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CHAPTER

Thermochemistry

CONTENTS

It is noticed that energy in the form of heat (thermal energy) is generally evolved or absorbed as a result of a chemical change.

Thermochemistry is the branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions.

We have studied in the previous chapter that every substance has a definite amount of energy known as the **intrinsic energy or internal energy, E.** Its exact value cannot be determined but the change in internal energy, ΔE, can be accurately measured experimentally.

When the internal energy of reactants (E_r) is greater than the internal energy of the products (E_p), the difference of internal energy, ΔE, is released as heat energy.

$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$

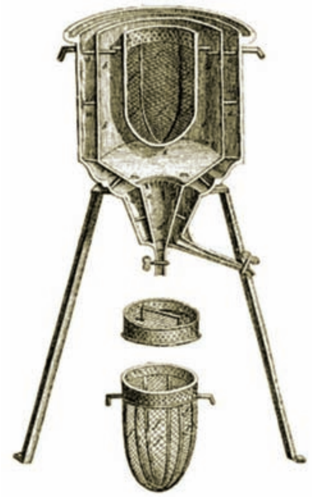
or

$$\Delta E = E_p - E_r$$

Such a reaction is called **exothermic reaction.** If the internal energy of the products (E_p) is greater than that of the reactants (E_r), heat is absorbed from the surroundings. Such a reaction is called **endothermic reaction.** The amount of heat released or absorbed in a chemical reaction is termed the **heat of reaction.**

HISTORY OF THERMOCHEMISTRY

In 1782 Antoine Lavoisier and Pierre-Simon Laplace laid the foundations of "thermochemistry" by showing that the heat evolved in a reaction is equal to the heat absorbed in the reverse reaction. They also investigated the specific heat and latent heat of a number of substances, and amounts of heat evolved in combustion. Similarly, in 1840 Swiss chemist Germain Hess formulated the principle that the evolution of heat in a reaction is the same whether the process is accomplished in one-step or in a number of stages. This known as Hess's law. With the advent of the mechanical theory of heat in the early 19th century, Hess's law came to be viewed as a consequence of the law of conservation of energy.



The world's first ice-calorimeter, used in the winter of 1782-83, by Antoine Lavoisier and Pierre-Simon Laplace, to determine the heat evolved in various chemical changes.

The energy changes in chemical reactions are largely due to the breaking of existing bonds between the atoms and the formation of new bonds. **Thus thermochemistry provides useful information regarding the bond energies.**

UNITS OF ENERGY CHANGES

The energy changes are usually expressed as the calorie (cal.), kilocalorie (1 kcal = 1000 cal), Joule (J) and kilojoule (kJ). It may be noted that 1 cal = 4.18 J and 1 kcal = 4.18 kJ.

ENTHALPY OF A REACTION

Thermochemical measurements are made either at (*a*) constant volume or (*b*) constant pressure. The magnitudes of changes observed under the two conditions are different.

The change in internal energy (ΔE) is the heat change accompanying a chemical reaction at constant volume because no external work is performed.

However at constant pressure not only does the change in internal energy take place but work is also involved because of expansion or contraction. In the laboratory most of the chemical reactions are carried out at constant pressure (atmospheric pressure) rather than at constant volume. In order to study the heat changes for reactions taking place at constant pressure and constant temperature, chemists have introduced a new term called **enthalpy.**

The enthalpy of a system is defined as the sum of the internal energy and the product of its pressure and volume. That is,

$$H = E + PV$$

where E is the internal energy, P is the pressure and V is the volume of the system. It is also called **Heat content.**

Just like internal energy, enthalpy is also a function of the state and it is not possible to measure its absolute value. However a change in enthalpy (ΔH) accompanying a process can be measured accurately and is given by the expression

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$
$$= H_p - H_r$$

Thus if ΔV be the change in volume in case of a reaction at constant temperature and pressure, the thermal effect observed will be the sum of the change in internal energy (ΔE) and the work done in expansion or contraction. That is,

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

Therefore, while the heat change in a process is equal to its change in internal energy ΔE at constant volume, it gives at constant pressure the enthalpy change ΔH. That is,

ΔE = Heat change in a reaction at constant volume

ΔH = Heat change in a reaction at constant pressure

For reactions involving solids and liquids only the change in volume (ΔV) is very small and the term $P \times \Delta V$ is negligible. For such reactions ΔH is equal to ΔE. In case of gases, however, we must specify whether the reaction has taken place at constant volume or at constant pressure because the value of $P \times \Delta V$ is appreciable. Most of such reactions are, however, studied at constant pressure and change in enthalpy (ΔH) is involved.

EXOTHERMIC AND ENDOTHERMIC REACTIONS

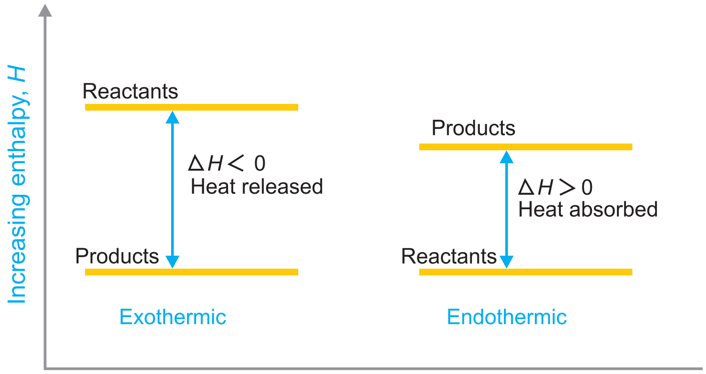
Let us consider a general reaction at constant pressure,

$$\mathrm{A + B \longrightarrow C + D}$$

If H_A, H_B, H_C and H_D be the enthalpies of A, B, C and D respectively, the heat of reaction at constant pressure *viz*., ΔH is equal to the difference in enthalpies of the products and the reactants *i.e.*,

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$
$$= (H_C + H_D) - (H_A + H_B)$$

The value of ΔH may be either zero, negative or positive. Where ΔH is zero, the enthalpies of the products and reactants being the same, the heat is evolved or absorbed. In case ΔH is negative, the sum of enthalpies of the products is less than that of the reactants and the difference in enthalpy is given out in the form of heat.



■ **Figure 8.1**
Enthalpy diagram for an exothermic and endothermic reaction.

Such reactions which are accompanied by the evolution of heat energy are called Exothermic reactions.

When ΔH is positive, the enthalpy or heat content of the reactants and an equivalent of heat is absorbed by the system from the surroundings.

EXAMPLES OF EXOTHERMIC AND ENDOTHERMIC PROCESSES

When trying to classify a process as exothermic or endothermic, watch how the temperature of the surroundings changes. An exothermic process releases heat, and causes the temperature of the immediate surroundings to rise. An endothermic process absorbs heat and cools the surroundings.

Exothermic processes	Endothermic processes
Making ice cubes	Melting ice cubes
Formation of snow in clouds	Conversion of frost to water vapour
Condensation of rain from water vapour	Evaporation of water
Mixing sodium sulfite and bleach	Baking bread
Rusting iron	Cooking an egg
Burning sugar	Producing sugar by photosynthesis
Forming ion pairs	Separating ion pairs
Mixing water and strong acids	Mixing water and ammonium nitrate
Mixing water with an anhydrous salt	Making an anhydrous salt from a hydrate
Crystallizing liquid salts (as in sodium acetate in chemical handwarmers)	Melting solid salts
Nuclear fission	Reaction of barium hydroxide octahydrate crystals with dry ammonium chloride
mixing water with calcium chloride	Reaction of thionyl chloride ($SOCl_2$) with cobalt(II) sulfate heptahydrate

Such reactions which are accompanied by absorption of heat are called Endothermic reactions.

Thus for an exothermic reaction $H_p < H_r$ and $\Delta H = -$ ve, for an endothermic reaction $H_p > H_r$ and $\Delta H = +$ve.

Sign of ΔH and ΔE

A negative sign of ΔH or ΔE shows that heat is evolved and the reaction is exothermic. A positive sign of ΔH or ΔE indicates that heat energy is absorbed and the reaction is endothermic.

TABLE 8.1. SIGN CONVENTIONS FOR ENERGY

Energy	Terms used	Sign
Released	Exothermic	–
Absorbed	Endothermic	+

Calculation of ΔH from ΔE and *vice versa*

The enthalpy change of a reaction at constant pressure (ΔH) and internal energy change (ΔE) are related to each other as

$$\Delta H = \Delta E + P \times \Delta V \qquad \ldots (i)$$

where ΔV is the change in volume due to expansion or contraction when measurement is done at constant pressure, P. Though heat changes of reactions are usually measured at constant pressure, it is sometimes necessary to carry out the reaction at constant volume as, for example, in the measurement of heat of combustion in a bomb calorimeter. The above relationship can be used, if desired, for the conversion of ΔH into ΔE and *vice versa*.

