 kg of carbon on combustion to CO_2 will produce heat $= \frac{394}{0 \cdot 012} \times 4 \cdot 8$

= 157600 kJ

0·012 kg of carbon on oxidation to CO produce heat = 111 kJ

∴ 3·2 kg of carbon on oxidation to CO will produce heat $= \frac{111}{0 \cdot 012} \times 3 \cdot 2$ kJ

= 29600 kJ

∴ Total heat produced = 157600 + 29600 = **1,87,200 kJ**

If oven were 100% efficient, all carbon would have been converted to CO_2.

Heat produced from 8 kg carbon would have been

$$= \frac{394}{0 \cdot 012} \times 8 = 262{,}667 \text{ kJ}$$

$$\therefore \% \text{ efficiency} = \frac{187{,}200}{262{,}667} \times 100 = 71 \cdot 3\%.$$

Problem 3. **Calculate the work of expansion when 100 g of water is electrolysed at a constant pressure of 1 atm and temperature of 25°C.**

Solution. Electrolysis of water takes place as

$$2\,H_2O\,(l) \longrightarrow 2\,H_2\,(g) + O_2\,(g)$$

Thus 2 moles of H_2O *i.e.* 2 × 18 = 36 *g* of H_2O on electrolysis produce 2 moles of H_2 gas and one mole of O_2 gas *i.e.* total 3 moles of the gases

∴ 100 *g* of water will produce gases

$$= \frac{3}{36} \times 100 = 8 \cdot 33 \text{ moles}$$

Volume occupied by 8·33 moles of gases at 25°C and 1 atm pressure is given by

$$V = \frac{nRT}{P}$$

$$= \frac{(8 \cdot 33 \text{ mole})\,(0 \cdot 0821 \text{ L atm K}^{-1} \text{ mol}^{-1})\,(298 \text{ K})}{1 \text{ atm}}$$

$$= 203 \cdot 8 \text{ L}$$

Taking the volume of liquid water as negligible (being 100 *m*L = 0·1 L), ΔV = 203·8 L

$$\therefore \quad W = -P_{ext}\,\Delta V$$

$$= -1 \text{ atm} \times 203 \cdot 8 \text{ L} = -203 \cdot 8 \text{ L atm}$$

$$= -203 \cdot 8 \times 101 \cdot 3 \text{ J} = -20 \cdot 6 \text{ kJ}$$

Problem 4. Work done in the expansion of an ideal gas from 4 dm^3 to 6 dm^3 against a constant external pressure of 2·5 atm was used to heat up 1 mole of water at 20°C. What will be the final temperature of water. Given that the specific heat of water = 4·184 $Jg^{-1} K^{-1}$.

Solution. As work is being done against constant external pressure, the process is irreversible. Hence

$$w = -P_{ext}\,\Delta V$$

$$= -2\cdot5 \text{ atm} \times (6-4)\, dm^3$$

$$= -5\cdot0 \text{ L atm} \qquad (1\, dm^3 = 1\text{ L})$$

$$= -5\cdot0 \times 101\cdot3 \text{ J } (1 \text{ L atm} = 101\cdot3 \text{ J})$$

$$= -506\cdot5 \text{ J}$$

For isothermal expansion of ideal gas, $\Delta E = 0$ so that $q = -w = 506\cdot5$ J.

This heat is used up to heat 1 mole of water. Applying the relation

$$q = m \times c \times \Delta T$$

$$506\cdot5 = 18 \times 4\cdot184 \times \Delta T$$

or $\Delta T = 6\cdot725$

∴ Final temperature

$$= 20°C + 6\cdot725 = 26\cdot725°C$$

Problem 5. An intimate mixture of ferric oxide, Fe_2O_3, and aluminium, Al, is used in solid fuel rockets. Calculate the fuel value per gram and fuel value per cc. of the mixture. Heats of formation and densities are as follows :—

$$\Delta H_f(Al_2O_3) = 399 \text{ kcal/mol}$$

$$\Delta H_f(Fe_2O_3) = 199 \text{ kcal/mol}$$

Density of Fe_2O_3 = 5·2 g/cc

Density of Al = 2·7 g/cc. ***(I.I.T. 1988)***

Solution. We aim at

$$Fe_2O_3 + 2Al \longrightarrow 2Fe + Al_2O_3,\ \Delta H = ?$$

$$\Delta H_{reaction} = [2 \times \Delta H_f(Fe) + \Delta H_f(Al_2O_3)] - \Delta H_f(Fe_2O_3) + 2 \times \Delta H_f(Al)]$$

$$= (0 + 399) - (199 + 0) = 200 \text{ kcal}$$

This is the heat change that takes place when 1 mole of Fe_2O_3 and 2 moles of Al combine

i.e. $(2 \times 56 + 3 \times 16) + 2 \times 27g = 214$ g of the mixture. Hence heat change per gram

$$= \frac{200}{214} = 0\cdot9346 \text{ kcal}$$

Further $\quad 160 \text{ g } Fe_2O_3 = \frac{160}{5\cdot2} = 30\cdot77$ cc

and $\quad 54 \text{ g Al} = \frac{54}{2\cdot7}$ cc $= 20$ cc

Total volume of the mixture = 50·77 cc

∴ Heat change per cc $= \frac{200}{50\cdot77}$

$= 3\cdot939$ kcal

Problem 6. An athlete is given 100 g of glucose ($C_6H_{12}O_6$) of energy equivalent to 1560 kJ. He utilizes 50 percent of this gained energy in the event. In order to avoid storage of energy in the body, calculate the weight of water he would need to perspire. The enthalpy of evaporation of water is 44 kJ/mol. ***(I.I.T. 1989)***

Solution. Energy left unutilized $= \frac{1560}{2}$ kJ

$= 780$ kJ

For losing 44 kJ of energy, water to be evaporated

$= 1$ mole $= 18$ g

∴ For losing 780 kJ of energy, water to be evaporated

$$= \frac{18}{44} \times 780 \text{ g} = 319 \text{ g}$$

Problem 7. The standard enthalpy of combustion at 25°C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are —241, —3800 and —3920 kJ/mol respectively. Calculate the heat of hydrogenation of cyclohexene.

(I.I.T. 1989, I.S.M. Dhanbad 1992 ; Bihar C.E.E. 2003)

Solution. We are given

$$(i)\ H_2 + \frac{1}{2}O_2 \longrightarrow H_2O,\ \Delta H = -241 \text{ kJ}$$

$$(ii)\ C_6H_{10} + \frac{17}{2}O_2 \longrightarrow 6CO_2 + 5H_2O,\quad \Delta H = -3800 \text{ kJ}$$

$$(iii)\ C_6H_{12} + 9O_2 \longrightarrow 6CO_2 + 6H_2O,\quad \Delta H = -3920 \text{ kJ}$$

We aim at $C_6H_{10} + H_2 \longrightarrow C_6H_{12}\quad \Delta H = ?$

Eqn. (*i*) + Eqn. (*ii*) —Eqn. (*iii*) gives the required result. **[Ans. —12 kJ]**

Problem 8. Calculate the standard heat of formation of carbon disulphide (*l*). Given that the standard heats of combustion of carbon (*s*), sulphur (*s*) and carbon disulphide (*l*) are —393·3, —293·72 and —1108·76 kJ mol^{-1} respectively. ***(Roorkee 1989)***

