11

CHEMICAL THERMODYNAMICS

When a chemical reaction occurs, it is accompanied by an energy change which may take any of several different forms. For example, the energy change involved in the combustion of fuels like kerosene, coal, wood, natural gas, etc., takes the form of heat and light. Electrical energy is obtained from chemical reactions in batteries. The formation of glucose, $C_6H_{12}O_6$ by the process of photosynthesis requires the absorption of light energy from the sun. Thus, we see that the energy change that accompanies a chemical reaction can take different forms. In this lesson, you shall study the reactions in which heat is either evolved or absorbed.

Objectives

After reading this lesson, you will be able to:

- define the commonly used terms in thermodynamics;

- differentiate between exothermic and endothermic reactions;

- explain the first law of thermodynamics;

- explain internal energy;

- define enthalpy and enthalpy change;

- state the relationship between enthalpy change and internal energy change;

- define enthalpy of formation, enthalpy of neutralisation and enthalpy of combustion;

- state the relationship between enthalpy of reaction and enthalpies of formation of reactants and products;

- solve numerical problems based on the enthalpy changes;

- state Hess's law;

- calculate enthalpy of a reaction using Hess's law;

- define bond enthalpy and bond dissociation enthalpy and

- calculate enthalpy of a reaction using bond enthalpy data.

11.1 Some Commonly Used Terms

In this lesson you would come across some frequently used terms. Let us understand the meaning of these terms first.

11.1.1 System and Surrounding

If we are studying the reaction of two substances A and B kept in a beaker, the reaction mixture of A and B is a system and the beaker and the room where it is kept are surroundings as shown in figure 11.1
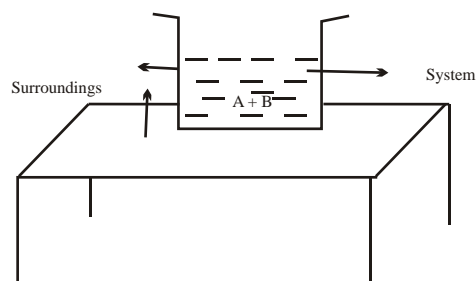

Fig 11.1 : *System and surroundings*

System is the part of the physical universe which is under study, while the rest of the universe is surroundings.

You know that hot tea/milk (let us call it a system) kept in a stoppered thermos flask remains hot for a couple of hours. If this flask is made of perfect insulating material, then there would be no exchange of matter or energy between the system and the surroundings. We call such a system an *isolated system.*

Isolated system is a system which can exchange neither matter nor energy with the surroundings.

If we keep hot tea/milk in a stoppered stainless steel flask, it will not remain hot after some time. Here energy is lost to the surroundings through the steel walls, but due to stopper, the matter will not be lost. We call this system a *closed system.*

Closed system is a system which can exchange energy but not matter with the surroundings.

If we keep stainless steel flask or thermos flask open, some matter will also be lost due to evaporation along with energy. We call such a system an open system. Plants, animals, human beings are all examples of open systems, because they continuously exchange matter (food, etc) and energy with the surroundings.

Open system is a system which can exchange both energy and matter with surroundings.

11.1.2. State of a System

We describe the state of a system by its measurable properties. For example, we can describe the state of a gas by specifying its pressure, volume, temperature etc. These variable properties are called state variables or state functions. Their values depend only on the initial and final state of the system and not on the path taken by the system during the change. When the state of a system changes, the change depends only on the initial and the final state of the system (Fig 11.2).
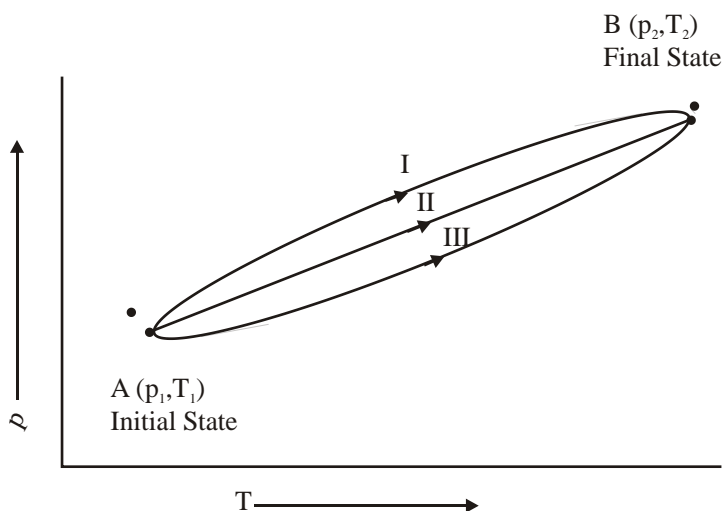
Fig. 11.2 : *Change of state from initial state to final state through three paths I, II and III. The difference $p_2 - p_1$ and $T_2 - T_1$ are independent of the path since pressure and temperature are state functions.*

State functions are those functions which depend only on the state of the system.

Change in state of a system is defined by giving the initial and the final state of the system. We can understand it by considering another example. We travel from one point to another. The distance travelled depends on the path or the route we take. But the separation between these two points on the earth is fixed. Thus, separation is a state function, but not the distance travelled.

11.1.3 Properties of a System

As stated earlier, the measurable properties of a system are called state variables. They may be further divided into two main types.

(i) **Extensive property** (variable) is one whose value depends upon the size of the system. For example, volume, weight, heat, etc.

(ii) **Intensive property** (variable) is one whose value is independent of the size of the system. For example, temperature, pressure, refractive index, viscosity, density, surface tension, etc.

You may note that an extensive property can become an intensive property by specifying a unit amount of the substance concerned. For example, mass and volume are extensive properties, but density (mass per unit volume) and specific volume (volume per unit mass) are intensive properties.

11.1.4 Types of Processes

Let us first understand what do we mean by a process. Suppose we want to raise the temperature of the system. We may do it by *heating* it. Here, heating is the process.

The method of bringing about a change in state is called process.

Processes could be of different types. The different types of processes are explained below.

i) **Isothermal process**: Ice melts at 273 K and 1 atm pressure. The temperature does not change as long as the process of melting goes on. Such processes are examples of isothermal process. We can define *isothermal process* as followes.

When the temperature of the system remains constant during various operations, then the process is said to be isothermal. This is attained either by removing heat from the system or by supplying heat to the system.

ii) **Adiabatic Process**: If an acid is mixed with a base in a closed thermos flask, the heat evolved is retained by the system. Such processes are known as adiabatic processes because the thermos flask does not allow exchange of heat between the system and the surroundings. Adiabatic process can be defined as follows:

In an adiabatic process there is no exchange of heat between the system and the surroundings. Thus, in adiabatic processes there is always a change in temperature.

iii) **Reversible Process:** In a reversible process, the initial and the final states are connected through a succession of equlibrium states. All changes occuring in any part of the process are exactly reversed when it is carried out in the opposite direction. Thus both the systems and its surroundings must be restored exactly to their original state, when the process has been performed and then reversed.