Let us consider a reaction

$$\text{aA} + \text{bB} \longrightarrow \text{cC} + \text{dD}$$

Change in number of moles

$$= \text{No. of moles of products} - \text{No. of moles of reactants}$$
$$= (\text{c} + \text{d}) - (\text{a} + \text{b})$$
$$= \Delta n$$

Let the volume occupied by one mole of the gas be V. Then, change in volume, ΔV = change in No. of moles × volume occupied by one mole of the gas.

$$\Delta V = \Delta n \times V$$

or $$P \times \Delta V = P(\Delta n \times V)$$

$$P \times \Delta V = PV \times \Delta n \qquad ...(ii)$$

But $$PV = RT \qquad \text{(for one mole of gas)}$$

Putting RT in place of PV in equation (ii) we get

$$P\Delta V = RT\,\Delta n$$

Substituting the value of $P\Delta V$ in equation (i) we get

$$\Delta H = \Delta E + \Delta n\, RT$$

It may be pointed out that while determining the value of ΔH, only the number of moles of gaseous reactants and products are taken into consideration. The value of gas constant R is taken either in calories or joules per degree per mol and is 1.987 cal (approximately 2 calories) or 8.314 joules.

SOLVED PROBLEM 1. The heat of combustion of ethylene at 17ºC and at constant volume is – 332.19 kcals. Calculate the heat of combustion at constant pressure considering water to be in liquid state. (R = 2 cal degree^{-1} mol^{-1})

SOLUTION

The chemical equation for the combustion of ethylene is

$$\underset{\text{1 mole}}{C_2H_4(g)} + \underset{\text{3 moles}}{3O_2(g)} \longrightarrow \underset{\text{2 moles}}{2CO_2(g)} + \underset{\text{negligible volume.}}{2H_2O(l)}$$

No. of moles of the products = 2

No. of moles of the reactants = 4

$$\therefore \qquad \Delta n = (2 - 4) = -2$$

We know that $$\Delta H = \Delta E + \Delta n\, RT$$

Given that $$\Delta E = -332.19 \text{ kcal}$$
$$T = 273 + 17 = 290 \text{ K}$$
$$R = 2 \text{ cals} = 2 \times 10^{-3} \text{ kcals}$$

$$\therefore \qquad \Delta H = -332.19 + 2 \times 10^{-3} \times -2 \times 290$$
$$\mathbf{= -333.3\ kcal}$$

SOLVED PROBLEM 2. The heat of combustion of carbon monoxide at constant volume and at 17ºC is – 283.3 kJ. Calculate its heat of combustion at constant pressure ($R = 8.314$ J degree^{-1} mol^{-1}).

SOLUTION

$$\underset{1\text{ mole}}{CO(g)} + \underset{\frac{1}{2}\text{ mole}}{\tfrac{1}{2}\,O_2(g)} \longrightarrow \underset{1\text{ mole}}{CO_2(g)}$$

No. of moles of products $= 1$

No. of moles of reactants $= 1\frac{1}{2}$

Δn = No. of moles of products – No. of moles of reactants

$$= 1 - 1\frac{1}{2} = -\frac{1}{2}$$

Given that $\Delta E = -283.3$ kJ

$T = (273 + 17) = 290$ K

and $R = 8.314$ J or 8.314×10^{-3} kJ

Substituting these values in the equation

$$\Delta H = \Delta E + \Delta n \times RT$$

we get

$$\Delta H = -283.3 + \left[-\frac{1}{2} \times (8.314 \times 10^{-3}) \times 290\right]$$

$$= -283.3 - 1.20$$

$$= -284.5 \text{ kJ}$$

∴ Heat of combustion of CO at constant pressure is – **284.5 kJ.**

SOLVED PROBLEM 3. The heat of formation of methane at 298 K at constant pressure is – 17.890 kcal. Calculate its heat of formation at constant volume. ($R = 1.987$ cal degree^{-1} mol^{-1})

SOLUTION

The thermochemical equation for the heat of formation of methane at 298 K at constant pressure is :

$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta H = -17.890 \text{ kcal}$$

No. of moles of gaseous products $= 1$

No. of moles of the gaseous reactants $= 2$

Change in No. of moles, $\Delta n = 1 - 2 = -1$

Given that $\Delta H = -17.890$ kcal; T = 25 + 273 = 298 K

and R = 1.987 cal = 1.987×10^{-3} kcal

Substituting these values in the equation

$$\Delta H = \Delta E + \Delta n \times RT$$

$$\Delta E = -17.89 + [-1 \times (1.987 \times 10^{-3}) \times 298]$$

$$= -18.482 \text{ kcal}$$

∴ The heat of formation of methane at constant volume is – **18.482 kcal.**

HOT PACKS / COLD PACKS

Heat therapy has become a standard treatment for ailing muscles among athletes, the disabled and elderly people. Heat packs provide relief by dilating the blood vessels of nearby muscles and allowing the soft tissue to stretch, and cold packs reduce the swelling and inflammation of injured body parts.Chemical advances have led to the development of very convenient types of heat packs and cold packs, which can now be found in most emergency first aid kits.

Hot Packs

There are a number of types of chemical heat packs used. Some packs consist of two plastic bags, the inner bag contains water, and the area between the inner bag and the outer bag is filled with a dry salt. When the inside bag is broken, the solid and the water react in an exothermic reaction, releasing heat. However, the most frequently used heat packs today involve one sealed plastic pouch containing a metal disk and a salt solution; commonly calcium chloride, magnesium sulfate, or sodium acetate.

Cold Packs

A cold pack comes in a plastic bag made of tough white plastic. This bag is filled with a smaller bag and ammonium nitrate crystals. The smaller bag contains water, and is made of a thin weak plastic, so it is easy to break. When a cold pack is used, it must be "broken" by rupturing the inner bag. Breaking the bag releases the water, which dissolves the ammonium nitrate. The water and ammonium nitrate react completely, and within fifteen to twenty the cold pack will no longer feel cold.

Cold packs make use of the heat transfer that occurs during chemical reactions, but in contrast to heat packs, utilize endothermic reactions. In the endothermic reaction between ammonium nitrate crystals and water, the heat required for the reaction to proceed from reactants to products is absorbed from the surrounding environment, resulting in a decrease in temperature of the pack noticeable to the touch.

THERMOCHEMICAL EQUATIONS

There are a number of factors which affect the quantity of heat evolved or absorbed during a physical or chemical transformation. One of these factors has already been discussed *viz.*, whether the change occurs at constant pressure or constant volume. The other factors are :

(1) Amount of the reactants and products
(2) Physical state of the reactants and products
(3) Temperature
(4) Pressure

An equation which indicates the amount of heat change (evolved or absorbed) in the reaction or process is called a Thermochemical equation.

It must essentially : (*a*) be balanced; (*b*) give the value of ΔE or ΔH corresponding to the quantities of substances given by the equation; (*c*) mention the physical states of the reactants and products. The physical states are represented by the symbols (*s*), (1), (*g*) and (aq) for solid, liquid, gas and gaseous states respectively.

Example of Thermochemical Equation

The equation :

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O \qquad \Delta H = -68.32 \text{ kcal}$$

indicates that when 1 mole of hydrogen reacts with 0.5 mole of oxygen, one mole of water is formed and 68.32 kcal of heat is evolved at constant pressure. If two moles of hydrogen are burnt, the heat evolved would be (2 × 68.32) kcals. This equation, however, is not a complete thermochemical equation because it does not specify whether water is in the form of steam or liquid. There is difference in the value of ΔH if water is in the liquid or gaseous state as shown below :

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -68.32 \text{ kcal}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta H = -57.80 \text{ kcal}$$

HEAT OF REACTION OR ENTHALPY OF REACTION

The heat of a reaction is simply the amount of heat absorbed or evolved in the reaction. We also know that the amount of heat absorbed or evolved at constant temperature and pressure is called enthalpy. Therefore **the amount of heat change during a reaction at constant temperature and pressure may also be called enthalpy change.** Its value depends upon the number of moles of the reactants which have reacted in the given chemical reaction. Thus,

Heat of reaction may be defined as the amount of heat absorbed or evolved in a reaction when the number of moles of reactants as represented by the balanced chemical equation change completely into the products. For example, the heat change for the reaction of one mole of carbon monoxide with 0.5 mole of oxygen to form one mole of carbon dioxide is – 284.5 kJ. This means that 284.5 kJ of heat is evolved during the reaction and is the heat of reaction. It can be represented as

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -284.5 \text{ kJ}$$

It is very important to note that heat of reaction varies with the change in temperature. Therefore, we must mention the temperature at which the reaction is taking place. It is also convenient for comparison to fix up some temperature as standard or reference. According to the conventions prevalent in thermodynamics, the temperature of 298 K under a pressure of one atmosphere has been fixed as the *standard state*. **The heat change accompanying a reaction taking place at 298 K and one atmospheric pressure is called the standard heat change or standard enthalpy change.** It is denoted by ΔH°.