Solution. We are given

$$(i)\ C(s) + O_2(g) \longrightarrow CO_2(g),\quad \Delta H = -393\cdot3 \text{ kJ}$$

$$(ii)\ S(s) + O_2(g)) \longrightarrow SO_2(g)\quad \Delta H = -293\cdot72 \text{ kJ}$$

$$(iii)\ CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g),\quad \Delta H = -1108\cdot76 \text{ kJ}$$

We aim at $C(s) + 2S(s) \longrightarrow CS_2(l),\ \Delta H = ?$

Eqn. (*i*) + 2 × Eqn. (*ii*) —Eqn. (*iii*) gives the required result **[Ans.** 128·02 kJ]

Problem 9. **A gas mixture of 3·67 litres of ethylene and methane on complete combustion at 25°C produces 6·11 litres of CO_2. Find out the amount of heat evolved on burning one litre of the mixture. The heats of combustion of ethylene and methane are —1423 and —891 kJ mol^{-1} at 25°C.**

(I.I.T. 1991)

Solution. Combustion reaction of ethylene and methane are

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O, \ \Delta H = -1423 \text{ kJ}$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O, \ \Delta H = -891 \text{ kJ}$$

Suppose volume of C_2H_4 in the mixture $= x$ litres.

Then volume of CH_4 in the mixture $= (3·67 - x)$ litres

From the above reactions :—

1 litre of C_2H_4 gives CO_2 = 2 litres

$\therefore$ x litres of C_2H_4 gives CO_2 = $2x$ litres

1 litre of CH_4 gives CO_2 = 1 litre

$\therefore$ $(3·67 - x)$ litres of CH_4 gives CO_2

$= (3·67 - x)$ litres

Total CO_2 produced $= 2x + (3·67 - x)$

$= (3·67 + x)$ litres

$\therefore \quad 3·67 + x = 6·11$

or $\quad x = 2·44$

$\therefore$ 1 litre of the mixture will contain C_2H_4

$$= \frac{2·44}{3·67} = 0·66 \text{ litre}$$

and $CH_4 = 1 - 0·66 = 0·34$ litre

22·4 litres of C_2H_4 give heat = 1423 kJ

$\therefore$ 0·66 litre of C_2H_4 will give heat

$$= \frac{1423}{22·4} \times 0·66 \text{ kJ} = 41·93 \text{ kJ}$$

22·4 litre of CH_4 give heat = 891 kJ

$\therefore$ 0·34 litre of CH_4 will give heat

$$= \frac{891}{22·4} \times 0·34 \text{ kJ} = 13·52 \text{ kJ}$$

$\therefore$ Total heat produced $= 41·93 + 13·52$

$= 55·45$ kJ

Problem 10. **Determine the enthalpy of the reaction $C_3H_8(g) + H_2(g) \longrightarrow C_2H_6(g) + CH_4(g)$ at 25°C using the given heat of combustion values under standard conditions.**

Compound	**H_2 (*g*)**	**CH_4 (*g*)**	**C_2H_6 (*g*)**	**C (graphite)**
ΔH° (kJ/mol)	**—285·8**	**—890·0**	**—1560·0**	**—393·5**

The standard heat of formation of C_3H_8 (*g*) is —103·8 kJ/mol. ***(I.I.T. 1992)***

Solution. We are given

(*i*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$,

$\Delta H = -285·8$ kJ

(*ii*) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$,

$\Delta H = -890$ kJ

(*iii*) $C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow$

$2CO_2(g) + 3H_2O(l)$, $\Delta H = -1560$ kJ

(*iv*) $C(s) + O_2(g) \longrightarrow CO_2(g)$,

$\Delta H = -393·5$ kJ

(*v*) $3C(s) + 4H_2(g) \longrightarrow C_3H_8(g)$,

$\Delta H = -103·8$ kJ

We aim at

$$C_3H_8(g) + H_2(g) \longrightarrow C_2H_6(g) + CH_4(g),$$

$\Delta H = ?$

5 × Eqn. (*i*) — Eqn. (*v*) — Eqn. (*ii*) — Eqn. (*iii*) + 3 × Eqn. (*iv*) gives the required result.

[**Ans.** —55·7 kJ mol^{-1}]

Problem 11. **In order to get maximum calorific output, a burner should have an optimum fuel value to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and $6x$ litre/hour of O_2) is to be readjusted for butane, C_4H_{10}. In order to get the same calorific output, what should be the rate of supply of butane and oxygen ? Assume that the losses due to incomplete combustion etc are the same for both the fuels and that the gases behave ideally. Heats of combustion :**

CH_4 = 809 kJ/mol,

C_4H_{10} = 2878 kJ/mol. ***(I.I.T. 1993)***

Solution. Combustion reaction of CH_4 and C_4H_{10} are

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + 809 \text{ kJ}$$

$$C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O + 2878 \text{ kJ}$$

Calorific value of $CH_4 = \frac{809}{16} = 50 \cdot 56 \text{ kJ g}^{-1}$

Calorific value of $C_4H_{10} = \frac{2878}{58} = 49 \cdot 62 \text{ kJ g}^{-1}$

$\therefore$ C_4H_{10} required to get the same calorific value as for x litres of $CH_4 = \frac{50 \cdot 56}{49 \cdot 62} \times x = 1 \cdot 0189\, x$ litres

Theoretically oxygen required $= \frac{13}{2} \times 1 \cdot 0189\, x$

$= 6 \cdot 623\, x$ litres.

Actual oxygen required $= 6 \cdot 623\, x \times 3$

$= 19 \cdot 869\, x$ litres

Hence C_4H_{10} and O_2 should be supplied at the rate of $1 \cdot 0189\, x$ litre/hour of C_4H_{10} and $19 \cdot 869\, x$ litre/hour of O_2.

Problem 12. **The enthalpy change involved in the oxidation of glucose is —2880 *k*J mol^{-1}. Twentyfive percent of this energy is available for muscular work. If 100 *k*J of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk after eating 120 *g* of glucose ?**

(I.I.T. 1997)

Solution. Energy available for muscular work

$= \frac{25}{100} \times 2880 \text{ kJ mol}^{-1}$

$= 720 \text{ kJ mol}^{-1}$

Molar mass of glucose $= 180 \text{ g mol}^{-1}$

$\therefore$ Energy available for muscular work from 120 *g* glucose

$= \frac{720}{180} \times 120 \text{ kJ} = 480 \text{ kJ}$

In 100 kJ of muscular work, distance walked = 1 km

$\therefore$ In 480 kJ of muscular work, distance walked

$= \frac{1}{100} \times 480$

$= \mathbf{4 \cdot 8 \text{ km}}$

Problem 13. **From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of $CO_2\,(g)$, $H_2O\,(l)$ and propene (*g*) are —393·5, —285·8 and 20·42 kJ mol^{-1} respectively. The enthalpy of isomerisation of cyclopropane to propene is $-$ 33·0 kJ mol^{-1}.**

(I.I.T. 1998)

Solution. We are given :

(*i*) $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$,

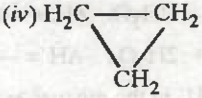
$\Delta H = -393 \cdot 5 \text{ kJ mol}^{-1}$

(*ii*) $H_2\,(g) + \frac{1}{2} O_2\,(g) \longrightarrow H_2O\,(l)$,

$\Delta H = -285 \cdot 8 \text{ kJ mol}^{-1}$

(*iii*) $3\,C\,(s) + 3\,H_2\,(g) \longrightarrow C_3H_6\,(g)$,

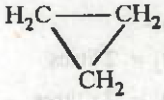
$\Delta H = +20 \cdot 42 \text{ kJ mol}^{-1}$

(*iv*)


$\longrightarrow C_3H_6\,(g)$

$\Delta H = -33 \cdot 0 \text{ kJ mol}^{-1}$

We aim at



$+ \frac{9}{2} O_2\,(g) \longrightarrow$

$3\,CO_2\,(g) + 3\,H_2O\,(l)$

Operating (*iv*) — (*iii*) + 3 × (*i*) + 3 × (*ii*), we get the required equation and

$\Delta H = -33 - 20 \cdot 42 + 3\,(-393 \cdot 5) + 3\,(-285 \cdot 8)$

$= \mathbf{-\,2091 \cdot 32 \text{ kJ mol}^{-1}}$.