Let us understand it by an example. Imagine a liquid in equlibrium with its vapour in a cylinder closed by a frictionless piston, and placed in a constant temperature bath as shown in figure. 11.3. If the external pressure on the piston is increased by an infinitesimally small amount, the vapours will condense, but the condensation will occur so slowly that the heat evolved will be taken up by the temperature bath. The temperature of the system will not rise, and the pressure above this liquid will remain constant. Although condensation of the vapor is taking place, the system at every instant is in the state of equilibrium. If the external pressure is made just smaller than the vapour pressure, the liquid will vaporize extremely slowly, and again temperature and pressure will remain constant.
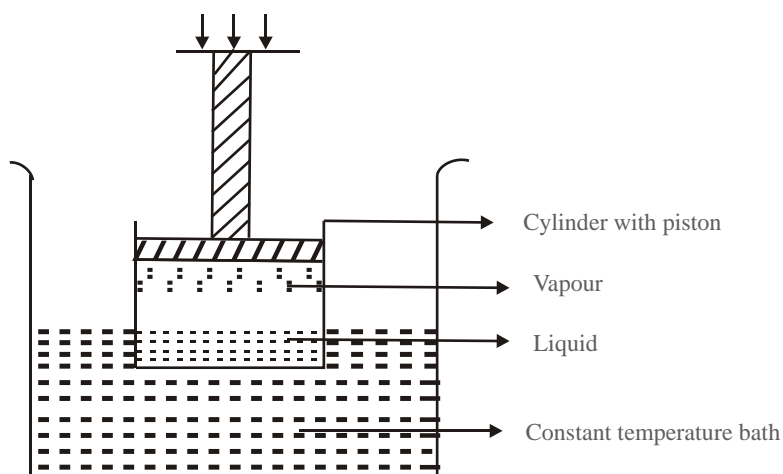
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Fig 11.3 : *Reversible process*

Reversible processes are those processes in which the changes are carried out so slowly that the system and surroundings are always in equilibrium.

iv) **Irreversible Processes**: In the above example rapid evaporation or condensation by the sudden decrease or incease of the external pressure, will lead to non-uniformity in temperature and pressure within the system and the equilibrium will be disturbed. Such processes are called as **irreversible processes.**

11.1.5 Standard States

You have seen that a system is described by the state variables. In order to compare the energies for different compounds, a standard set of conditions is chosen. This refers to the condition of 1 bar pressure at any specified temperature, with a substance in its most stable form.

11.2 Exothermic and Endothermic Reactions

(i)   Add a few cm^3 of dilute hydrocholoric acid in a test tube containing a few pieces of granulated zinc and observe the evolution of a gas. Feel the test tube. It would be hot.

(ii)   You must have observed that when some water is added to quick lime to prepare white wash, a lot of heat is evolved.

(iii) When a fuel like cooking gas or coal is burnt in air, heat is evolved besides light. Many chemical reactions lead to release of energy (heat) to the surroundings. We call these type of rections as *exothermic reactions.*

Exothermic reactions are those reactions which proceed with the evolution of heat.

Let us now consider the following reactions:

(i)   Add a small amount of solid ammonium chloride in a test tube half-filled with water. Shake and feel the test tube. It will feel cold.

(ii)   Similarly repeat this experiment with potassium nitrate and feel the test tube, it will feel cold.

(iii)   Mix barium hydroxide with ammonium chloride in small quantities in water taken in a test tube. Feel the test tube. It will be cold.

In all the above processes we see that heat is absorbed by the system from the surroundings. Such reactions are called *endothermic reactions.*

Endothermic reactions are those reactions which proceed with the absorption of heat from the surroundings.

11.3 Thermochemical Equations

You are familiar with equations for chemical reactions. Now we shall write the chemical equations which will specify heat energy changes and states of the reactants and products. These are called the thermochemical equations. For writing these equations, we follow the conventions listed below:

(i)   The heat evolved or absorbed in a reaction is affected by the physical state of the reacting substances. Therefore, gaseous, liquid and solid states are represented by putting symbols (g), (l), and (s) along side the chemical formulae respectively.

For example, to represent burning of methane in oxygen, we write

$$CH_4(g) + 2O_2 (g) \rightarrow CO_2 (g) + 2H_2O (l) + heat$$

In writing thermochemical reactions, we denote the amount of heat evolved or absorbed by a symbol ΔH. The amount of heat evolved or absorbed is written after the equation followed by semicolon. ΔH is negative for exothermic reactions and it is positive for endothermic reactions.

For example:

An exothermic reaction is written as

$$CH_4 (g) + 2O_2 (g) \rightarrow CO_2 (g) + 2H_2O (l) ; \Delta H = - 891 \text{ kJ}$$
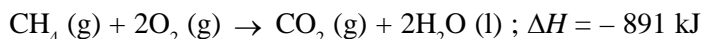
Whereas an endothermic reaction is written as

$$H_2 (g) + I_2 (g) \rightarrow 2HI (g) ; \Delta H = 52.2 \text{ kJ}$$

(ii)   In case of elements which exhibit allotropy, the name of allotropic modification is mentioned. For example,

C (graphite), C (diamond), etc.

(iii)   The substances in aqueous solutions are specified using the symbol (aq). For example NaCl (aq) stands for an aqueous solution of sodium chloride.

(iv)   Thermochemical equations may be balanced even by using fractional coefficients, if so required. The coefficients of the substances of the chemical equation indicate the number of moles of each substance involved in the reaction and the ΔH values given correspond to these quantities of substances.

(v)   In case the coefficients are multipied or divided by a factor, ΔH value must also be multiplied or divided by the same factor. In such cases, the ΔH value will depend upon the coefficients. For example, in equation.

$$H_2 \text{ (g)} + \tfrac{1}{2}O_2 \text{ (g)} \rightarrow H_2O \text{ (g)} ; \Delta H = -242 \text{ kJ}$$
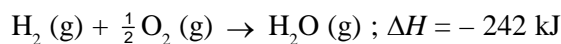
If coefficients are multiplied by 2, we would write the equation

$$2H_2 \text{ (g)} + O_2 \text{ (g)} \rightarrow 2H_2O \text{ (g)} ; \Delta H = 2\,(-242) = -484 \text{ kJ}$$
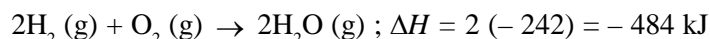
11.4 The First Law of Thermodynamics

You have learnt that chemical reactions are accompanied by energy changes. How do we determine these energy changes? You know that we cannot create or destroy energy. Energy only changes from one form to another. This is the observation made by many scientists over the years. This observation has taken the form of first law of thermodynamics. It has been found valid for various situations. We state this law as follows:

Energy can neither be created nor destroyed. The total energy of the universe or an isolated system is constant.