VARIATION OF HEAT (OR ENTHALPY) OF REACTION WITH TEMPERATURE

The heat of reaction changes with change in temperature of a gas due to variation in its specific heat. The equations representing the variation of heat change of reaction with temperature are known as **Kirchoff's equations.**

At constant volume, the heat of reaction, ΔE, is given by the relation

$$\Delta E = E_2 - E_1$$

where E_1 and E_2 are the internal energies of the reactants and products.

Differentiating this equation with respect to temperature at constant volume, we get

$$\left[\frac{d(\Delta E)}{dT}\right]_v = \left(\frac{dE_2}{dT}\right)_v - \left(\frac{dE_1}{dT}\right)_v \qquad ...(1)$$

But we have already seen that

$$\left(\frac{dE}{dT}\right)_v = C_v$$

$$\therefore \qquad \frac{d(\Delta E)}{dT} = (C_v)_2 - (C_v)_1 = \Delta C_v \qquad ...(2)$$

where $(C_v)_2$ and $(C_v)_1$ are heat capacities of the products and reactants respectively. Or, **change in heat of reaction at constant volume per degree change in temperature is equal to the difference in heat capacities at constant volume of products and reactants.**

Integrating the above equation between temperatures T_1 and T_2, we have

$$\Delta E_2 - \Delta E_1 = \int_{T_1}^{T_2} \Delta C_v \, dT$$

or $$\Delta E_2 - \Delta E_1 = \Delta C_v [T_2 - T_1] \qquad ...(3)$$

where ΔE_2 and ΔE_1 are heats of reaction at temperatures T_2 and T_1 respectively.

Similarly, at **constant pressure** the heat of reaction ΔH is given by the reaction

$$\Delta H = H_2 - H_1$$

where H_2 is the heat content (enthalpy) of the products and H_1 being that of the reactants.

Differentiating with respect to temperature at constant pressure, we have

$$\left(\frac{d(\Delta H)}{dT}\right)_P = \left(\frac{dH_2}{dT}\right)_P - \left(\frac{dH_1}{dT}\right)_P \qquad ...(4)$$

According to the equation, Chapter 7, we have

$$\left(\frac{dH}{dT}\right)_P = C_P$$

$$\therefore \qquad \left(\frac{d(\Delta H)}{dT}\right)_P = (C_P)_2 - (C_P)_1 = \Delta C_P \qquad ...(5)$$

where $(C_P)_2$ and $(C_P)_1$ are the heat capacities of products and reactants respectively.

or $$d(\Delta H) = \Delta C_P \times dT$$

Change in heat of reaction at constant pressure per degree change of temperature is equal to difference in heat capacities of products and reactants at constant pressure.

Integrating the equation between temperature T_1 and T_2, we have

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \, dT$$

or $$\Delta H_2 - \Delta H_1 = \Delta C_p [T_2 - T_1] \qquad ...(6)$$

The relations (2), (3), (5) and (6) were first derived by Kirchoff and are called **Kirchoff's equations.** These equations may be used for calculating heat of reaction at a given temperature when it is known at some other temperature and when the heat capacities of products and reactants are known.

SOLVED PROBLEM 1. The heat of reaction $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$ at 27ºC is – 22.1 kcal. Calculate the heat of reaction at 77ºC. The molar heat capacities at constant pressure at 27ºC for hydrogen, chlorine and HCl are 6.82, 7.70 and 6.80 cal mol^{-1} respectively.

SOLUTION

Here,

$$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl \qquad \Delta H = -22.1 \text{ kcal}$$

ΔC_p = Heat capacities of products – Heat capacities of reactants

$$\begin{aligned}
&= 6.80 - \left[\frac{1}{2}(6.82) + \frac{1}{2}(7.70)\right] \\
&= 6.80 - 7.26 = -0.46 \text{ cal} = -0.46 \times 10^{-3} \text{ kcal} \\
T_2 &= 273 + 77 = 350 \text{ K}; T_1 = 273 + 27 = 300 \text{ K} \\
T_2 - T_1 &= (350 - 300) \text{ K} = 50 \text{ K}
\end{aligned}$$

Substituting these values in Kirchoff's equation, we have

$$\begin{aligned}
\Delta H_2 - \Delta H_1 &= \Delta C_p (T_2 - T_1) \\
&= -22.1 + (-0.46 \times 10^{-3}) \times 50 \\
&= -22.1 + (-0.023) \\
&= -22.123 \text{ kcal}
\end{aligned}$$

∴ Heat of reaction at 77ºC is – **22.123 kcal**

SOLVED PROBLEM 2. The heat of reaction $N_2 + 3H_2 \rightarrow 2NH_3$ at 27ºC was found to be –21.976 kcal. What will be the heat of reaction at 50ºC ?

The molar heat capacities at constant pressure and at 27ºC for nitrogen, hydrogen and ammonia are 6.8, 6.77 and 8.86 cal mol^{-1} degree^{-1}.

SOLUTION

Here,

$$\begin{aligned}
\Delta H &= -21.976 \text{ kcal} \\
T_2 &= 273 + 50 = 323 \text{ K} \\
T_1 &= 273 + 27 = 300 \text{ K} \\
[T_2 - T_1] &= (323 - 300) \text{ K} = 23 \text{ K}
\end{aligned}$$

ΔC_p = Heat capacities of products – Heat capacities of reactants

$$\begin{aligned}
&= (2 \times 8.86) - [6.8 + (3 \times 6.77)] \\
&= 17.72 - (6.8 + 20.31) = -9.39 \text{ cal} \\
&= -9.39 \times 10^{-3} \text{ kcal}
\end{aligned}$$

Substituting these values in Kirchoff's equation, we have

$$\begin{aligned}
\Delta H_2 &= \Delta H_1 + (T_2 - T_1)\, \Delta C_p \\
&= -21.976 + [23 \times (-9.39 \times 10^{-3})] \\
&= -21.976 + (-0.216) = -22.192 \text{ kcal}
\end{aligned}$$

∴ Heat of reaction at 50ºC is = **22.192 kcal**

DIFFERENT TYPES OF HEAT (ENTHALPY) OF REACTION

The heat or enthalpy changes accompanying chemical reactions are expressed in different ways, depending on the nature of the reaction. These are discussed below.

HEAT OF FORMATION

The heat of formation of a compound is defined as :

The change in enthalpy that takes place when one mole of the compound is formed from its elements.

It is denoted by ΔH_f. For example, the heat of formation of ferrous sulphide and acetylene may be expressed as :

$$\mathrm{Fe}\,(s) + \mathrm{S}(s) \longrightarrow \mathrm{FeS}(s) \qquad \Delta H_f = -24.0\ \mathrm{kcal}$$

$$2\mathrm{C}(s) + \mathrm{H_2}(g) \longrightarrow \mathrm{C_2H_2}(g) \qquad \Delta H_f = +53.14\ \mathrm{kcal}$$

Similarly, the reaction between gaseous hydrogen and gaseous chlorine to form gaseous hydrogen chloride is represented by the equation

$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \longrightarrow 2\mathrm{HCl}(g) \qquad \Delta H = -44.0\ \mathrm{kcal}$$

It may be noted in this case that – 44.0 kcal is not the heat of formation of hydrogen chloride because this amount of heat is evolved when two moles of hydrogen chloride are formed. The heat of formation of hydrogen chloride, therefore, would be – 44.0/2 = – 22.0 kcal and the equation can be written as

$$\tfrac{1}{2}\,\mathrm{H_2}(g) + \tfrac{1}{2}\,\mathrm{Cl_2}(g) \longrightarrow \mathrm{HCl}(g) \qquad \Delta H_f = -22.0\ \mathrm{kcal}$$

STANDARD HEAT OF FORMATION

The standard heat of formation of a compound is defined as :

The change in enthalpy that takes place when one mole of a compound is formed from its elements, all substances being in their standard states (298 K and 1 atm pressure).

The standard heat of formation of some compounds are given in Table 8.2.

TABLE 8.2. STANDARD HEAT OF FORMATION OF SOME COMPOUNDS

Substance	ΔH_f^o kcal mol^{-1}	Substance	ΔH_f^o kcal mol^{-1}
$H_2O(g)$	– 57.84	$CH_4\,(g)$	– 17.89
$H_2O(l)$	– 68.38	$C_2H_6\,(g)$	– 20.23
$HCl(g)$	– 22.08	$C_6H_6\,(g)$	+ 11.86
$HBr(g)$	– 8.70	$C_2H_2\,(g)$	+ 53.14
$NH_3(g)$	– 11.02	$CH_3OH\,(l)$	– 57.17
$CO_2(g)$	– 94.13	$C_2H_5OH\,(l)$	– 66.26
$SO_2(g)$	– 71.00	$CH_3COOH\,(l)$	– 115.83

By convention the standard heat of formation of all elements is assumed to be zero.