Problem 14. **Estimate the average S—F bond energy in SF_6. The standard heat of formation values of $SF_6\,(g)$, S (*g*) and F (*g*) are :— 1100, 275 and 80 kJ mol^{-1} respectively.**

(I.I.T. 1999)

Solution. We are given

(*i*) $\frac{1}{8} S_8\,(s) + 3\,F_2\,(g) \longrightarrow SF_6\,(g)$,

$\Delta H = -1100 \text{ kJ}$

(*ii*) $\frac{1}{8} S_8\,(s) \longrightarrow S\,(g)$, $\Delta H = 275 \text{ kJ}$

(*iii*) $\frac{1}{2} F_2\,(g) \longrightarrow F\,(g)$, $\Delta H = 80 \text{ kJ}$

We aim at $\frac{1}{6} [SF_6\,(g) \longrightarrow S\,(g) + 6\,F\,(g)]$

Eqn. (*ii*) + 6 (*iii*)—(*i*) gives

$SF_6\,(g) \longrightarrow S\,(g) + 6\,F\,(g)$,

$\Delta H = 275 + 6 \times 80 - (-1100) = 1855 \text{ kJ}$

$\therefore$ Average S—F bond energy

$= \frac{1855}{6}$

$= \mathbf{309 \cdot 16 \text{ kJ mol}^{-1}}$

MULTIPLE CHOICE QUESTIONS

For CBSE– PMT (Preliminary), IIT Screening, AIEEE, AIIMS, AFMC, DPMT, CPMT, BHU and All Other Competitive Examinations

1. Internal energy of a substance/system is
(*a*) State function
(*b*) Path function
(*c*) Neither state function nor path function
(*d*) Both state function as well as path function

2. The relationship between enthalpy and internal energy change is
(*a*) $\Delta E = \Delta H + P\,\Delta V$ (*b*) $\Delta H = \Delta E + P\,\Delta V$
(*c*) $\Delta H = -\Delta E - P\,\Delta V$ (*d*) $P\,\Delta V = \Delta E + \Delta H$

3. When a reaction is carried out in a closed vessel
(*a*) $q_p < q_v$ (*b*) $q_p > q_v$
(*c*) $q_p = q_v$ (*d*) $q_v = 0$.

4. The bond energies of H—H and Cl—Cl are 430 kJ mol^{-1} and 242 kJ mol^{-1} respectively. ΔH_f for HCl is 91 kJ mol^{-1}. The bond energy of HCl will be
(*a*) 427 kJ (*b*) 245 kJ
(*c*) 285 kJ (*d*) 766 kJ.

5. The relationship between free energy change (ΔG) and entropy change (ΔS) at constant temperature (T) is
(*a*) $\Delta G = \Delta H + T\,\Delta S$
(*b*) $\Delta H = \Delta G + T\,\Delta S$
(*c*) $T\,\Delta S = \Delta G + \Delta H$
(*d*) $\Delta G = -\Delta H - T\,\Delta S$

6. If heat of dissolution of anhydrous $CuSO_4$ and $CuSO_4 . 5H_2O$ are —15·89 kcal and + 2·80 kcal respectively, then the heat of hydration of $CuSO_4$ to form $CuSO_4 . 5H_2O$ is
(*a*) —13·09 kcal (*b*) – 18·69 kcal
(*c*) + 13·09 kcal (*d*) + 18·69 kcal.

7. The difference between heats of reaction at constant pressure and at constant volume for the reaction
$2\,C_6H_6\,(l) + 15\,O_2\,(g) \longrightarrow 12\,CO_2\,(g) + 6\,H_2O\,(l)$
at 25°C in kJ is
(*a*) –7·43 (*b*) + 3·72
(*c*) —3·72 (*d*) + 7·43. *(I.I.T. 1991)*

8. Which of the following equations correctly represents the standard heat of formation (ΔH_f^0) of methane ?
(*a*) $C\,(\text{diamond}) + 2\,H_2\,(g) \longrightarrow CH_4\,(g)$
(*b*) $C\,(\text{graphite}) + 2\,H_2\,(g) \longrightarrow CH_4\,(l)$
(*c*) $C\,(\text{graphite}) + 2\,H_2\,(g) \longrightarrow CH_4\,(g)$
(*d*) $C\,(\text{graphite}) + 4\,H \longrightarrow CH_4\,(g)$ *(I.I.T. 1992)*

9. The enthalpy of vaporization of liquid water using the data

$$H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(l)\,;\quad \Delta H = -285\cdot77 \text{ kJ/mole}$$

$$H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(g)\,;\quad \Delta H = -241\cdot84 \text{ kJ/mole is}$$

(*a*) + 43·93 kJ/mol (*b*) – 43·93 kJ/mol
(*c*) + 527·61 kJ/mol (*d*) – 527·61 kJ/mol.
(I.I.T. 1993)

10. Under the same conditions how many ml of 1 M KOH and 0·5M H_2SO_4 solutions, respectively, when mixed to form a total volume of 100 ml, produces the highest rise in temperature ?
(*a*) 67, 33 (*b*) 33, 67
(*c*) 40, 60 (*d*) 50, 50.
(I.I.T. 1993 ; Haryana C.E.E.T. 2000)

11. The heat of neutralization of aqueous hydrochloric acid by NaOH is *x* kcal/mol of HCl. Calculate the heat of neutralisation per mol of aqueous acetic acid.
(*a*) 0·5 *x* kcal (*b*) *x* kcal
(*c*) 2*x* kcal
(*d*) cannot be calculated from the given data.
(I.S.M. Dhanbad, 1994)

12. The enthalpy change for a given reaction at 298 K is – *x* cal/mol. If the reaction occurs spontaneously at 298 K, the entropy change at that temperature
(*a*) can be negative but numerically larger than $x / 298$ cal K^{-1}

ANSWERS

1. *a* **2.** *b* **3.** *c* **4.** *b* **5.** *b* **6.** *b* **7.** *a* **8.** *c* **9.** *a* **10.** *d*
11. *d*

(*b*) can be negative, but numerically smaller than $x / 298$ cal K^{-1}

(*c*) cannot be negative

(*d*) cannot be positive. (*I.S.M. Dhanbad 199*[illegible])

13. ΔH°_f of CO_2 (*g*), CO (*g*), N_2O (*g*) and NO_2 (*g*) in kJ/mol are respectively —393, —110, 81 and 34. Calculate the ΔH in kJ of the following reaction :

$2NO_2(g) + 3CO(g) \longrightarrow N_2O(g) + 3CO_2(g)$

(*a*) 836 (*b*) 1460

(*c*) —836 (*d*) —1460.