Mathematically the first law of thermodynamics is stated as:

$$\Delta U = q + w \tag{11.1}$$

where ΔU = change in internal energy, q = heat absorbed by the system, and w = work done on the system. These terms are explained as:

11.4.1 Internal Energy (U)

Every system has a definite amount of energy. This amount is different for different substances. It includes translational, vibrational and rotational energies of molecules, energy of electrons and nuclei.

The internal energy may be defind as the sum of the energies of all the atoms, molecules or ions contained in the system.

It is a state variable. It is not possible to measure the absolute values of internal energy. However, we can calculate the change in internal energy. If the internal energy of the system in the initial state is U_1 and that in the final state is U_2, then change in internal energy ΔU is independent of the path taken from the intial to the final state.

We can write this change as:

$$\Delta U = U_2 - U_1$$

The internal energy of the system can be changed in two ways :

Notes

(i) either by allowing heat to flow into the system or out of the system; and

(ii) by work done on the system or by the system

11.4.2 Heat(q) and Work(w)

Heat and work are not state functions. This is because the values of both q and w depend upon the way in which the change is carried out.

Since the law deals with the transfer of heat and work, we assign some signs to these quantities. Any thing which increases the internal energy of a system is given a positive sign.

Heat given to the system (q) and work done on the system (w) are given positive signs. Let us illustrate this with an example.

If a certain change is accompanied by absorption of 50 kJ of heat and expenditure of 30 kJ of work,

$$q = + 50 \text{ kJ}$$

$$w = - 30 \text{ kJ}$$

Change in internal energy $\Delta U = (+ 50 \text{ kJ}) + (- 30 \text{ kJ}) = = + 20 \text{ kJ}$

Thus the system has undergone a net increase in the internal energy of –20 kJ.

Change in the internal energy of the surroundings wll be 20 kJ.

11.4.3 Work of Expansion

Let us assume that pressure p is constant and the volume of the system changes from V_1 to V_2. The work done by a system is given as

$$w = - p \ (V_2 - V_1) = - p \ \Delta \ V \tag{11.2}$$

(Here we have taken minus sign, because the work is done by the system). Let us substitute the expression given for w in equation 11.1.

We get

$$\Delta \ U = q - p \ \Delta \ V \tag{11.3}$$

If the process is carried ot at constant volume, i.e. $\Delta \ V = 0$, then

$$\Delta \ U = q_v \tag{11.4}$$

The subscript v in q_v denotes that volume is constant.

The equation 11.4 shows that we can determine internal energy change if we measure the heat gained or lost by the system at constant volume. However, in chemistry, the chemical reactions are generally carried out at constant pressure (atmospheric presure). What do we do then? Let us define another state function, called, enthalpy.

11.4.4 Enthalpy(H)

For measuring heat lost or gained at constant pressure, we define a new state function called enthalpy. It is denoted by the symbol H and is given by

$$H = U + p\,V \qquad (11.5)$$

Enthalpy change, ΔH, is given by

$$\Delta H = \Delta U + \Delta(pV) \qquad (11.6)$$

$$\text{or } \Delta H = \Delta U + p\,\Delta V + V\,\Delta p$$

If the change is carried out at constant pressure, then $\Delta p = 0$. The equation 11.6 will become

$$\Delta H = \Delta U + p\,\Delta V \text{ (at constant pressure)} \qquad (11.7)$$

Substituting the value of ΔU from equation 11.3 in equation 11.7, we get

$$\Delta H = q - p\,\Delta V + p\,\Delta V$$

$$= q \text{ (at constant pressure)}$$

We denote q at constant pressure by q_p hence

$$\Delta H = q_p \qquad (11.8)$$

Equation 11.8 shows that by measuring heat lost or gained at constant pressure, we can measure enthalpy change for any process.

11.4.5 Relation between ΔH and ΔU

For liquids and solids, the difference between $\Delta_r H$ and $\Delta_r U$ is not significant but for gasses, the difference is significant as we will see here.

Let V_A be the total volume of the gaseous reactants,

V_B the total volume of the gaseous products,

n_A the number of moles of gaseous reactants,

and n_B the number of moles of gaseous products, at constant pressure and temperature.

Then, using ideal gas law, we can write

$$p\,V_A = n_A\,RT \qquad (11.9)$$

$$p\,V_B = n_B\,RT \qquad (11.10)$$

Subtracting equation 11.9 from equation 11.10, we get

$$p\,V_B - pV_A = n_B\,RT - n_A\,RT = (n_B - n_A)\,RT$$

$$p\,(V_B - V_A) = p\,\Delta V = \Delta n_g RT$$

At constant pressure

$$\Delta H = \Delta U + p\,\Delta V$$

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

Here Δn_g = (number of moles of gaseous products) - (number of moles of gaseous reactants)

Thus we can find the value of ΔH from ΔU or vice versa.

Chemistry

For solids and liquids ΔV is very small. We can neglect the term $p \Delta V$, hence ΔH is nearly the same as ΔU.

Intext Questions 11.1

1. Which of the following is false ?

   (a) The reaction

   $H_2(g) + Cl_2(g) \rightarrow 2HCl(g) + 185$ kJ

   is endothermic.

   (b) Enthalpy change is a state function.

   (c) Standard state condition for a gaseous system is 1 bar pressure at a specified temperature.

2. For the reaction at 298 K,

   $\dfrac{1}{2} N_2(g) + \dfrac{3}{2} H_2(g) \rightarrow NH_3(g)$; $\Delta H = -46$ kJ

   (a) What is the value of Δn_g ?

   ....

   (b) Calculate the value of ΔU at 298 K?

   ....

3. Which of the following will increase the internal energy of a system?

   (a) Heat given to the system

   (b) Work done by the system

   ....
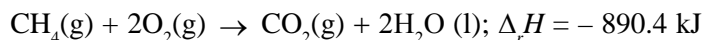
11.5 Standard Enthalpy of Reactions

Let as denote total enthalpy of reactants as $H_{reactants}$ and total enthalpy of products as $H_{products}$. The difference between these enthalpies, ΔH, is the enthalpy of the reaction

$\Delta_r H = H_{products} - H_{reactants}$

When $H_{products}$ is greater than $H_{reactants}$ then ΔH is positive and heat is absorbed in the reaction, and the reaction will be endothermic. For example,

$H_2(g) + I_2(g) \rightarrow 2HI(g)$; $\Delta_r H = 52.5$ kJ

When $H_{products}$ is less than $H_{reactants}$ then ΔH is negative and heat is evolved in the reaction, and the reaction will be exothermic. For example,

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O \ (l); \Delta_r H = -890.4 \ kJ$

Enthalpy of a reaction changes with pressure and temperature. It is convenient to report enthalpies of the reactions in terms of standard state of substances as we have defined earlier. When substances are in their standard states, we call the enthalpy of reaction as *standard enthalpy of reaction*. It is defined as the enthalpy change for a reaction, when the reactants and the products are in their standard states. It is donoted by $\Delta_r H^0$.