Standard Heat of Reaction (ΔH^o) from Standard Heat of Formation (ΔH_f^o)

We can calculate the heat of reaction under standard conditions from the values of standard heat of formation of various reactants and products. **The standard heat of reaction is equal to the standard heat of formation of products minus the standard heat of formation of reactants.**

That is,

$$\Delta H^\circ = \begin{bmatrix}\text{Total standard heat}\\ \text{of formation of products}\end{bmatrix} - \begin{bmatrix}\text{Total standard heat}\\ \text{of formation of reactants}\end{bmatrix}$$

$$\Delta H^o = \Delta H_f^o \text{ (products)} - \Delta H_f^o \text{ (reactants)}$$

Let us consider a general reaction

$$\text{aA} + \text{bB} \longrightarrow \text{cC} + \text{dD}$$

The standard heat of reaction is given by

$$\Delta H^o = \Delta H_f^o \text{ (products)} - \Delta H_f^o \text{ (reactants)}$$

$$= [\text{c} \times \Delta H_f^o \text{ (C)} + \text{d} \times H_f^o \text{ (D)}] - [\text{a} \times \Delta H_f^o \text{ (A)} + \text{b} \times \Delta H_f^o \text{ (B)}]$$

SOLVED PROBLEM 1. Calculate ΔH^o for the reaction

$$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$$

given that ΔH_f^o for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are – 393.5, – 111.31 and – 241.80 kJ mol^{-1} respectively.

SOLUTION

Here we have

$$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$$

$$\Delta H^o = \Delta H_f^o \text{ (products)} - \Delta H_f^o \text{ (reactants)}$$

$$= [\Delta H_f^o [CO\,(g)] + \Delta H_f^o [H_2O(g)]] - [\Delta H_f^o [CO_2\,(g)] + \Delta H_f^o [H_2(g)]]$$

$$= [-111.3 + (-241.8)] - [-393.5 + 0]$$

$$= -353.1 + 393.5$$

$$= \mathbf{40.4\ kJ}$$

SOLVED PROBLEM 2. The standard heats of formation of $C_2H_5OH(l)$, $CO_2(g)$ and $H_2O(l)$ are – 277.0, –393.5 and –285.5 kJ mol^{-1} respectively. Calculate the standard heat change for the reaction

$$C_2H_5OH(l) + 3O_2(l) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

SOLUTION

We know that :

$$\Delta H^o = \Delta H_f^o \text{ (products)} - \Delta H_f^o \text{ (reactants)}$$

In the present case

$$\Delta H^o = [2 \times \Delta H_f^o [CO_2(g)] + 3 \times \Delta H_f^o [H_2O(l)]]$$

$$- \Delta H_f^o [C_2H_5OH(l)] + 3 \times \Delta H_f^o [O_2(g)]]$$

$$= [2 \times (-393.5) + 3 \times -285.5] - [-277.0 - 0]$$

$$= -1643.5 - (-277)$$

$$= \mathbf{-\ 1366.5\ kJ}$$

HEAT OF COMBUSTION

The heat of combustion of a substance is defined as : **the change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen.**

It is denoted by ΔH_c. As for example, heat of combustion of methane is – 21.0 kcal (= 87.78 kJ) as shown by the equation

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_c = -21.0 \text{ kcal}$$

Now consider the chemical equations

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -94.3 \text{ kcal}$$

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H = -26.0 \text{ kcal}$$

It may be noted that – 94.3 kcal and not – 26.0 kcal is the heat of combustion of carbon as the combustion is complete only in the first reaction. In the second case, oxidation has converted carbon to carbon monoxide and is by no means complete as carbon monoxide can be further oxidised to carbon dioxide.

It should be noted clearly that the **heat of combustion of a substance (ΔH_c) is always negative.** Heat energy is evolved during the process of combustion *i.e.*, $\Delta H_c = -$ ve.

APPLICATIONS OF THE HEAT OF COMBUSTION

(1) **Calculation of heat of formation.** Since the heats of combustion of organic compounds can be determined with considerable ease, these are employed to calculate their heats of formation. The direct determination of these is often impossible.

(2) **Calorific value of foods and fuels.** The calorific value is defined as : **the amount of heat produced in calories (or joules) when one gram of a substance is completely burnt.**

It is expressed in cal g^{-1} or kcal g^{-1} or kJ g^{-1}. Let us compare the calorific values of methane and ethane. Their heats of combustion are – 890.3 kJ and – 1559.7 kJ. These combustion reactions are expressed as

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_c = -890.3 \text{ kJ}$$

$$C_2H_6(g) + 3\tfrac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H_c = -1559.7 \text{ kJ}$$

In case of methane heat produced per gram is 890.3/16 = 55.64 kJ g^{-1} while for ethane it is –1559.7/30 = 51.90 kJ g^{-1}. Thus methane has better fuel efficiency than ethane as it produces more heat per gram.

(3) **Deciding constitution.** Heat of combustion of organic compounds is to a large extent an additive property, as shown by the fact that in a homologous series the difference between the heats of combustion of successive members is nearly constant and is equal to 158 cals. Constants corresponding to the heats of combustion of various atoms and linkages have been worked out. The heat of combustion of an organic substance can be calculated from its probable structural formula by adding up the values of the constants corresponding to the atoms and linkages involved therein. If the value so obtained comes out to be the same as the experimental value of the heat of combustion of the compound, the assumed formula must be correct. In this way Kekule's formula for benzene with alternate double and single linkages has been supported as the calculated value of the heat of combustion of benzene according to this formula agrees with the actual heat of combustion. Heat of combustion of organic compounds has thus proved very valuable in deciding their chemical constitution.

SOLVED PROBLEM. Calculate the standard heat of formation of propane (C_3H_8) if its heat of combustion is – 2220.2 kJ mol^{-1}. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are – 393.5 and – 285.8 kJ mol^{-1} respectively.

SOLUTION

We are given

$$(i)\quad C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H_c = -2220.2\text{ kJ}$$

$$(ii)\quad C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5\text{ kJ}$$

$$(iii)\quad H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -285.8\text{ kJ}$$

We should manipulate these equations in a way so as to get the required equation

$$3C(s) + 4H_2(g) \longrightarrow C_3H_8(g) \qquad \Delta H = ?$$

Multiplying equation (*ii*) by 3 and equation (*iii*) by 4 and adding up we get

$$3C(s) + 3O_2(g) \longrightarrow 3CO_2(g) \qquad \Delta H = -1180.5\text{ kJ}$$

$$4H_2(g) + 2O_2(g) \longrightarrow 4H_2O(l) \qquad \Delta H = -1143.2\text{ kJ}$$

$$(iv)\quad 3C(s) + 4H_2(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H = -2323.7\text{ kJ}$$

Subtracting equation (*i*) from equation (*iv*), we have

$$3C(s) + 4H_2(g) + 5O_2(g) - 5O_2(g) \longrightarrow C_3H_8(g) \qquad \Delta H = -103.5\text{ kJ}$$

∴ The heat of formation of propane is **– 103.5 kJ mol^{-1}.**

HEAT OF SOLUTION

Heat changes are usually observed when a substance is dissolved in a solvent. When a reaction takes place in solution, the heat of solution of reactants and products must be taken into consideration. The heat of solution is defined as : **the change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent at a given temperature.**

For example, when one mole of copper sulphate is dissolved in water so that we get one molar solution, the heat absorbed is 78.5 kJ. If the solution so obtained is further diluted, there will again be a change in enthalpy. If we go on diluting the solution, a stage will come when further dilution produces no thermal effect. This state is called the state of infinite dilution. To avoid the quantity of the solvent, we have to incorporate the idea of infinite dilution in our definition which may be stated as : **the heat of solution is the change in enthalpy when one mole of a substance is dissolved in a solvent so that further dilution does not give any change in enthalpy.**

The heat of solution can also be expressed as :

$$KCl(s) + H_2O(l) \longrightarrow KCl(aq) \qquad \Delta H = -4.4\text{ kcal}$$

$$MgSO_4(s) + H_2O(l) \longrightarrow MgSO_4(aq) \qquad \Delta H = -20.28\text{ kcal}$$

The heat of solution of an electrolyte may be due to energy change involved during ionisation or some hydrate formation as in case of sulphuric acid. Usually heat is absorbed when ions are torn apart from each other in the process of solution and heat is evolved during hydrate formation. With a salt as sodium chloride the heat of separation of ions just equals the heat of hydration and there is very little heat effect.

HEAT OF NEUTRALISATION

The heat of neutralisation is defined as : **the change in heat content (enthalpy) of the system when one gram equivalent of an acid is neutralised by one gram equivalent of a base or *vice versa* in dilute solution.**

The following may be considered as typical examples of the heat of neutralisation.

$$\begin{aligned}
HNO_3(aq) + NaOH(aq) &\longrightarrow NaNO_3(aq) + H_2O(l) && \Delta H = -13.69 \text{ kcal}\\
HNO_3(aq) + KOH(aq) &\longrightarrow KNO_3(aq) + H_2O(l) && \Delta H = -13.87 \text{ kcal}\\
HCl(aq) + NaOH(aq) &\longrightarrow NaCl(aq) + H_2O(l) && \Delta H = -13.68 \text{ kcal}\\
HCl(aq) + LiOH(aq) &\longrightarrow LiCl(aq) + H_2O(l) && \Delta H = -13.70 \text{ kcal}
\end{aligned}$$

It may be concluded from the above data that **the heat of neutralisation of a strong acid and strong base is –13.7 kcal, no matter which acid or base is employed.** This regularity has been explained satisfactorily with the help of the theory of ionisation. If HA and BOH represent any strong acid and any strong base respectively and equivalent amounts of these in dilute solution be mixed, we have

$$H^+(aq) + \overset{-}{A}(aq) + \overset{+}{B}(aq) + OH^-(aq) \longrightarrow \overset{-}{A}(aq) + \overset{+}{B}(aq) + H_2O(l) \qquad \Delta H = -13.7 \text{ kcal}$$

Disregarding the ions which are present on both sides of the equation, we get

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H = -13.7 \text{ kcal}$$

Thus the heat of neutralisation of an acid and a base is merely the heat of formation of water from hydrogen and hydroxyl ions.