(*I.S.M Dhanbad, 1994*)

14. Given that $C + O_2 \longrightarrow CO_2, \quad \Delta H^\circ = -x\,kJ$

$2\,CO + O_2 \longrightarrow 2\,CO_2, \quad \Delta H^\circ = -y\,kJ$

The enthalpy of formation of carbon monoxide will be

(*a*) $y - 2x$ (*b*) $\frac{2x - y}{2}$

(*c*) $\frac{y - 2x}{2}$ (*d*) $2x - y$

(*C.B.S.E. P.M.T. 1997*)

15. Standard molar enthalpy of formation of CO_2 is equal to

(*a*) zero

(*b*) the standard molar enthalpy of combustion

(*c*) the sum of standard molar enthalpies of formatioin of CO and O_2

(*d*) the standard molar enthalpy of combustion of carbon (graphite). (*I.I.T. 1997*)

16. Molar heat capacity of water in equilibrium with ice at constant pressure is

(*a*) zero

(*b*) infinity

(*c*) 40·45 kJ K^{-1} mol^{-1}

(*d*) 75·48 JK^{-1} mol^{-1}. (*I.I.T. 1997*)

17. In the reaction : $S + 3/2\,O_2 \longrightarrow SO_3 + 2x$ kcal and $SO_2 + 1/2\,O_2 \longrightarrow SO_3 + y$ kcal, the heat of formation of SO_2 is

(*a*) $(x + y)$ (*b*) $(x - y)$

(*c*) $(2x + y)$ (*d*) $(2x - y)$.

(*C.B.S.E. P.M.T. 1999*)

18. At constant T and P, which one of the following statements is correct for the reaction

$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$?

(*a*) ΔH = ΔE

(*b*) ΔH < ΔE

(*c*) ΔH > ΔE

(*d*) ΔH is independent of the physical state of the reactants. (*M.P. C.E.E. 1999*)

19. Heat of neutralisation of strong acid against strong base is constant and equals to

(*a*) 13·7 kcal (*b*) 57 kJ

(*c*) $5{\cdot}7 \times 10^4$ J (*d*) All of the above.

(*M.P. C.E.E. 1999*)

20. The following is (are) endothermic reaction (s)

(*a*) Combustion of methane

(*b*) Decomposition of water

(*c*) Dehydrogenation of ethane to ethylene

(*d*) Conversion of graphite to diamond.

(*I.I.T. 1999*)

21. If ΔE is the heat of reaction for

$C_2H_5OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(l)$

at constant volume, the ΔH (heat of reaction at constant pressure) at constant temperature is

(*a*) ΔH = ΔE − RT (*b*) ΔH = ΔE − 2 RT

(*c*) ΔH = ΔE + 2 RT (*d*) ΔH = ΔE + RT.

(*C.B.S.E. P.M.T. 2000*)

22. Internal energy does *not* include

(*a*) nuclear energy (*b*) vibrational energy

(*c*) rotational energy

(*d*) energy of gravitational pull. (*A.I.I.M.S. 2000*)

23. Which of the following reactions is endothermic ?

(*a*) $N_2 + O_2 \longrightarrow 2NO$

(*b*) $H_2 + Cl_2 \longrightarrow 2\,HCl$

(*c*) $H_2SO_4 + 2\,NaOH \longrightarrow Na_2SO_4 + 2\,H_2O$

(*d*) None of these. (*A.F.M.C. 2000*)

24. Amount of heat required to change 1 *g* ice at 0°C to 1 *g* steam at 100°C is

(*a*) 616 cal (*b*) 12 kcal

(*c*) 717 cal (*d*) none of these.

(*Haryana C.E.E.T. 2000*)

25. The ΔH_f° for CO_2 (*g*), CO (*g*) and H_2O (*g*) are —393·5, — 110·5 and − 241·8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$ is

ANSWERS

12. *b* **13.** *c* **14.** *c* **15.** *d* **16.** *b* **17.** *d* **18.** *b* **19.** *d* **20.** *b,c,d* **21.** *a*

22. *d* **23.** *a* **24.** *c*

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

(*a*) 524·1 [✓ (*b*) 41·2]
(*c*) —262·5 (*d*) — 41·2. (*I.I.T. 2000*)

26. In thermodynamics, a process is called reversible when
(*a*) surroundings and system change into each other
(*b*) there is no boundary between system and surroundings
[✓ (*c*) the surroundings are always in equilibrium with the system]
(*d*) the system changes into the surroundings spontaneously (*I.I.T. 2001*)

27. Which one of the following statements is false ?
[✓ (*a*) Work is a state function]
(*b*) Temperature is a state function
(*c*) Change in the state is completely defined when the initial and final states are specified
(*d*) Work appears at the boundary of the system. (*I.I.T. 2001*)

28. Change in enthalpy for the reaction
$2\,H_2O_2\,(l) \longrightarrow 2\,H_2O\,(l) + O_2\,(g)$
if heat of formation of $H_2O_2\,(l)$ and $H_2O\,(l)$ are —188 kJ mol^{-1} and —286 kJ mol^{-1} respectively, is
[✓ (*a*) —196 kJ mol^{-1}] (*b*) + 196 kJ mol^{-1}
(*c*) + 948 kJ mol^{-1} (*d*) – 948 kJ mol^{-1}
(*C.B.S.E. P.M.T. 2001*)

29. Enthalpy of $CH_4 + \frac{1}{2}O_2 \longrightarrow CH_3OH$ is negative. If enthalpy of combustion of CH_4 and CH_3OH are x and y respectively, then which relation is correct ?
(*a*) $x > y$ [✓ (*b*) $x < y$]
(*c*) $x = y$ (*d*) $x \geq y$
(*C.B.S.E. P.M.T. 2001*)

30. If order to decompose 9 *g* water, 142·5 kJ heat is required. Hence the enthalpy of formation of water is
(*a*) +285 kJ [✓ (*b*) —285 kJ]
(*c*) +142·6 kJ (*d*) —142·5 kJ
(*K.C.E.T. 2001*)

31. The heats of combustion of graphite and carbon monoxide respectively are —393·5 kJ mol^{-1} and —283 kJ mol^{-1}. Therefore the heat of formation of carbon monoxide in kJ mol^{-1} is
(*a*) +172·5 [✓ (*b*) —110·5]
(*c*) —1070 (*d*) —676·5
(*e*) +110·5
(*Kerala C.E.E. 2001 ; A.I.E.E.E. 2004*)

32. Compounds with high heat of formation are less stable because
(*a*) it is difficult to synthesize them
[✓ (*b*) energy rich state leads to instability]
(*c*) high temperature is required to synthesize them
(*d*) molecules of such compounds are distorted
(*K.C.E.T. 2002*)

33. The heat required to raise the temperature of a body by 1 K is called
(*a*) specific heat [✓ (*b*) thermal capacity]
(*c*) water equivalent (*d*) molar heat capacity
(*A.I.E.E.E. 2002*)

34. In a reaction involving only solids and liquids, which of the following is true ?
(*a*) ΔH < ΔE [✓ (*b*) ΔH = ΔE]
(*c*) ΔH > ΔE (*d*) ΔH = ΔE + RT Δ*n*
(*Tamil Nadu C.E.T. 2002*)

35. C (diamond) ⟶ C (graphite), ΔH = – ve. This shows that
[✓ (*a*) Graphite is more stable than diamond]
(*b*) Diamond is more stable than graphite
(*c*) Both are equally stable
(*d*) Stability cannot be predicted.
(*Manipal P.M.T. 2002*)