Notes

11.5.1 Enthalpy of formation ($U_f H°$)

The enthalpy change when one mole of a pure compound is formed from its elements in their most stable states is called the enthalpy of formation and is denoted by $U_f H^0$.

When the reacting elements and the products formed are all in their standard states, the enthalpy change accompanying the chemical reaction is called the standard enthalpy of formation and is denoted by $\Delta_f H^0$. By convention, we take the standard enthalpy of formation of an element in its most stable state as zero.

For example:

$$C_{(Graphite)} + O_2(g) \rightarrow CO_2 \ (g) \ ; \Delta_f H^0 = -393.5 \ kJ \ mol^{-1}$$
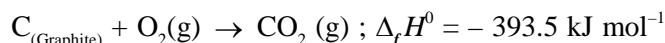
This means that carbon dioxide is formed from its elements in their most stable states. Carbon in the form of graphite and at room temperature and gasesous O_2 and CO_2 being at 1 bar.

11.5.2 Enthalpy of Combustion ($U_{comb} H°$)

Enthalpy of combustion is the enthalpy change (heat evolved) accompanying the complete combustion of 1 mole of a substance in oxygen at a given temperature and 1 bar pressure.

For example :

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \ ; \Delta_{comb} H^0 = -1365.6 \ kJ$$
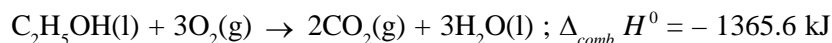
Enthalpy of combutsion of $C_2H_5OH(l)$ is $-1365.6 \ kJ \ mol^{-1}$

11.5.3 Enthalpy of Neutralization ($U_{neut} H°$)

Enthalpy of neutralization is the enthalpy change (heat evolved) when one mole of hydrogen ions (H^+)is neutralized by one mole of hydroxyl ions (OH^-) in dilute aqueous medium to form water.

For example:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O \ (l) \ ; \Delta_{neut} H = -57 \ kJ/mol$$
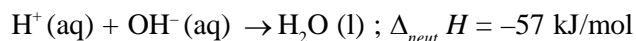
Enthalpy of neutralization of a strong acid with a strong base is always constant having a value of -57 kJ. However, enthalpy of neutralization of strong acid with a weak base or weak acid with a strong base will be different, because of varying degree of ionization of weak acids and bases.

## 11.6 Laws of Thermochemistry

There are two laws of thermochemistry : The Lavoisiter–Laplace law and the Hess's Law of Constant Heat Summation.

Lavoisier – Laplace Law : When a chemical equation is reversed, the sign of $\Delta_r H$ is changed. For example,

$$N_2 \text{ (g)} + O_2 \text{ (g)} \rightarrow 2NO \text{ (g)}; \Delta_r H = 180.5 \text{ kJ}$$

$$2NO \text{ (g)} \rightarrow N_2 \text{ (g)} + O_2 \text{ (g)}; \Delta_r H = -180.5 \text{ kJ}$$

Hess's Law of constant heat summation: Hess's law states that the enthalpy of reaction is independent of the number and the nature of the intermediate steps.

You have learnt that standard enthalpy change of the reaction

$$C \text{ (graphite)} + O_2(g) \rightarrow CO_2(g)$$
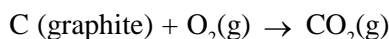
is equal to $- 393.5$ kJ mol^{-1}. This value can be determined with the help of a calorimeter. However, there are some reactions for which the direct measurement of enthalpy in the laboratory is not possible. For example the standard enthalpy change for the reaction,

$$C \text{ (graphite)} + \frac{1}{2} O_2 \text{ (g)} \rightarrow CO \text{ (g)}$$
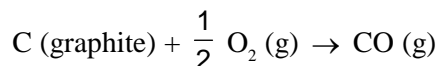
cannot be to determined with the help of calorimeter because the combustion of carbon is incomplete unless an excess of oxygen is used. If excess of oxygen is used, some of the CO is oxidized to CO_2. How can then we determine the enthalpy change for such reactions when direct measurement is not possible?

Since ΔH is a state function, it is not dependent on the way the reactions are carried out. Let us carry out the reactions as follows.

(1) First carry out the following reaction and let $\Delta_r H_1^0$ be the enthalphy change of the reaction.

$$C \text{ (graphite)} + O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)}; \Delta_r H_1^0 = -393.5 \text{ kJ/mol.}$$

(2) Now let us write the reaction for which we have to determine the enthalpy change of the reaction and let it be $\Delta_r H_2^o$

$$C \text{ (graphite)} + \frac{1}{2} O_2 \text{ (g)} \rightarrow CO(g); \Delta_r H_2^0 = ?$$
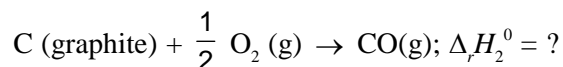
(3) Let us carry out the following reactions and let $\Delta_r H_3^0$ be the enthalpy change of the reaction

$$CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g); \Delta_r H_3^0 = - 283.0 \text{ kJ}$$
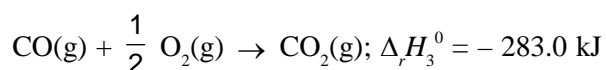
We have obtained the products $CO_2(g)$ from carbon and oxygen through two routes, namely first as in step (1) and second as in step (2) + (3).
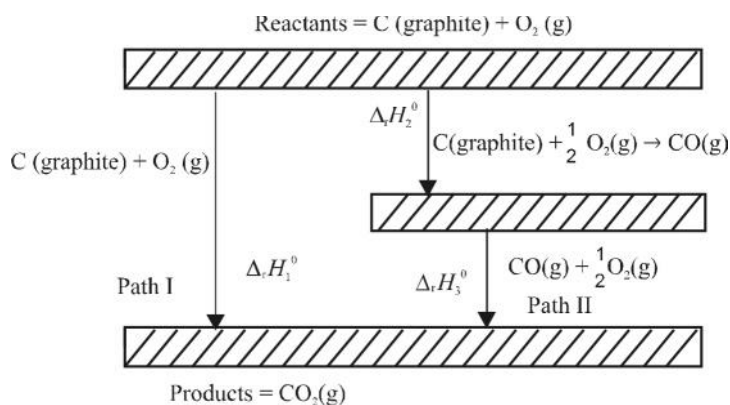
According to Hess's Law