When weak acids or weak bases are neutralised by strong bases or strong acids respectively, the heat of neutralisation differs widely from – 13.7 kcal. This is shown by the following examples :

$$\begin{aligned}
HCl(aq) + NH_4OH(aq) &\longrightarrow NH_4Cl(aq) + H_2O(l) && \Delta H = -12.3 \text{ kcal}\\
HCN(aq) + NaOH(aq) &\longrightarrow NaCN(aq) + H_2O(l) && \Delta H = -12.3 \text{ kcal}\\
HNO_3(aq) + NH_4OH(aq) &\longrightarrow NH_4NO_3(aq) + H_2O(l) && \Delta H = -12.3 \text{ kcal}\\
HCOOH(aq) + NH_4OH(aq) &\longrightarrow HCOONH_4(aq) + H_2O(l) && \Delta H = -11.9 \text{ kcal}
\end{aligned}$$

In such cases the neutralisation process involves not only the union of hydrogen and hydroxyl ions but also the dissociation of the weak acid or base. The measured heat of neutralisation is, therefore, equal to the heat given out in the union of $H^+ (aq)$ and $OH^- (aq)$ ions plus the heat accompanying the dissociation of weak acid or weak base. The neutralisation of NH_4OH with HCl, for example, can be represented as :

$$\begin{aligned}
NH_4OH(aq) &\longrightarrow NH_4^+(aq) + OH^-(aq) && \Delta H = Q \text{ kcal}\\
\text{and} \quad H^+(aq) + OH^-(aq) + Cl^-(aq) &\longrightarrow H_2O(l) + Cl^-(aq) && \Delta H = -13.7 \text{ kcal}
\end{aligned}$$

$$NH_4OH(aq) + H^+(aq) + Cl^-(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq) + H_2O(l) \quad \Delta H = Q - 13.7 \text{ kcal}$$

But the measured heat of neutralisation is – 12.3 kcals. Therefore,

$$\begin{aligned}
Q - 13.7 &= -12.3\\
Q = 13.7 - 12.3 &= 1.4 \text{ kcal}
\end{aligned}$$

Hence the heat of dissociation of NH_4OH is 1.4 kcal *i.e.*, 1.4 kcal of heat is absorbed when one mole of ammonium hydroxide is dissociated into ions. In general, **the heat of dissociation of a weak acid or weak base may be defined as the change in enthalpy of the system when one mole of it is dissociated into ions.**

ENERGY CHANGES DURING TRANSITIONS OR PHASE CHANGES

The three states of matter – solid, liquid and gas differ from one another in the arrangement of their constituent particles. The magnitudes of intermolecular forces acting between the particles in these states are also different. It is a common observation that when a solid is converted into the liquid state, energy is to be supplied. This energy is spent in breaking the intermolecular forces in the solid which are of high magnitude. Whenever there is a change in the state of matter (solid → liquid or liquid → gas), the process is called phase change or transition. It is also accompanied by the change in enthalpy or heat content of the system.

HEAT OF FUSION

It is defined as : **the heat change (or enthalpy change) when one mole of a solid substance is converted into the liquid state at its melting point.**

As an example, we can take the melting of one mole of ice at its melting point, 0ºC or 273 K. The process can be represented as

$$\underset{\text{ice}}{H_2O(s)} \longrightarrow \underset{\text{water}}{H_2O(l)} \qquad \Delta H = +1.43 \text{ kcal}$$

and is accompanied by the absorption of 1.43 kcal of heat. From the values of fusion of various substances we can compare their magnitudes of intermolecular forces. **Greater the heat of fusion of a substance higher the magnitude of intermolecular forces.**

HEAT OF VAPOURISATION

The heat of vapourisation is defined as : **the heat change (or enthalpy change) when one mole of liquid is converted into vapour or gaseous state at its boiling point.**

For example, when one mole of water is converted into steam at 100ºC or 373 K, the heat absorbed is 9.71 kcal which is the heat of vaporisation of water. The change can be represented as :

$$\underset{\text{water}}{H_2O(l)} \longrightarrow \underset{\text{steam}}{H_2O(g)} \qquad \Delta H = +9.71 \text{ kcal}$$

The heats of vaporisation of ethyl alcohol (C_2H_5OH) and benzene (C_6H_6) are 7.29 kcal mol^{-1} and 7.36 kcal mol^{-1} respectively. The values of heats of vaporisation can also be used for the comparison of the magnitude of intermolecular forces of attraction in liquids.

HEAT OF SUBLIMATION

Sublimation is a process when a solid changes directly into gaseous state without changing into liquid state. It occurs at a temperature below the melting point of the solid. Heat of sublimation is defined as : **the heat change (or enthalpy change) when one mole of a solid is directly converted into the gaseous state at a temperature below its melting point.**

For example, the heat of sublimation of iodine is 14.92 kcal mol^{-1}. It can be represented as

$$I_2(s) \longrightarrow I_2(g) \qquad \Delta H = +14.92 \text{ kcal}$$

HEAT OF TRANSITION

The heat of transition is defined as : **the change in enthalpy which occurs when one mole of an element changes from one allotropic form to another.**

For example, the transition of diamond into amorphous carbon may be represented as

$$C_{\text{diamond}} \longrightarrow C_{\text{amorphous}} \qquad \Delta H = +3.3 \text{ kcal}$$

Similarly,

$$S_{\text{monoclinic}} \longrightarrow S_{\text{rhombic}} \qquad \Delta H = -0.016 \text{ kcal}$$

and $$P_{\text{white}} \longrightarrow P_{\text{red}} \qquad \Delta H = -1.028 \text{ kcal}$$

where – 0.016 kcal and – 1.028 kcal are heats of transition of monoclinic sulphur to rhombic sulphur and white phosphorus to red phosphorus respectively.

HESS'S LAW OF CONSTANT HEAT SUMMATION

We have already seen that heat changes in chemical reactions are equal to the difference in internal energy (ΔE) or heat content (ΔH) of the products and reactants, depending upon whether the reaction is studied at constant volume or constant pressure. Since ΔE and ΔH are functions of the state of the system, the heat evolved or absorbed in a given reaction must be independent of the manner in which the reaction is brought about. Thus it depends only on the initial state and final states of the system and not the manner or the steps in which the change takes place. This generalisation is known as **Hess's Law** and may be stated as : **If a chemical change can be made to take place in two or more different ways whether in one step or two or more steps, the amount of total heat change is same no matter by which method the change is brought about.**

The law also follows as a mere consequence of the first law of thermodynamics. Let us suppose that a substance A can be changed to Z directly.

$$\mathrm{A} \longrightarrow \mathrm{Z} + Q_1 \qquad \Delta H_1 = -Q_1$$

where Q_1 is the heat evolved in the direct change. When the same change is brought about in stages :

$$\begin{aligned} \mathrm{A} &\longrightarrow \mathrm{B} + q_1 & \Delta H_2 &= -q_1 \\ \mathrm{B} &\longrightarrow \mathrm{C} + q_2 & \Delta H_2 &= -q_2 \\ \mathrm{C} &\longrightarrow \mathrm{Z} + q_3 & \Delta H_2 &= -q_3 \end{aligned}$$

the total evolution of heat = $q_1 + q_2 + q_3 = Q_2$

According to Hess's law $Q_1 = Q_2$. If it be not so, let $Q_2 > Q_1$. Then by transforming A to Z through stages and retransforming directly back to A, there would be gain of heat energy = $Q_2 - Q_1$. By repeating the process again and again an unlimited heat energy will be developed in an isolated system. This goes against the first law of thermodynamics. Hence Q_1 must be equal to Q_2.