36. In a closed insulated container, a liquid is stirred with a paddle to increase the temperature. Which of the following is true ?
[✓ (*a*) ΔE = W ≠ 0, *q* = 0]
(*b*) ΔE = W = *q* ≠ 0
(*c*) ΔE = 0, W = *q* ≠ 0
(*d*) W = 0, ΔE = *q* ≠ 0 (*C.B.S.E. P.M.T. 2002*)

37. An adiabatic expansion of an ideal gas always has
(*a*) decrease in temperature
[✓ (*b*) *q* = 0] (*c*) W = 0
(*d*) ΔH = 0 (*M.P. P.M.T. 2002*)

38. The amount of energy released when 20 ml of 0·5 M NaOH are mixed with 100 ml of 0·1 M HCl is *x* kJ. The heat of neutralization (in kJ mol^{-1}) is

ANSWERS

25. *b* **26.** *c* **27.** *a* **28.** *a* **29.** *b* **30.** *b* **31.** *b* **32.** *b* **33.** *b* **34.** *b*
35. *a* **36.** *a* **37.** *b*

(*a*) —100 x (*b*) —50 x

(*c*) + 100 x (*d*) + 50 x

(Manipal P.M.T. 2002)

39. Enthalpy of neutralization of HCl with NaOH is x. The heat evolved when 500 ml of 2 N HCl are mixed with 250 ml of 4 N NaOH will be

(*a*) 500 x (*b*) 100 x

(*c*) x (*d*) 10 x *(A.F.M.C. 2002)*

40. One mole of a non-ideal gas undergoes a change of state (2·0 atm, 3·0 L, 95 K) ⟶ (4·0 atm, 5·0 L, 245 K) with a change in internal energy, $\Delta U = 30{\cdot}0$ L atm. The change in enthalpy (ΔH) of the process in L atm is

(*a*) 40·0 (*b*) 42·3

(*c*) 44·0

(*d*) not defined because pressure is not constant

(I.I.T. 2002)

41. Which of the following reaction defines ΔH_f°?

(*a*) $C_{(diamond)} + O_2(g) \longrightarrow CO_2(g)$

(*b*) $\frac{1}{2} H_2(g) + \frac{1}{2} F_2(g) \longrightarrow HF(g)$

(*c*) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

(*d*) $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$ *(I.I.T. 2003)*

42. For the reaction

$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$

at constant temperature, $\Delta H - \Delta E$ is

(*a*) + RT (*b*) – 3 RT

(*c*) + 3 RT (*d*) – RT

(C.B.S.E. P.M.T. 2003)

43. For which one of the following equations is $\Delta H^\circ_{reaction}$ equal to ΔH°_f for the product ?

(*a*) $N_2(g) + O_3(g) \longrightarrow N_2O_3(g)$

(*b*) $CH_4(g) + 2Cl_2(g) \longrightarrow CH_2Cl_2(l) + 2HCl(g)$

(*c*) $Xe(g) + 2F_2(g) \longrightarrow XeF_4(g)$

(*d*) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$

(C.B.S.E. Med. 2003)

44. The enthalpy change for a reaction does not depend upon

(*a*) use of different reactants for the same products

(*b*) the nature of intermediate reaction steps

(*c*) the differences in the initial and final temperatures of the involved substances

(*d*) the physical state of the reactants and products

(A.I.E.E.E. 2003)

45. ΔH_f of graphite is 0·23 kJ/mole and ΔH_f for diamond is 1·896 kJ/mole. $\Delta H_{transition}$ from graphite to diamond is

(*a*) 1·66 kJ/mole (*b*) 2·1 kJ/mole

(*c*) 2·33 kJ/mole (*d*) 1·5 kJ/mole

(B.H.U. 2003)

46. The bond energies of C—C, C = C, H—H and C—H linkages are 350, 600, 400 and 410 kJ per mole respectively. The heat of hydrogenation of ethylene is

(*a*) -170 kJ mol^{-1} (*b*) -260 kJ mol^{-1}

(*c*) -400 kJ mol^{-1} (*d*) -450 kJ mol^{-1}

(A.I.E.E.E. 2003)

47. One gram of sample of NH_4NO_3 is decomposed in a bomb calorimeter. The temperature of the calorimeter increases by 6·12 K. The heat capacity of the system is 1·23 kJ/g/deg. What is the molar heat of decomposition for NH_4NO_3 ?

(*a*) —7·53 kJ/mol (*b*) —398·1 kJ/mol

(*c*) —16·1 kJ/mol (*d*) —602 kJ/mol

(A.I.I.M.S. 2003)

48. How much energy is released when 6 moles of octane is burnt in air ? Given ΔH_f° for $CO_2(g)$, $H_2O(g)$ and $C_8H_{18}(l)$ respectively are – 490, – 240 and + 160 kJ mol^{-1}

(*a*) – 6·2 kJ (*b*) – 37·4 kJ

(*c*) – 35·5 kJ (*d*) – 20·0 kJ

(A.I.I.M.S. 2004)

49. If the bond energies of H—H, Br—Br and H—Br are 433, 192 and 364 kJ mol^{-1} respectively, the ΔH° for the reaction $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$ is

(*a*) – 261 kJ (*b*) + 103 kJ

(*c*) + 261 kJ (*d*) – 103 kJ

(C.B.S.E. P.M.T. 2004)

50. The work done during the expansion of a gas from a volume of 4 dm³ to 6 dm³ against a constant external pressure of 3 atm is (1 L atm = 101·32 kJ)

ANSWERS

38. *a* **39.** *c* **40.** *c* **41.** *b* **42.** *b* **43.** *c* **44.** *b* **45.** *a* **46.** *a* **47.** *d*

48. *b* **49.** *d*

(*a*) – 6 J
(*b*) – 608 J
(*c*) + 304 J
(*d*) – 304 J *(C.B.S.E. P.M.T. 2004)*

51. Two moles of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is
(*a*) 11·4 kJ
(*b*) – 11·4 kJ
(*c*) 0 kJ
(*d*) 4·8 kJ *(I.I.T. 2004)*

52. An ideal gas expands in volume from $1 \times 10^{-3} m^3$ to $1 \times 10^{-2} m^3$ at 300 K against a constant pressure of 1×10^5 Nm^{-2}. The work done is
(*a*) – 900 J
(*b*) – 900 kJ
(*c*) 270 kJ
(*d*) 900 kJ *(A.I.E.E.E. 2004)*

53. During isothermal expansion of ideal gas, its
(*a*) Internal energy increases
(*b*) Enthalpy increases
(*c*) Enthalpy reduces to zero
(*d*) Enthalpy remains unchanged *(U.P.C.P.M.T. 2004)*

54. Internal energy is
(*a*) partly potential and partly kinetic
(*b*) totally kinetic
(*c*) totally potential
(*d*) none of these *(A.F.M.C. 2004)*

55. Among te following intensive property is
(*a*) mass
(*b*) volume
(*c*) surface tension
(*d*) enthalpy *(A.F.M.C. 2004)*

56. When 50 cm^3 of 0·2 N H_2SO_4 is mixed with 50 cm^3 of 1 N KOH, the heat liberated is
(*a*) 11·46 kJ
(*b*) 57·3 kJ
(*c*) 573 kJ
(*d*) 573 J *(Karnataka C.E.T. 2004)*