$$\Delta_r H_1^0 = \Delta_r H_2^0 + \Delta_r H_3^0$$
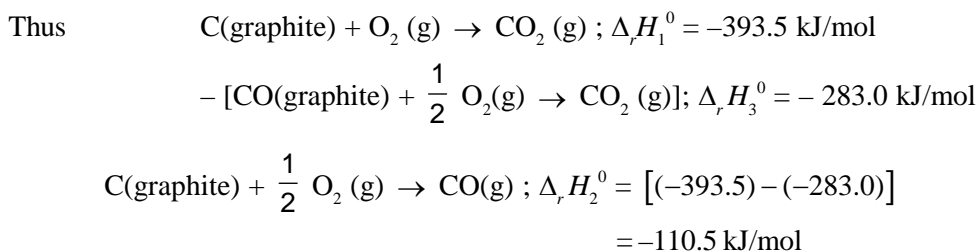
or

$$\Delta_r H_2^0 = \Delta_r H_1^0 - \Delta_r H_3^0$$

Fig 11.4 shows alternate paths for the conversion of carbon and oxygen to carbon dioxide.
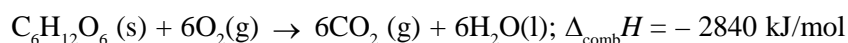
Notes

Fig 11.4 : *Alternate paths for the conversion of carbon and oxygen to carbon dioxide*

The result of Hess's law is that thermochemical equations can be added and substracted just like algebraic equations to get the desired reaction. A useful practical application of this law is that we can calculate enthalpy changes for the reactions which cannot be studied directly as in the above case.

To obtain the enthalpy change for the reactions, we algebraically combine the known values of $\Delta_r H^0$ in the same way as the reactions themselves,

Thus
$$C(graphite) + O_2 (g) \rightarrow CO_2 (g) ; \Delta_r H_1^0 = -393.5 \text{ kJ/mol}$$

$$- [CO(graphite) + \frac{1}{2} O_2(g) \rightarrow CO_2 (g)]; \Delta_r H_3^0 = -283.0 \text{ kJ/mol}$$

$$C(graphite) + \frac{1}{2} O_2 (g) \rightarrow CO(g) ; \Delta_r H_2^0 = \left[(-393.5) - (-283.0)\right]$$

$$= -110.5 \text{ kJ/mol}$$

Example 11.1 The heat evolved in the combustion of glucose is shown in the following equation:

$$C_6H_{12}O_6 (s) + 6O_2(g) \rightarrow 6CO_2 (g) + 6H_2O(l); \Delta_{comb}H = -2840 \text{ kJ/mol}$$

How much energy will be required for the production of 1.08 g of glucose?

Soluton: Glucose will be prepared by the reverse reaction.

$$6CO_2(g) + 6H_2O (l) \rightarrow C_6H_{12}O_6 (s) + 6CO_2 (g) ; \Delta H = 2840 \text{ kJ}.$$
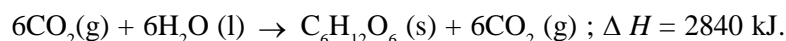
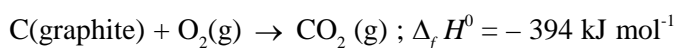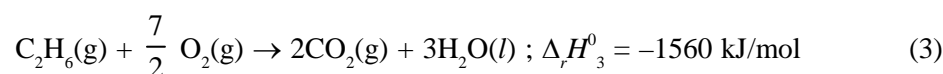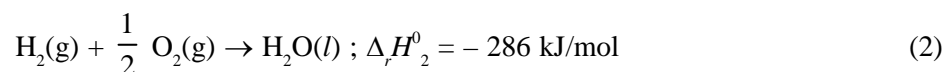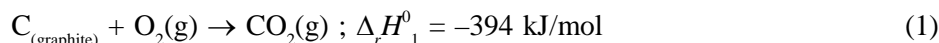This equation refers to 1 mol of glucose (180 g of glucose).

Notes

Production of 180 g of glucose requires 2840 kJ of energy. Therefore, production of 1.08 g will require;

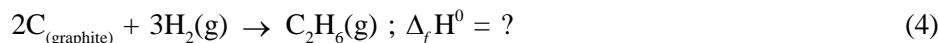$$\frac{2840 \text{ kJ}}{180 \text{ g}} \times 1.08 \text{ g} = 17.04 \text{ kJ}$$

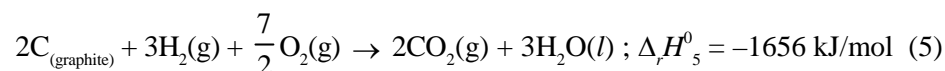**Example 11.2** Calculate the standard enthalpy of formation of ethane, given that

$$C(graphite) + O_2(g) \rightarrow CO_2(g) ; \Delta_f H^0 = -394 \text{ kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(\ell); \Delta_f H^0 = -286 \text{ kJ mol}^{-1}$$

$$C_2H_6(g) + \frac{7}{2} O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell); \Delta_r H^0 = -1560 \text{ kJ mol}^{-1}$$

Solution: Given that

$$C_{(graphite)} + O_2(g) \rightarrow CO_2(g) ; \Delta_r H^0_{\ 1} = -394 \text{ kJ/mol} \qquad (1)$$

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) ; \Delta_r H^0_{\ 2} = -286 \text{ kJ/mol} \qquad (2)$$

$$C_2H_6(g) + \frac{7}{2} O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) ; \Delta_r H^0_{\ 3} = -1560 \text{ kJ/mol} \qquad (3)$$
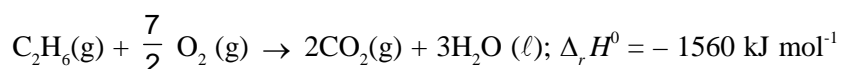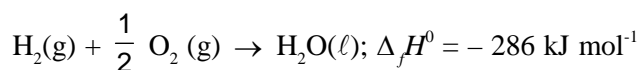
The required equation is
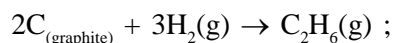
$$2C_{(graphite)} + 3H_2(g) \rightarrow C_2H_6(g) ; \Delta_f H^0 = ? \qquad (4)$$

To obtain the above equation, mulitply equations (1) by 2 and equation (2) by 3 and then add both the equations we get

$$2C_{(graphite)} + 3H_2(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) ; \Delta_r H^0_{\ 5} = -1656 \text{ kJ/mol} \quad (5)$$

(where $\Delta_r H^0_{\ 5} = 2\Delta_r H^0_{\ 1} + 3\Delta_r H^0_{\ 2} = 2 \times (-394) + 3 \times (-286) = -1656$ kJ/mol)

Subtract equation (3) from equation (5) to get the equation (4)

$$2C_{(graphite)} + 3H_2(g) \rightarrow C_2H_6(g) ;$$

where $\Delta_f H^0 = -1656 - (-1560) = -96$ kJ/mol

Thus, standard enthalpy of formation of ethane is –96 kJ/mol

Intext Questions 11.2

1. Which of the following is true?

   (a) Enthalpy of formation is the heat evolved or absorbed when one gram of a substance is formed from its elements in their most stable states.
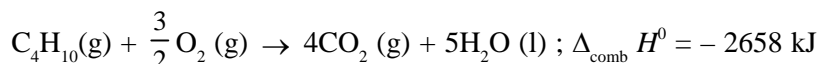
(b) When one mole of H+ (aq) and 1 mole of OH⁻ (aq) react, 57.1 kJ of energy is absorbed.