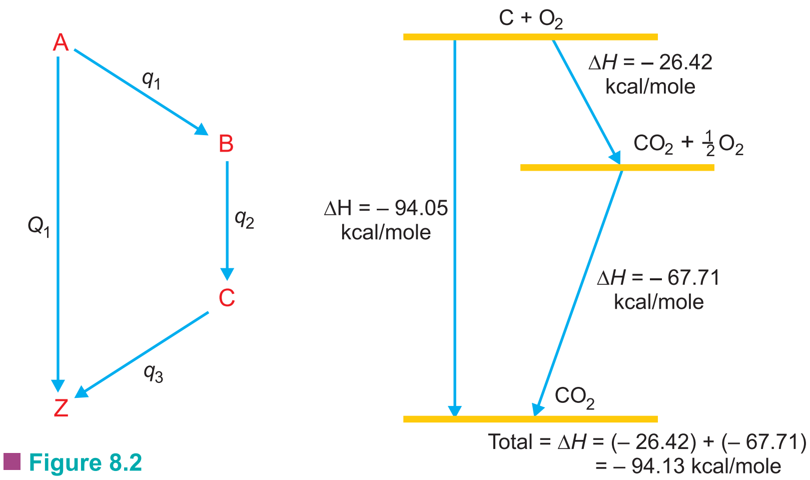


Figure 8.2
Illustration of Hess's Law.

Hess's law has been tested experimentally and shown to be true.

Illustrations of Hess's Law

(1) **Burning of carbon to CO_2.** Carbon can be burnt to carbon dioxide directly or it may first be changed to carbon monoxide which may then be oxidised to carbon dioxide.

1st way :

$$\mathrm{C}(s) + \mathrm{O}_2(g) \longrightarrow \mathrm{CO}_2(g) \qquad \Delta H = -94.05 \text{ kcal}$$

2nd way :

$$\begin{aligned} \mathrm{C}(s) + \tfrac{1}{2}\mathrm{O}(g) &\longrightarrow \mathrm{CO}_2(g) & \Delta H &= -26.42 \text{ kcal} \\ \mathrm{CO}(g) + \tfrac{1}{2}\mathrm{O}_2(g) &\longrightarrow \mathrm{CO}(g) & \Delta H &= -67.71 \text{ kcal} \end{aligned}$$

$$\textit{overall change} \quad \mathrm{C}(s) + \mathrm{O}_2(g) \longrightarrow \mathrm{CO}_2(g) \qquad \Delta H = -94.13 \text{ kcal}$$

It is evident from above that the total heat energy evolved is the same in the two cases (Fig. 8.2)

(2) **Formation of Sodium hydroxide from Na.** The formation of sodium hydroxide from metallic sodium presents another example of Hess's law. The process can be carried out in two ways.

1st way :

$$\begin{array}{rcll} 2Na(s) + \tfrac{1}{2}O_2(g) & \longrightarrow & Na_2O(s) & \Delta H = -100 \text{ kcal} \\ Na_2O(s) + H_2O(l) & \longrightarrow & 2NaOH(aq) & \Delta H = -56 \text{ kcal} \\ \hline 2Na(s) + H_2O(l) + \tfrac{1}{2}O_2(g) & \longrightarrow & 2NaOH(aq) & \Delta H = -156 \text{ kcal} \end{array}$$

2nd way :

$$\begin{array}{rcll} 2Na(s) + 2H_2O(l) & \longrightarrow & 2NaOH(aq) + H_2(g) & \Delta H = -88 \text{ kcal} \\ H_2(g) + \tfrac{1}{2}O_2(g) & \longrightarrow & H_2O(g) & \Delta H = -68.5 \text{ kcal} \\ \hline 2Na(s) + H_2O(l) + \tfrac{1}{2}O_2(g) & \longrightarrow & 2NaOH(aq) & \Delta H = -156.5 \text{ kcal} \end{array}$$

It may be observed that the total heat evolved in carrying the reaction in two different ways is the same. The difference of 0.5 kcal is within the experimental error.

It is obvious from the above examples that by the addition of a series of chemical equations we can obtain not only the resultant products of this series of reactions but also the net heat effect. It is, therefore, clear that : **thermochemical equations may be multiplied, added or subtracted like ordinary algebraic equations.** For this reason, Hess's law has been of great service in the indirect determination of heats of formation.

APPLICATIONS OF HESS'S LAW

(1) **Determination of heat of formation of substances which otherwise cannot be measured experimentally.** The substances like methane, carbon monoxide, benzene, etc., cannot be prepared by uniting their elements. Therefore it is not possible to measure the heats of formation of such compounds directly. These can be determined indirectly by using Hess's law. This will be illustrated by the following examples.

SOLVED PROBLEM 1. Calculate the heat of formation of potassium hydroxide from the following data.

$$\begin{array}{lrcll} (i) & K(s) + H_2O\,(aq) & \longrightarrow & KOH + \tfrac{1}{2}H_2 & \Delta H = -48.0 \text{ kcal} \\ (ii) & H_2(g) + \tfrac{1}{2}O_2(g) & \longrightarrow & H_2O(l) & \Delta H = -68.5 \text{ kcal} \\ (iii) & KOH(s) & \longrightarrow & KOH(aq) & \Delta H = -14.0 \text{ kcal} \end{array}$$

SOLUTION

We should aim at finding the value of ΔH for the equation, which is the heat of formation.

$$K(s) + \tfrac{1}{2}O_2(g) + \tfrac{1}{2}H_2(g) \longrightarrow KOH(s) \qquad \Delta H = ?$$

Adding equations (*i*) and (*ii*) and subtracting equation (*iii*) will give

$$K(s) + H_2O(l) + H_2(g) + \tfrac{1}{2}O_2(g) - KOH(s) \longrightarrow KOH(aq) + \tfrac{1}{2}H_2(g) + H_2O(l) - KOH(aq)$$

$$\begin{aligned} \Delta H &= -48.0 + (-68.5) - (-14.0) \\ &= -102.5 \text{ kcal} \end{aligned}$$

or $$K(s) + \tfrac{1}{2}H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow KOH(s) \qquad \Delta H = -102.5 \text{ kcal}$$

Thus heat of formation of KOH is – **102.5 kcal**

SOLVED PROBLEM 2. The heat of combustion of ethyl alcohol is – 330 kcal. If the heat of formation of $CO_2(g)$ and $H_2O(l)$ be – 94.3 kcal and – 68.5 kcal respectively, calculate the heat of formation of ethyl alcohol.

SOLUTION

We are given

$$(a) \quad C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H = -330.0 \text{ kcal}$$

$$(b) \quad C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -94.3 \text{ kcal}$$

$$(c) \quad H_2(g) + \tfrac{1}{2} O_2(g) \longrightarrow H_2O(l) \quad \Delta H = -68.5 \text{ kcal}$$

We have to manipulate these equations so as to get the required equation :

$$2C(s) + 3H_2(g) + \tfrac{1}{2} O_2(g) \longrightarrow C_2H_5OH(l) \quad \Delta H = ?$$

where ΔH is the heat of formation of ethyl alcohol.

Multiplying equation (*b*) by 2 and equation (*c*) by 3 and adding up these, we get

$$2C(s) + 3H_2(g) + \tfrac{3}{2} O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

$$\Delta H = -394.1 \text{ kcal}$$

Subtracting equation (*c*) from the above equation, we have

$$2C(s) + 3H_2(g) + \tfrac{1}{2} O_2(g) \longrightarrow C_2H_5OH(l)$$

$$\Delta H = -394.1 - (-330.0)$$

Thus the heat of formation of ethyl alcohol is **– 64.1 kcal.**

SOLVED PROBLEM 3. Determine ΔH of the reaction

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

from the following data :

$$(i) \quad C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393.7 \text{ kJ}$$

$$(ii) \quad H_2(g) + \tfrac{1}{2} O_2(g) \longrightarrow H_2O(l) \quad \Delta H = -285.7 \text{ kJ}$$

$$(iii) \quad CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = -890.3 \text{ kJ}$$

SOLUTION

Multiplying equation (*ii*) by 2 and adding to equation (*i*), we get

$$(iv) \quad C(s) + O_2(g) + 2H_2(g) + O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta H = (2 \times -285.7) + (-393.7)$$

$$= -965.1 \text{ kJ}$$

On subtracting equation (*iii*) from equation (*iv*), we get

$$C(s) + 2H_2(g) = CH_4(g) \quad \Delta H = -965.1 - (-890.3)$$

$$\Delta H = -74.8 \text{ kJ}$$

Thus the heat of formation of methane is – **74.8 kJ.**

(2) **Determination of Heat of Transition**

The heat of transition of one allotropic form to another can also be calculated with the help of Hess's law. For example, the enthalpy of transition from monoclinic sulphur to rhombic sulphur can be calculated from their heats of combustion which are :

$$(i) \quad S_{\text{rhombic}} + O_2(g) \longrightarrow SO_2(g) \quad \Delta H = -291.4 \text{ kJ}$$

$$(ii) \quad S_{\text{monoclinic}} + O_2(g) \longrightarrow SO_2(g) \quad \Delta H = -295.4 \text{ kJ}$$

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

$$S_{\text{rhombic}} - S_{\text{monoclinic}} + O_2(g) - O_2(g) \longrightarrow SO_2(g) - SO_2(g)$$

or

$$\Delta H = -291.4 - (-295.4)$$

$$S_{\text{rhombic}} = S_{\text{monoclinic}} \qquad \Delta H = 4.0 \text{ kJ}$$

Thus heat of transition of rhombic sulphur to monoclinic sulphur is **4.0 kJ.**

(3) **Determination of heats of various reactions**

By using Hess's law we can calculate the heats or enthalpies of many reactions which otherwise cannot be measured directly. For example, from the following equations the enthalpy of dimerisation of NO_2 can be calculated.