57. The enthalpy of the reaction $H_2O\,(g) + \frac{1}{2} O_2\,(g) \longrightarrow H_2O\,(g)$ is ΔH_1 and that of $H_2\,(g) + \frac{1}{2} O_2\,(g) \longrightarrow H_2O\,(l)$ is ΔH_2. Then
(*a*) $\Delta H_1 < \Delta H_2$
(*b*) $\Delta H_1 + \Delta H_2 = 0$
(*c*) $\Delta H_1 > \Delta H_2$
(*d*) $\Delta H_1 = \Delta H_2$ *(Karnataka C.E.T. 2004)*

58. The enthalpy of combustion of methane at 25°C is 890 kJ. The heat liberated when 3·2 *g* of methane is burnt in air is
(*a*) 445 kJ
(*b*) 278 kJ
(*c*) – 890 kJ
(*d*) 178 kJ *(Karnataka C.E.T. 2004)*

59. If for (*i*) $C + O_2 \longrightarrow CO_2$ (*ii*) $C + 1/2\,O_2 \longrightarrow CO$ (*iii*) $CO + 1/2\,O_2 \longrightarrow CO_2$ the heats of reaction are Q, – 12 and – 10 respectively. Then Q =
(*a*) – 2
(*b*) 2
(*c*) – 22
(*d*) – 16 *(Orissa J.E.E. 2004)*

60. 1 mole of H_2SO_4 is mixed with 2 moles of NaOH. The heat evolved will be
(*a*) 57·3 kJ (*b*) 2 × 57·3 kJ
(*c*) 57·3/2 kJ (*d*) cannot be predicted *(J & K C.E.T. 2004)*

61. The enthalpy of a monoatomic gas at T kelvin is
(*a*) $\frac{7}{2}$ RT (*b*) $\frac{3}{2}$ RT
(*c*) $\frac{1}{2}$ RT (*d*) $\frac{1}{2} mv^2$
(*e*) $\frac{5}{2}$ RT *(Karnataka C.E.T. 2004)*

62. $CH_2 = CH_2\,(g) + H_2\,(g) \longrightarrow CH_3 - CH_3\,(g)$. The heat of reaction is [bond energy of C—C = 80 kcal, C = C = 145 kcal, C—H = 98 kcal, H—H = 103 kcal
(*a*) – 14 kcal
(*b*) – 28 kcal
(*c*) – 42 kcal
(*d*) – 56 kcal *(Bihar C.E.C.E. 2004)*

A N S W E R S

50. *b* **51.** *c* **52.** *a* **53.** *c* **54.** *a* **55.** *c* **56.** *d* **57.** *a* **58.** *d* **59.** *c*
60. *b* **61.** *e* **62.** *b*

HINTS/EXPLANATIONS to Multiple Choice Questions

4. $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow HCl,$

$$\Delta H = 91 \text{ kJ mol}^{-1} \text{ (Given)}$$

$$\Delta H_{\text{Reaction}} = \left[\frac{1}{2}\text{B.E. }(H_2) + \frac{1}{2}\text{B.E. }(Cl_2)\right] - \text{B.E. (HCl)}$$

$$91 = \left[\frac{1}{2} \times 430 + \frac{1}{2} \times 242\right] - \text{B.E. (HCl)}$$

or B.E. (HCl) = (215 + 121)—91

= 245 kJ

5. $\Delta G = \Delta H - T\Delta S$ or $\Delta H = \Delta G + \Delta TS$

6. See solved example on page 5/31.

(*i*) $CuSO_4\,(s) + aq. \longrightarrow CuSO_4\,(aq),$

$\Delta H = -15{\cdot}89$ kcal

(*ii*) $CuSO_4 . 5\,H_2O + aq. \longrightarrow CuSO_4\,(aq),$

$\Delta H = +2{\cdot}80$ kcal

Eqn. (*i*)—Eq. (*ii*) directly gives the required result.

7. $\Delta n_g = 12 - 15 = -3,$

$\Delta H - \Delta E = \Delta n_g RT$

$= -3 \times 8{\cdot}314 \times 298 \text{ J} = -7{\cdot}43 \text{ kJ}$

9. Aim : $H_2O\,(l) \longrightarrow H_2O\,(g), \Delta H = ?$

Eqn. (*ii*)—Eqn. (*i*) gives the required result.

10. In the first three cases, amount neutralized is less than 50 ml and hence heat evolved is less.

11. It will be less than *x* because acetic acid is a weak acid but exact value cannot be predicted.

12. $\Delta G = \Delta H - T\Delta S = -x - 298 \times \Delta S$. For ΔG to be —ve, ΔS can be negative but ΔS should be less than $x / 298$.

13. $\Delta H_{\text{Reaction}} = [\Delta H°_f(N_2O + 3\,\Delta H°_f(CO_2)] - [2\,\Delta H°_f(NO_2) + 3\,\Delta H°_f(CO)]$

$= [81 + 3\,(-393)] - 2\,(34) + 3\,(-110)]$

$= -836$ kJ

14. Aim : $C + \frac{1}{2}O_2 \longrightarrow CO, \Delta H = ?$

Eqn. (*i*)—$\frac{1}{2}$ Eqn. (*ii*) gives the required result.

15. Aim : $C\,(gr) + O_2\,(g) \longrightarrow CO_2\,(g), \Delta H° = ?$

This is same as molar enthalpy of combustion of graphite.

16. $C_p = \frac{dq}{\Delta T}$. At equilibrium, as $\Delta T = 0$,

$C_p = \infty$

17. Eqn. (*i*)—Eqn. (*ii*) gives the required result.

18. $\Delta n_g = (n_p - n_r)_g = 1 - 1\frac{1}{2} = -\frac{1}{2}.$

$\Delta H = \Delta E + \Delta n_g RT.$

As Δn_g is —ve, $\Delta H < \Delta E$

21. $\Delta n_g = 2 - 3 = -1.$

Hence $\Delta H = \Delta E - RT$

24. 1 g ice at 0°C $\xrightarrow{80 \text{ cal}}$ 1 g water at 0°C $\xrightarrow{100 \text{ cal}}$

1 g water at 100°C $\xrightarrow{537 \text{ cal}}$ 1 g steam at 100°C.

Total heat required = 80 + 100 + 537

= 717 cal.

25. $\Delta H°_{\text{Reaction}} = [\Delta H°_f(CO) + \Delta H°_f(H_2O)] - [\Delta H_f(CO_2) + \Delta H_f(H_2)]$

$= [(-110{\cdot}5) + (-241{\cdot}8)] - [(-393{\cdot}5) + 0]$

$= +41{\cdot}2$ kJ

28. $\Delta H_{\text{Reaction}} = [2\,\Delta H°_f(H_2O + \Delta H°_f(O_2)] - 2\,\Delta H°_f(H_2O_2)$

$= [2\,(-286) + 0] - 2\,(-188) = -196$ kJ

29. (*i*) $CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O, \quad \Delta H = x$

(*ii*) $CH_3OH + \frac{1}{2}O_2 \longrightarrow CO_2 + 2\,H_2O, \quad \Delta H = y$

(*i*)—(*ii*) gives the required eqn. *i.e.* for the given reaction, $\Delta H = x - y.$

As $\Delta H = -\text{ve}, x < y$

30. For decomposition of 1 mol H_2O (18 g), heat required = 2 × 142·5 kJ = 285 kJ

i.e. $H_2O\,(l) \longrightarrow H_2\,(g) + \frac{1}{2}O_2\,(g),$

$\Delta H = +285$ kJ

Hence for the reverse reaction, $\Delta H = -285$ kJ

31. Given : (*i*) $C\,(gr) + O_2\,(g) \longrightarrow CO_2\,(g),$

$\Delta H = -393{\cdot}5$ kJ

(*ii*) $CO\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow CO_2\,(g),$

$\Delta H = -283$ kJ

Aim : $C\,(gr) + \frac{1}{2}O_2\,(g) \longrightarrow CO\,(g), \quad \Delta H = ?$

Eqn. (*i*)—Eqn. (*ii*) gives the required result.