(c) In the thermochemical equation,
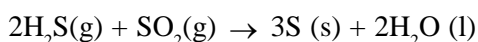
C(graphite) + O_2 (g) → CO_2(g) ; $\Delta_f H^0$ = –394 kJ mol⁻¹

$\Delta_f H^0$ is known as enthalpy of formation of CO_2(g)

2. Calculate the enthalpy change for complete combustion of 29.0 g of butane, if

$$C_4H_{10}(g) + \frac{3}{2} O_2 \text{ (g)} \rightarrow 4CO_2 \text{ (g)} + 5H_2O \text{ (l)} ; \Delta_{comb} H^0 = - 2658 \text{ kJ}$$

3. Calculate the standard enthalpy of the reaction

$2H_2S(g) + SO_2(g) \rightarrow 3S \text{ (s)} + 2H_2O \text{ (l)}$

given that

$\Delta_f H^0 \text{ (H}_2\text{S)} = - 20.6 \text{ kJ mol}^{-1}$

$\Delta_f H^0 \text{ (SO}_2\text{)} = - 296.9 \text{ kJ mol}^{-1}$

$\Delta_f H^0 \text{ (H}_2\text{O)} = - 289.9 \text{ kJ mol}^{-1}$
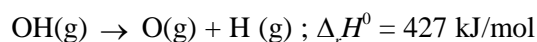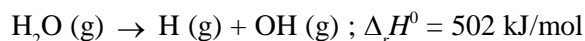
11.7 Bond Enthalpies

In a chemical reaction, you have seen that energy is either absorbed or evolved. Do you know the origin of this change in energy? You know that bonds are broken and new bonds are formed in chemical reactions. Energy changes take place in breaking some bonds of the reactants and in forming new bonds of the products. So the energy changes in a chemical reaction are a result of energy changes in breaking and forming of bonds. Let us consider the gaseous reactions, because in these, we encounter the energy changes due to breaking and forming of bonds only.

At high temperature, hydrogen molecules dissociate into atoms as

$H_2(g) \rightarrow H \text{ (g)} + H(g) ; \Delta_r H = 435 \text{ kJ/mol}$
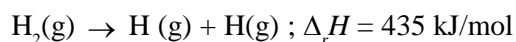
The heat absorbed in this reaction is used to break the chemical bonds holding the hydrogen atoms together in the H_2 molecules. For a diatomic molecule like $H_2(g)$, we define **bond dissociation energy as the enthalpy change of the reaction in which one mole of the gaseous molecules are dissociated into gaseous atoms.**

Now, let us consider a polyatomic molecule like $H_2O(g)$. The dissociation may involve fragmenting the molecules into an atom and a group of atoms, called a radical, as in

$H_2O \text{ (g)} \rightarrow H \text{ (g)} + OH \text{ (g)} ; \Delta_r H^0 = 502 \text{ kJ/mol}$

$OH(g) \rightarrow O(g) + H \text{ (g)} ; \Delta_r H^0 = 427 \text{ kJ/mol}$

In the first reaction, one of the two OH bonds in H_2O (g) dissociates with an enthalpy change of 502 kJ/mol and in the second reaction, second OH bond dissociates with an enthalpy change of 427 kJ/mol. It is clear that the dissociation energy of the O – H bond is sensitive to its environment. However, the difference is not very large. We take the

Notes

Notes

average value (464.5 kJ/mol in this case) in case of polyatomic molecules and call it bond enthalpy.

Bond enthalpy is defined as the average amount of enthalpy change involved in the dissociation of one mole of bonds present in different gaseous compounds.

Now you know the distincton between bond dissociation enthalpy and bond enthalpy. Bond dissociation enthalpy refers to breaking a particular bond in a particular molecule whereas bond enthalpy is the average value of bond dissociation energies for a given type of bond. The bond enthalpies of some bonds are listed in table 11.1.

By using bond enthalpies (B.E.) it is possible to estimate the energy released when a gaseous molecule is formed from its gaseous atoms. For example, the energy released at constant pressure for the reaction ($\Delta_r H$),

$$3H(g) + C(g) + Cl(g) \rightarrow CH_3Cl(g)$$
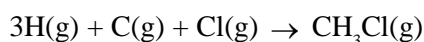
is the sum of the energies of three C – H bonds, and one C – Cl bond, all taken with a negative sign because energy is released. Using the values of bond enthalpies (B.E.) from table 11.1 we get,

$$\Delta_r H = -3 \times \text{B.E. (C – H)} - \text{B.E. (C – Cl)}$$

$$= (-3 \times 415 - 335) \text{ kJ mol}^{-1}$$

$$= (-1245 - 335) \text{ kJ mol}^{-1}$$

$$= -1574 \text{ kJ mol}^{-1}$$

We will now show you how to use bond enthalpy data to estimate the enthalpy of a reaction, when direct calorimetric data are not available. Note that in section 11.7 we used enthalpy of formation data to estimate enthalpy of a reaction. In principle, bond enthalpy data can be used to calculate $\Delta_r H$ for a chemical reaction occuring in gaseous state by making use of difference in energy absorbed in breaking the bonds in reactants and energy released in formation of bonds in products.

$$\Delta_r H = \Sigma \text{ B.E. (reactants)} - \Sigma \text{ B.E. (products)} \qquad (11.10)$$

Table 11.1 : Average Bond enthalpies

BOND	BOND ENTHALPY /(kJ mol^{-1})
H – H	435
C – H	415
C – Br	284
C – C	356
C = C	598
Br – Br	193
Cl – Cl	242
C – Cl	339
F – F	155
H – Cl	431
H – O	462
H – N	390

BOND	BOND ENTHALPY /(kJ mol^{-1})
H – F	563
H – Br	366
H – I	296
C – O	355
C = O	723
C – N	391
C = N	619
C $\equiv$ N	878
C $\equiv$ C	832

Example 11.3: Use bond enthalpy data given in table 11.1 to calculate the enthalpy of the reaction.