(*i*) $N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H = 67.9 \text{ kJ}$

(*ii*) $N_2(g) + 2O_2(g) \longrightarrow N_2O_4(g) \qquad \Delta H = 9.3 \text{ kJ}$

Subtracting equation (*i*) from equation (*ii*) we have

$$2NO_2(g) \longrightarrow N_2O_4(g) \qquad \Delta H = (9.3 - 67.9) \text{ kJ}$$

$$= -58.6 \text{ kJ}$$

Thus the heat of dimerisation of NO_2 is – **58.6 kJ.**

BOND ENERGY

When a bond between two atoms is formed, there is a release of energy. The same amount of energy is absorbed when the bond is broken.

The bond energy is defined as the average amount of energy required to break all bonds of a particular type in one mole of the substance.

Thus the bond energy of H – H bond is the energy required to break all the bonds in one mole of the gas. It is expressed in kcal mol^{-1} or kJ mol^{-1}. For example, the bond energy of H – H bond is 433 kJ mol^{-1} or 103.58 kcal mol^{-1}. The bond energies of some common bonds are listed below :

Bond	Bond Energy
Cl–Cl	243 kJ mol^{-1}
O=O	499.0 kJ mol^{-1}
C–H	414.0 kJ mol^{-1}
O–H	460.0 kJ mol^{-1}

Bond Energy is a Measure of Strength of the Bond

In other words, bond energy is the force with which the atoms are bonded together. It depends upon :

(*i*) Size of the atom

(*ii*) Electronegativity

(*iii*) Bond length

A knowledge of bond enthalpy is useful for calculating heats of reaction for gaseous reactions for which no thermal data is available and which involve substances having covalent bonds.

Suppose we desire to determine the bond energy of C–H bond in methane. For this purpose we need to know the enthalpy change for the reaction

$$C(g) + 4H(g) \longrightarrow CH_4(g)$$

This is obtained by combining the heat of formation of methane from $C(s) + H_2(g)$ with the heat of sublimation of carbon *i.e.*, $C(s) \rightarrow C(g)$ and the heat of dissociation of hydrogen into atoms *i.e.*, $H_2(g)$

$\rightarrow 2H(g)$, which have been determined by spectroscopic methods. The value so obtained is 398 kcal mol^{-1} (or 1663.64 kJ mol^{-1}). This represents the bond energy of four C–H bonds. Since all the bonds in methane are identical, the bond energy of C–H bond is 398/4 = 99.5 kcal mol^{-1}.

In a similar manner the bond energies of other types of bonds have been calculated. **When a bond is broken, the bond energy is positive because heat is absorbed.** It is written with a minus sign when a bond is formed and heat is evolved. The calculation of heat of reaction with the help of bond energies is illustrated in the following examples.

SOLVED PROBLEM 1. Given that energies for H–H, O=O and O–H bonds are 104, 118 and 111 kcal mol^{-1} respectively, calculate the heat of the reaction

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

SOLUTION

In this reaction, two O–H bonds are formed and one H–H bond is broken. Therefore we can write for ΔH

$$\begin{aligned}\Delta H &= -2\,\Delta H\,(O-H) + \Delta H\,(H-H) + \tfrac{1}{2}\,\Delta H\,(O=O)\\ &= (-2\times 111) + 104 + \left(\tfrac{1}{2}\times 118\right)\\ &= -222 + 104 + 59\\ &= -59 \text{ kcal mol}^{-1}\end{aligned}$$

$\therefore$ The heat of the given reaction is – **59.0 kcal mol^{-1}**

SOLVED PROBLEM 2. Calculate the bond energy of HCl, given that H–H bond energy is 433 kJ mol^{-1}, Cl – Cl bond energy is 242 kJ mol^{-1} and ΔH_f for HCl is – 91 kJ mol^{-1}.

SOLUTION

Given :

(*i*) $\tfrac{1}{2}H_2(g) + Cl_2(g) \longrightarrow HCl(g) \qquad \Delta H = -91 \text{ kJ}$

(*ii*) $H_2(g) \longrightarrow 2H(g) \qquad \Delta H = +433 \text{ kJ}$

(*iii*) $Cl_2(g) \longrightarrow 2Cl(g) \qquad \Delta H = +242 \text{ kJ}$

Multiplying equation (*i*) by 2, we get

(*iv*) $H_2(g) + 2Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H = -182 \text{ kJ}$

Adding equation (*ii*) and (*iii*), we have

(*v*) $H_2(g) + Cl_2(g) \longrightarrow 2H(g) + 2Cl(g) \qquad \Delta H = +675 \text{ kJ}$

Subtracting equation (*iv*) from (*v*), one has

$$2HCl(g) \longrightarrow 2H(g) + 2Cl(g) \qquad \Delta H = +857 \text{ kJ}$$

Dividing this equation by 2 we get

$$HCl(g) \longrightarrow H(g) + Cl(g) \qquad \Delta H = 428.5 \text{ kJ}$$

Thus the bond energy of H–Cl is 428.5 kJ.

MEASUREMENT OF THE HEAT OF REACTION

The experimental measurement of the heat of reaction or enthalpy change is known as **calorimetry.** The name evidently finds its origin in the unit of heat–the calorie. The heat given out or absorbed in a chemical reaction is measured in a suitable apparatus called a **calorimeter.** These calorimeters vary considerably in their construction and designs. They are adapted to suit the requirements of a particular reaction under study. For instance, to measure the heats of reactions involving (*i*) solutions only, (*ii*) gases, (*iii*) very reactive chemicals etc., different types of calorimeters are employed. We discuss below two of the common type of calorimeters.

Water Calorimeter

This is a convenient apparatus for finding the heat changes accompanying chemical reactions taking place in solutions.

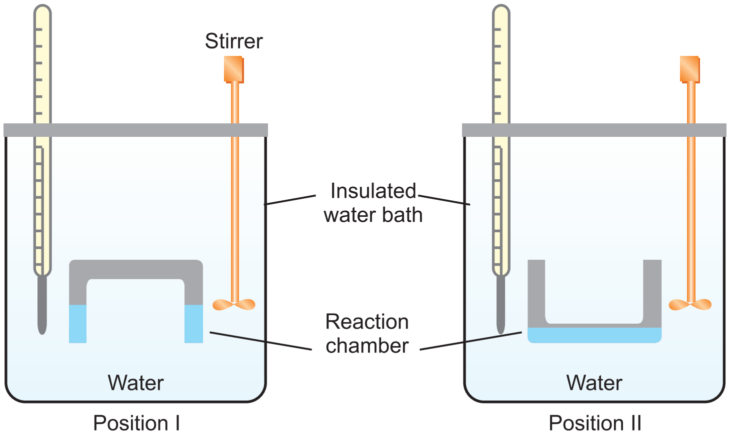


Figure 8.3
Water Calorimeter.

The apparatus consists essentially of a water-bath with thermally insulated walls. A reaction chamber consisting of two limbs is suspended in the water-bath. Through the lid of the water-bath pass (*a*) *thermometer* that records the temperature variations and (*b*) a *stirrer* that stirs water in the water-bath. A known quantity of water (say *W* gms) is taken in the water-bath and its temperature is noted. The reacting substances are filled in the two limbs as shown in Fig. 8.3. The reacting chamber is now turned upside down (position II) to allow the solutions to mix. They react and the heat produced during the reaction is taken up by water, raising its temperature. If the rise in temperature (Final reading – Initial reading) is t ºC, the heat absorbed by water 'Q' is given by

$$Q = W \times 1 \times t \text{ calories}$$

But heat produced in the reaction is equal to that absorbed by water, hence heat of the reaction can be calculated.

Bomb Calorimeter

This apparatus was devised by Berthelot (1881) to measure the heat of combustion of organic compounds. A modified form of the apparatus shown in Fig. 8.4 consists of a sealed combustion chamber, called a *bomb*, containing a weighed quantity of the substance in a dish along with oxygen under about 20 atm pressure. The *bomb* is lowered in water contained in an insulated copper vessel. This vessel is provided with a stirrer and a thermometer reading up to 1/100th of a degree. It is also surrounded by an outer jacket to ensure complete insulation from the atmosphere. The temperature of water is noted before the substance is ignited by an electric current. After combustion, the rise in temperature of the system is noted on the thermometer and heat of combustion can be calculated from the heat gained by water and the calorimeter.