34. $\Delta H = \Delta E + P\Delta V$. For solids and liquids, $\Delta V = 0$.

35. Graphite will have lower energy and hence greater stability.

36. As container is closed and insulated, the process is adiabatic so that $q = 0$. As

$$\Delta E = q + W. \quad \therefore \quad \Delta E = W \neq 0.$$

37. For adiabatic expansion, $q = 0$.

38. 20 ml of $0{\cdot}5$ M NaOH $= 20 \times 0{\cdot}5$

$= 10$ millimoles

$= 10$ milliequivalents

100 ml of $0{\cdot}1$ M HCl $= 100 \times 0{\cdot}1$

$= 10$ millimoles

$= 10$ milli equivalents

Thus 10 milli eq. on neutralization give heat $= x$ kJ

$\therefore$ 1 g eq. *i.e.* 1000 milli eq. will give heat $= 100x$ kJ

i.e. $\Delta H_{\text{neut.}} = -100x$ kJ

39. 500 ml of 2 N HCl ≡ 1000 ml of 1 N HCl

250 ml of 4 N NaOH ≡ 1000 ml of 1 N NaOH

$\therefore$ By definition, heat evolved $= x$ kJ

40. $H = U + PV$

As pressure is not constant,

$$\Delta H = H_2 - H_1$$
$$= (U_2 + P_2V_2) - (U_1 + P_1V_1)$$
$$= (U_2 - U_1) + (P_2V_2 - P_1V_1)$$
$$= 30 + (4 \times 5 - 2 \times 3) = 44 \text{ L atm}$$

41. ΔH_f° is the enthalpy change when 1 mole of the substance is formed from its elements in the standard state. Reaction (*a*) does not represent ΔH_f° because standard state of carbon is graphite and not diamond.

42. $\Delta n_g = n_p - n_r = 3 - 6 = -3$

$$\Delta H = \Delta E + \Delta n_g RT$$

or $\Delta H - \Delta E = \Delta n_g RT = -3 RT$.

43. For (*c*), $\Delta H^\circ_{\text{reaction}} = \Delta H^\circ_f(\text{XeF}_4) - [\Delta H^\circ_f(\text{Xe}) + 2\,\Delta H^\circ_f(\text{F}_2)]$

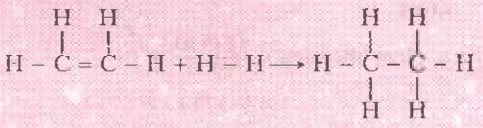
Enthalpies of formation of elementary substances, Xe and F_2 are taken as zero.

44. (*b*) by Hess's law.

45. Graphite ⟶ Diamond

$$\Delta H_{\text{reaction}} = \Delta H_f(\text{diamond}) - \Delta H_f(\text{graphite})$$
$$= 1{\cdot}896 - 0{\cdot}23 = 1{\cdot}666 \text{ kJ/mole.}$$

46. Aim : $CH_2 = CH_2 + H_2 \longrightarrow CH_3 - CH_3$



$$H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H + H-H \longrightarrow H-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H$$

$$\Delta H_{\text{reaction}} = \Sigma \text{ B.E. (Reactants)} - \Sigma \text{ B.E. (Products)}$$
$$= [\text{B.E.}(4\ C-H) + \text{B.E.}(C=C) + \text{B.E.}(H-H)$$
$$- [\text{B.E.}(6\ C-H) + \text{B.E.}(C-C)]$$
$$= \text{B.E.}(C=C) + \text{B.E.}(H-H)$$
$$- 2\,\text{B.E.}(C-H) - \text{B.E.}(C-C)$$
$$= 600 + 400 - 2 \times 410 - 350 \text{ kJ}$$
$$= 1000 - 1170 = -170 \text{ kJ.}$$

47. Heat evolved from decomposition of 1 g $NH_4NO_3 = 1{\cdot}23 \times 6{\cdot}12$ kJ

Heat evolved from 1 mol of NH_4NO_3 (80 g)

$$= 1{\cdot}23 \times 6{\cdot}12 \times 80 \text{ kJ}$$
$$= 602 \text{ kJ.}$$

48. $C_8H_{18} + \frac{25}{2} O_2 \longrightarrow 8\,CO_2 + 9\,H_2O$

$$\Delta H^\circ_{\text{Reaction}} = [8\,\Delta H_f^\circ(CO_2) + 9\,\Delta H_f^\circ(H_2O)]$$
$$- [\Delta H_f^\circ(C_8H_{18}) + \frac{25}{2}\Delta H_f^\circ(O_2)]$$
$$= [8(-490) + 9(-240)] - \left[160 + \frac{25}{2} \times 0\right]$$
$$= -3920 - 2160 - 160 = -6240 \text{ kJ mol}^{-1}$$

$\therefore$ For 6 moles, enthalpy of combustion

$$= -6240 \times 6 = -37400 \text{ J} = -37{\cdot}4 \text{ kJ}$$

49. $\Delta H^\circ_{\text{Reaction}} = \Sigma \text{ B.E. (Reactants)}$

$$- \Sigma \text{ B.E. (Products)}$$
$$= (433 + 192) - 2(364) = -103 \text{ kJ.}$$

50. Work done $= -P_{\text{ext}} \times \Delta V = -3(6-4)$ L atm

$$= -6 \text{ L atm} = -6 \times 101{\cdot}32 \text{ J} = -608 \text{ J.}$$

51. $\Delta H = \Delta(E + PV) = \Delta E + \Delta(RT) = \Delta E + R\Delta T$

For isothermal expansion of ideal gas, $\Delta E = 0$

$(\because \Delta E = C_v\,\Delta T \text{ and } \Delta T = 0)$

$\therefore \Delta H = 0 + 0 = 0$

52. $W = -P\Delta V = -10^5 \text{ Nm}^{-2}(10^{-2} - 10^{-3}) \text{ m}^3$

$$= -10^5 \times 10^{-3}(10 - 1) \text{ Nm}$$
$$= -900 \text{ Nm} = -900 \text{ J}$$

53. See MCQ 51.

56. 50 cm^3 of $0{\cdot}2$ N H_2SO_4

$$= 50 \times 0{\cdot}2 \text{ Meq} = 10 \text{ Meq}$$

50 cm^3 of 1 N KOH $= 50 \times 1$ Meq $= 50$ Meq

Thus 10 Meq of H_2SO_4 will neutralize 10 Meq of KOH

$\therefore$ Heat liberated $= \frac{57 \cdot 3 \text{ kJ}}{1000} \times 10$

$= 0 \cdot 573 \text{ kJ} = 573 \text{ J}.$

57. When H_2O (*g*) changes to H_2O (*l*) *i.e.* condensation takes place, heat is evolved *i.e.* ΔH_2 is greater than ΔH_1.

58. 16 *g* CH_4 produce heat = 890 kJ.