$$CH_3 \text{ (g)} + Cl_2 \text{ (g)} \rightarrow CH_3Cl \text{ (g)} + HCl \text{ (g)}$$
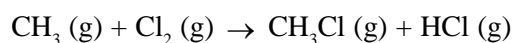
Solution: 1. Write the equation using structural formula

$$
\begin{array}{c}
\text{H} \\
| \\
\text{H – C – H} \\
| \\
\text{H}
\end{array}
\quad + \quad \text{Cl – Cl} \rightarrow
\begin{array}{c}
\text{H} \\
| \\
\text{H – C – Cl} \\
| \\
\text{H}
\end{array}
+ \text{H – Cl}
$$
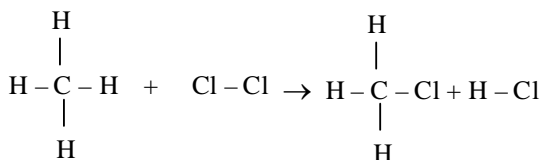
2. List the bonds broken and bonds formed under the equation as shown

$$
\begin{array}{c}
\text{H} \\
| \\
\text{H – C – H} \\
| \\
\text{H}
\end{array}
+ \text{Cl – Cl} \rightarrow
\begin{array}{c}
\text{H} \\
| \\
\text{H – C – Cl} \\
| \\
\text{H}
\end{array}
+ \text{H – Cl}
$$
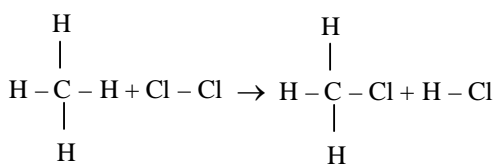
number of bonds broken	number of bonds formed
C – H = 4	C – Cl = 1
Cl – Cl = 1	H – Cl = 1
	C – H = 3

3. Look up the values of bond enthalpies for the bonds in the reactants and products and list them as shown

Reactants	Products
B.E. (C – H) = 435 kJ mol^{-1}	B.E. (Cl – C) = 339 kJ mol^{-1}
B.E. (Cl – Cl) = 242 kJ mol^{-1}	B.E. (H – Cl) = 431 kJ mol^{-1}
	B.E. (C – H) = 435 kJ/mol

4. Use equation 11.10,

Enthalpy of the rection $\Delta_r H = \Sigma$ B.E. (reactants) - Σ B.E. (products)

$= 4[\text{B.E. (C} - \text{H)} + \text{B.E. (C} - \text{Cl)}] - [\text{B.E. (C} - \text{Cl)} + \text{B.E. (H} - \text{Cl)} + 3 \text{ B.E. (C} - \text{H)}]$
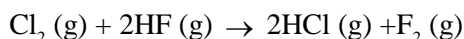
$= [4 \times 435 + 242] - [339 + 431 + 3 \times 435] = -93 \text{ kJ}$

Now let us take one example in which we calculate the enthalpy of a reaction using

(i) Enthalpy of formation data

(ii) Bond enthalpy data.

Example 11.4: Calculate $\Delta_r H°$ for the reaction

$$\text{Cl}_2 \text{ (g)} + 2\text{HF (g)} \rightarrow 2\text{HCl (g)} + \text{F}_2 \text{ (g)}$$

(a) Using enthalpy of formation data

$$\Delta_f H° \text{ (HCl)} = -92.5 \text{ kJ}$$

$$\Delta_f H° \text{ (HF)} = -269 \text{ kJ}$$

(b) Using bond enthalpy data

B.E. (H – Cl) = 431 kJ mol^{-1}

B.E. (F – F) = 155 kJ mol^{-1}

B.E. (H – F) = 563 kJ mol^{-1}

B.E. (Cl – Cl) = 242 kJ mol^{-1}

Solution : (a) Using enthalpy of formation of compounds,

$$\Delta_r H = [2\Delta_f H^0 \text{ (HCl)} + \Delta_f H \text{ (F}_2\text{)}] - [2\Delta_f H^0 \text{ (HF)} + U_f H^0 (\text{Cl}_2)]$$

$$= [2\text{x} (-92.5) + 0] - [2\text{x} - (269) + 0] \text{ kJ}$$

$$= -185 \text{ kJ} + 538 \text{ kJ}$$

$$= +353 \text{ kJ}$$

(b) Using bond enthalpies

$$\Delta_r H^0 = \Sigma \text{ B.E. (reactants bonds)} - \Sigma \text{ B.E. (products bonds)}$$

$$= [\text{B.E. (Cl} - \text{Cl)} + 2\text{B.E. (H} - \text{F)}] - [2 \text{ B.E. (H} - \text{Cl)} + \text{B.E. (F} - \text{F)}]$$

$$= [242 + 2 (563)] \text{ kJ} - [2 \times 431 + 155] \text{ kJ}$$

$$= 1368 \text{ kJ} - 1017 \text{ kJ}$$

$$\Delta_r H^0 = 351 \text{ kJ}$$

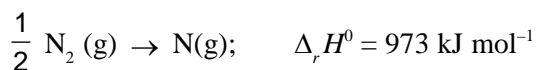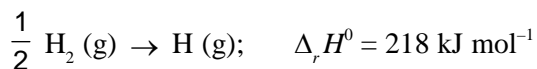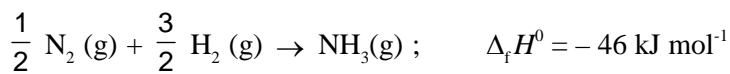$\Delta_r H^0$ calculated by these two different methods are nearly the same.

Notes

Intext Questions 11.3

1. Write True or false

(a) Enthalpy of a reaction is equal to the sum of the enthalpy of formation of products minus the sum of the enthalpy of formation of the reactants.

(b) Enthalpy of formation of any elementary substance is equal to zero.

(c) If a reaction can be carried out in several steps, the enthalpy change for the overall reaction is equal to enthalpy change in the last step.

(d) Bond enthalpy and bond dissociation energy are same for polyatomic molecules.

2. Calculate the bond enthalpy of N – H in NH_3 (g), given

$$\frac{1}{2}\ N_2\ (g) + \frac{3}{2}\ H_2\ (g)\ \rightarrow\ NH_3(g)\ ;\qquad \Delta_f H^0 = -\ 46\ \text{kJ mol}^{-1}$$

$$\frac{1}{2}\ H_2\ (g)\ \rightarrow\ H\ (g);\qquad \Delta_r H^0 = 218\ \text{kJ mol}^{-1}$$

$$\frac{1}{2}\ N_2\ (g)\ \rightarrow\ N(g);\qquad \Delta_r H^0 = 973\ \text{kJ mol}^{-1}$$

3. Calculate the enthalpy of the reaction

$$H_2\ (g) + Cl_2\ (g)\ \rightarrow\ 2HCl\ (g)$$

given;

Bond enthalpy (H - H) = 435 kJ mol⁻¹

Bond enthalpy (Cl - Cl) = 242 kJ mol⁻¹

Bond enthalpy (H - Cl) = 431 kJ mol⁻¹

What You Have Learnt

- System is the part of the physical universe which is under study, while the rest of the universe is surroundings.

- Isolated system is a system which can exchange neither matter nor energy with the surroundings.

- Closed system is a system which can exchange energy but not the matter with the surroundings.

- Open system is a system which can exchange both energy and matter with the surroundings.

- State functions are those functions which depend only on the state of the system.
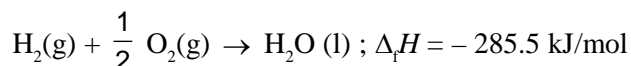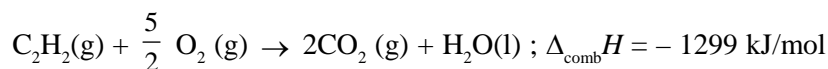
Notes

- Extensive properties depend upon the size of the system whereas intensive properties do not depend upon the size of the system.

- When the temperature of the system is kept constant during various operations then the process is said to be isothermal.

- In an adiabatic process there is no exchange of heat between the system and the surroundings.

- Reversible processes are those processes in which the changes are carried out so slowly that the system and surrounding are always in equilibrium.

- Exothermic reactions are those reactions which proceed with the evolution of heat.

- Endothermic reactions are those which proceed with absorption of heat from the surroundings.

- First law of Thermodynamics states that energy can neither be created nor destroyed.

- Internal energy is the sum of the energies of all the atoms, molecules or ions contained in the system.

- The state function enthalpy (H) is given by the relation $H = U + PV$.

- When a chemical equation is reversed, the sign of ΔH is also reversed.

- The enthalpy of reaction is independent of the number and nature of the intermediate steps.

- Bond enthalpy is the average amount of bond dissociation enthalpies for a given type of bond present in different gaseous compounds, when one mole of bonds is broken in the gaseous state.
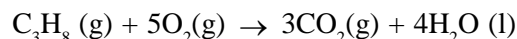
Terminal Exercise

1. Enthalpy of combustion of ethyl alcohol, C_2H_5OH, is $- 950$ kJ mol^{-1}. How much heat is evolved when one gram of ethyl alcohol burns?

2. Given :

   $$C_2H_2(g) + \frac{5}{2} O_2 (g) \rightarrow 2CO_2 (g) + H_2O(l) \; ; \Delta_{comb}H = - 1299 \text{ kJ/mol}$$

   $$C(graphite) + O_2 (g) \rightarrow CO_2(g) \; ; \Delta_f H = - 393 \text{ kJ/mol}$$

   $$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O (l) \; ; \Delta_f H = - 285.5 \text{ kJ/mol}$$
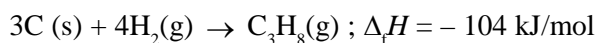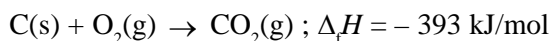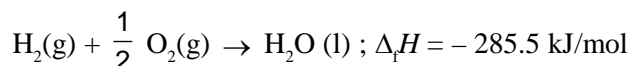
   Calculate enthalpy of formation of $C_2H_2(g)$

3. Calculate the enthalpy of combustion of propane

   $$C_3H_8 (g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O (l)$$

Given the following:

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O \text{ (l)} ; \Delta_f H = -285.5 \text{ kJ/mol}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) ; \Delta_f H = -393 \text{ kJ/mol}$$
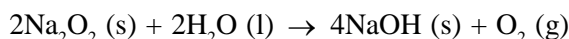
$$3C \text{ (s)} + 4H_2(g) \rightarrow C_3H_8(g) ; \Delta_f H = -104 \text{ kJ/mol}$$

4. When two moles of H_2 and one mole of O_2 react to produce two moles of gaseous water at 373 K and 1 bar pressure, a total of 484 kJ are evolved. What are (a) ΔH and (b) ΔU for the production of a single mole of H_2O (g).

5. Calculate enthalpy of the reaction:

$$2Na_2O_2 \text{ (s)} + 2H_2O \text{ (l)} \rightarrow 4NaOH \text{ (s)} + O_2 \text{ (g)}$$

Enthalpies of formation of NaOH (s), Na_2O_2 (s) and H_2O (l) are -426.4 kJ mol^{-1}, 504 kJ mol^{-1} and -285 kJ mol^{-1} respectively.

6. Calculate the heat of formation of gaseous ethyl alcohol,

$$2C(\text{graphite}) + 3H_2(g) + \frac{1}{2} O_2(g) \rightarrow C_2H_5OH \text{ (g)}$$
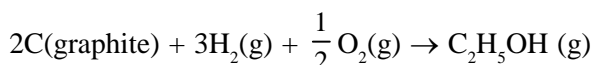
given that enthalpy of sublimation of graphite is 714 kJ/mol and bond enthalpies of H – H, O = O, C – C, C – H, C – O and O – H are respectively 435 kJ/mol^{-1}, 498 kJ/mol^{-1}, 347 kJ/mol^{-1}, 415 kJ/mol^{-1}, 355 kJ/mol^{-1} and 462 kJ/mol^{-1} respectively.

Answers to Intext Questions

11.1

1. (a)

2. (a) $\Delta n = 1 - \frac{1}{2} - \frac{3}{2} = -1$

    (b) $\Delta U = \Delta H - \Delta n \text{ RT}$

    $= 46000 \text{ (J mol}^{-1}) - (-1) (8.314 \text{ Jk}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})$

    $= -46000 \text{ (J mol}^{-1}) + 2247.6 \text{ (J mol}^{-1})$

    $= -43.5 \text{ kJ mol}^{-1}$

3. (a)

11.2

1. (c)

2. -1329 kJ

3. $\Delta_r H^0 = 2 \Delta_f H^0 \text{ (H}_2\text{O)} - 2\Delta_f H^0 \text{ (H}_2\text{S)} - \Delta_f H^0 \text{ (SO}_2)$

    $= -241.7$ kJ

11.3

1.   (a) T

   (b) T

   (c) F

   (d) F

2. $\Delta rH^0 = \Sigma$ B.E. (reactant bonds) $- \Sigma$ B.E. (products bonds)

   or $- 46$ (kJ mol^{-1}) = 3×218 (kJ mol^{-1}) + 973 (kJ mol^{-1}) $-$ B.E. (NH$_3$(g) Bonds)

   B.E. (NH$_3$(g) Bonds) = 1673 kJ mol^{-1}

   B.E. (N $-$ H) = 557.7 kJ mol^{-1}

3. $\Delta_r H^0 = - 185$ kJ mol^{-1}