$\therefore$ 3·2 *g* CH_4 will produce heat

$= \frac{890}{16} \times 3 \cdot 2 = 178 \text{ kJ}$

59. Eqn. (*ii*) + Eqn. (*iii*) gives the required result.

60. 1 mole of H_2SO_4 = 2 g eq. of H_2SO_4.

61. For monoatomic gas $E = \frac{3}{2} RT$

$$H = E + PV = E + RT$$

$$= \frac{3}{2} RT + RT = \frac{5}{2} RT \text{ mol}^{-1}$$

62. $\Delta H_{\text{Reaction}} = \Sigma$ B.E. (Reactants)

$- \Sigma$ B.E. (Products)

$= [\text{B.E. } (C = C) + 4 \text{ B.E. } (C - H) + \text{B.E. } (H - H)]$

$- [\text{B.E. } (C - C) + 6 \text{ B.E. } (C - H)]$

$= [145 + 4 \times 98 + 103] - [80 + 6 \times 98] = - 28 \text{ kcal}.$

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The questions given below consist of an 'Assertion' in column 1 and the 'Reason' in column 2. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

(*b*) If both assertion and reason are CORRECT but reason is not the CORRECT explanation of the assertion.

(*c*) If assertion is CORRECT but the reason is INCORRECT.

(*d*) If assertion is INCORRECT but reason is CORRECT.

(*e*) If both assertion and reason are INCORRECT.

	Assertion	Reason
1.	The value of enthalpy of neutralization of a weak acid and a strong base is numerically less than 57·1 kJ.	All the OH^- ions furnished by 1 *g* equivalent of a strong base are not completely neutralized by the H_3O^+ ions from the weak acid.
2.	Standard enthalpy of graphite is lower than that of diamond.	Standard enthalpy of elements is taken to be zero arbitrarily.
3.	Enthalpy of combustion is negative.	Combustion reaction can be exothermic or endothermic.
4.	Absolute value of H cannot be determined.	Absolute value of E cannot be determined.
5.	Endothermic compounds are more stable than the exothermic compounds.	Endothermic reactions have positive enthalpy of formation.
6.	Enthalpy of vaporisation is always endothermic.	Water is an exothermic compound.
7.	Enthalpy of neutralization is always exothermic.	Neutralization involves reaction between an acid and a base.
8.	Enthalpy of neutralization for both HNO_3 and HCl with NaOH is 57·1 kJ per mole.	NaOH is a strong electrolyte. *(A.I.I.M.S. 1997)*

True/False Statements

Which of the following statements are not true ? Rewrite them correctly.

1. An isolated system is that which can exchange energy but not matter with the surroundings.
2. An extensive property depends upon the amount of the substance.
3. In an isothermal process, temperature remains constant because no heat can enter or leave the system.

4. The work done on the system is positive whereas the heat absorbed by the system is positive.
5. Internal energy change is the heat change at constant volume whereas the enthalpy change is the heat change at constant pressure.
6. Internal energy is a state function but enthalpy is not a state function.
7. The standard state of a substance is 0°C and 1 atm pressure.
8. The S.I. unit of heat is 'calorie'.
9. The absolute value of internal energy of a substance cannot be determined.
10. W is positive when the work is done on the system.
11. Enthalpy of combustion is the amount of heat evolved when the number of moles as represented by the balanced equation have been completely oxidized.
12. The total amount of heat evolved or absorbed in a reaction depends upon the number of steps in which the reaction takes place.
13. The enthalpy of combustion of carbon (graphite) is not equal to that of carbon (diamond)
14. Enthalpy of solution is always positive.
15. The total amount of heat evolved or absorbed in a reaction depends upon the number of steps in which the reaction takes place.
16. The enthalpy of combustion of carbon (graphite) is not equal to that of carbon (diamond).

Fill In The Blanks

1. A system which can exchange only energy but not matter with the surroundings is called......
2. A thermodynamic property which depends only on the nature of the substance is called ....
3. A process which is carried out .... is called a reversible process.
4. Law of conservation of energy is also known as ....
5. The heat change occurring at constant pressure is called ......
6. The difference between molar heat capacity at constant pressure and that at constant volume for one mole of an ideal gas is equal to...... .
7. (*a*) A system is said to be ..... if it can neither exchange matter nor energy with the surroundings.

   (*b*) The heat content of the products is more than that of the reactants in an .... reaction. ***(I.I.T. 1993)***
8. When Fe(*s*) is dissolved in aqueous hydrochloric acid in a closed vessel, the work done is..........
9. Enthalpy is an..........property.
10. The part of the universe chosen for study of energy changes is called..........whereas the rest of the universe is called ....
11. The energy stored within a substance is called its...
12. A reaction in which heat is absorbed is called an ....
13. The enthalpy of any element in the standard state is taken as......
14. Heat of neutralization of an acid is the amount of heat evolved when .... of .... is neutralized by .... of the ....
15. $\Delta H_{\text{sublimation}}$ = ... + ...
16. The enthalpy of combustion of benzene is —3264 kJ mol^{-1}. The heat evolved in the combustion of 39 g of benzene will be ....
17. Coal and petroleum are called .... fuels.
18. The heat content of the products is more than that of the reactants in an ..... reaction.
19. The enthalpy of neutralisation of a weak acid is.......... than that of a strong acid. The difference of the latter from the former is known as enthalpy of..........of the weak acid. ***(Bihar C.E.E. 1998)***

Matching Type Questions

Match the entries of column A with appropriate entries of column B :

(*a*)

A	B
1. System can exchange both matter and energy with the surroundings.	1. Closed system
2. System can exchange neither matter nor energy with the surroundings.	2. Open system
3. System can exchange energy with the surroundings but not matter.	3. Isolated system
4. System can exchange matter with the surroundings but not energy.	4. No such system exists.

(*b*)

A	B
1. A process which is carried out infinitesimally slowly.	1. Isochoric process.
2. A process is carried out such that temperature remains constant.	2. Isobaric process.
3. A process in which no heat enters or leaves the system.	3. Isothermal process.
4. A process in which the volume is kept constant.	4. Reversible process.
5. A process in which pressure is kept constant.	5. Adiabatic process.

ANSWERS

ASSERTION-REASON TYPE QUESTIONS

1. (*a*) **2.** (*b*) **3.** (*c*) **4.** (*a*) **5.** (*d*) **6.** (*b*) **7.** (*a*) **8.** (*b*)

TRUE/FALSE STATEMENTS

1, 3, 6, 8, 10, 11, 13, 14, 15.

FILL IN THE BLANKS

1. Closed system **2.** Intensive property **3.** Infinitesimally slowly **4.** First law of thermodynamics **5.** Enthalpy change **6.** gas constant, R **7.** (*a*) closed (*b*) endothermic **8.** zero **9.** extensive **10.** system, surroundings **11.** internal energy **12.** endothermic reaction **13.** zero **14.** one gram equivalent, the acid, excess base **15.** ΔH_{fusion}, $\Delta H_{vaporisation}$ **16.** 1632 kJ **17.** fossil. **18.** endothermic **19.** less, ionization.

MATCHING TYPE QUESTIONS

(*a*) 1-2, 2-3, 3-1, 4-4 (*b*) 1-4, 2-3, 3-5, 4-1, 5-2.

HINTS/EXPLANATIONS to Assertion-Reason Type Questions

4. H = E + PV. As absolute value of E cannot be determined, so absolute value of H cannot be determined.

5. Endothermic compounds are less stable because their enthalpies of formation are positive.

8. Enthalpy of neutralisation is same for HNO_3 and HCl with NaOH because both are strong.