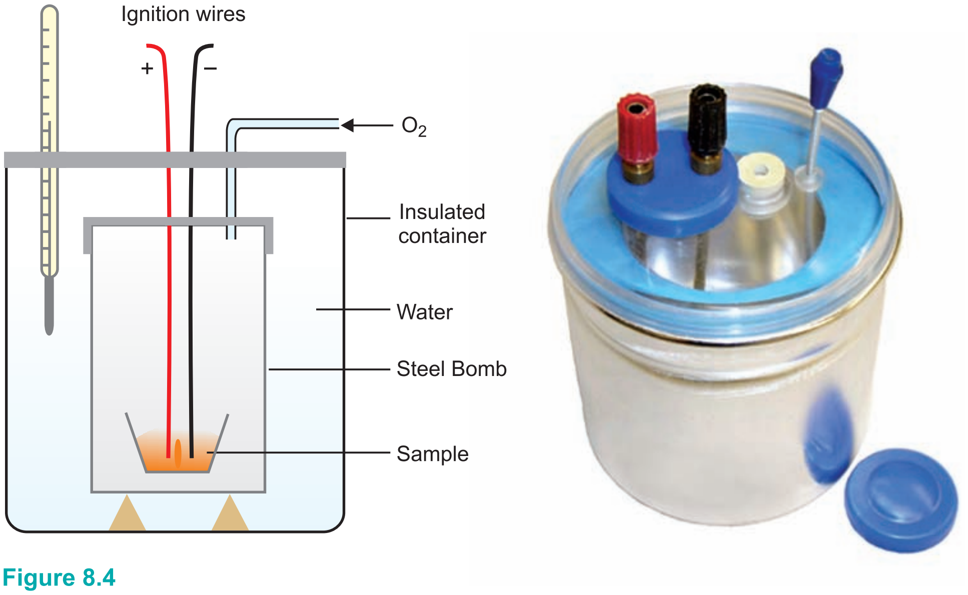


Figure 8.4
Bomb Calorimeter.

EXAMINATION QUESTIONS

1. Define or explain the following terms :
   - (*a*) Thermochemistry
   - (*b*) Internal energy
   - (*c*) Enthalpy of a reaction
   - (*d*) Thermochemical equations
   - (*e*) Heat of reaction
   - (*f*) Standard heat of reaction
   - (*g*) Heat of formation
   - (*h*) Standard heat of formation
   - (*i*) Heat of combustion
   - (*j*) Heat of solution
   - (*k*) Heat of neutralisation
   - (*l*) Heat of vaporisation
   - (*m*) Heat of sublimation
   - (*n*) Heat of transition
   - (*o*) Hess's law
   - (*p*) Bond energy
2. (*a*) Explain the terms : heat of reaction at constant pressure and heat of reaction at constant volume. How are they related?

   (*b*) If the heat of formation of methane at constant pressure is –17.9 kcal per mole at 25°C, what is its value at constant volume?

   Answer. (*b*) –17.308 kcal
3. Given the heats of combustion of ethylene, hydrogen and ethane as 337.2, 68.3 and 372.8 kcal respectively, calculate the heat of reaction at 78°C for

   $$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

   Answer. –32.7 kcal
4. ΔH values for the combustion reaction of ethyl alcohol, carbon and hydrogen are –330, –94.3 and –68.5 kcal respectively. Calculate the heat of formation of ethyl alcohol.

   Answer. – 64.1 kcal

5. (*a*) State Hess' Law of constant heat summation and explain some of its important applications.

(*b*) Calculate the heat of formation of benzene at 25°C, if the heats of combustion of benzene, carbon and hydrogen are – 780.98, – 94.05 and – 68.32 kcal respectively at 25°C.

Answer. 11.72 kcal

6. Graphite and diamond are two forms of carbon. The enthalpy of combustion of graphite at 25°C is –393.51 kJ mol^{-1} and that of diamond is –395.41 kJ mol^{-1}. What is the enthalpy change in the process Graphite $\longrightarrow$ Diamond at the same temperature?

Answer. 1.90 kJ mol^{-1}

7. (*a*) State and explain heat of formation, heat of combustion with examples.

(*b*) The standard heats of formation of CO(g) and H_2O(g) at 25°C are 100.5 kJ and –241.8 kJ per mole respectively. Calculate the heat change of the following reaction at this temperature.

$$H_2O(g) + C(s) \longrightarrow H_2(g) + CO(g)$$

Answer. (*b*) 342.3 kJ

8. The heat of combustion of liquid benzene is –326.7 kJ. The heat of formation of CO_2 and H_2O are –393.5 kJ and –286.2 kJ respectively. Calculate the heat of formation of liquid benzene.

Answer. –2826.1 kJ

9. Explain the term enthalpy of ionisation. The enthalpy of neutralisation of HCl with NaOH is –57.3 kJ mol^{-1} and that of neutralisation of CH_3COOH with NaOH is –55.2 kJ mol^{-1}. Calculate the enthalpy of ionisation of CH_3COOH.

Answer. +2.1 kJ

10. Calculate the standard enthalpy of formation of naphthalene ($C_{10}H_8$) when the standard enthalpy of combustion of naphthalene is –5153 kJ and the standard enthalpies of formation of CO_2 and H_2O are –393.5 kJ mol^{-1} and –285.8 kJ mol^{-1} respectively.

Answer. +74.8 kJ

11. (*a*) Discuss the variation of heat of reaction with temperature.

(*b*) Calculate the heat of formation of carbon disulphide. The heat of combustion of CS_2, Sulphur and Carbon are –26.5 kcal, –94.3 kcal and –71.08 kcal respectively at 25°C.

Answer. (*b*) –233.18 kcal

12. (*a*) Derive Kirchoff's equation.

(*b*) Bond energies of F_2 and Cl_2 are 36.6 and 580 kcal/mole respectively. Heat liberated in the reaction

$$F_2 + Cl_2 \longrightarrow 2FCl$$

is 26.6 kcal. Find the bond energy of F—Cl bond.

Answer. (*b*) 295 kcal

13. (*a*) Define the heat of reaction. Derive the relationship between heat of reaction at constant volume and at constant pressure.

(*b*) The heat of combustion of glucose at 17°C and at constant pressure is –651000 calories. Calculate heat of combustion at constant volume at 17°C.

Answer. (*b*) – 651000 cals

14. 2.0 g of C_6H_6 was burnt in excess of O_2 in a bomb calorimeter :

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

If the temperature rise is 40°C and the heat capacity of the system is 2.0 kJ K^{-1}, calculate the enthalpy of combustion of C_6H_6 at constant volume and constant pressure.

Answer. – 2.4414 kJ mol^{-1}; –24410.283 kJ mol^{-1} (*Guru Nanak Dev BSc, 2002*)

15. The enthalpies of combustion of benzene, Carbon and hydrogen are –3267.7 kJ, –393.5 kJ and –286.2 kJ respectively. Calculate the enthalpy of formation of benzene.

Answer. – 48.1 kJ (*Nagpur BSc, 2002*)

16. Calculate heat of fusion of benzene at its freezing point, 278 K, if the rate of change of melting point with pressure is 0.0129 K atm^{-1} and ΔV is 0.059 cm^{-3} g^{-1}. (Mol. wt. of benzene is 78)

Answer. 99.174 kJ mol^{-1} (*Aligarh BSc, 2002*)

17. Define enthalpy of Neutralisation. When 100 ml of 1N HCl is neutralised by equivalent amount of NaOH, 5.273 kJ of heat is evolved. Calculate the heat of neutralisation of HCl.

Answer. 52.73 kJ (*Nagpur BSc, 2002*)

18. Determine ΔH of the reaction :

$$C(s) + 2H_2(g) \rightarrow CH_4(g)$$

from the following data :

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

(*ii*) $H_2(g) + ½O_2(g) \rightarrow H_2O(\ell)$ $\Delta H = -285.7$ kJ

(*iii*) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O$ $\Delta H = -890$ kJ

Answer. –74.9 kJ (*Guru Nanak Dev BSc, 2002*)

19. (*a*) State Hess's law of constant heat summation and describe its applications.

(*b*) Calculate ΔH for the reaction :

$$C_{(graphite)} + 2H_2(g) \rightarrow CH_4(g)$$

from the following data.

(*i*) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H = -890.35$ kJ

(*ii*) $H_2(g) + ½O_2(g) \rightarrow H_2O(\ell)$ $\Delta H = -286.2$ kJ

(*iii*) $C_{(graphite)} + O_2(g) \rightarrow CO(g)$ $\Delta H = -393.51$ kJ

Answer. –75.56 kJ (*Allahabad BSc, 2002*)

20. (*a*) Show that

$$\Delta H = \Delta V + \Delta nRT$$

(*b*) If the heat of formation of methane at constant pressure is –17.9 kcal per mole at 25°C, what is its value at constant volume?

Answer. (*b*) -173.078 kcal mol^{-1} (*Guru Nanak Dev BSc, 2002*)

21. Define bond energy. Calculate ΔH for the reaction :

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$$

from the following values of bond energies :

Bond	C–H	O=O	C=O	O–H	C=C
Bond Energy (kJ)	414	499	724	460	619

Answer. – 960 kJ (*Nagpur BSc, 2002*)

22. Calculate the standard enthalpy of formation of *n*-butane, given that the standard enthalpies of combustion of *n*-butane, $c_{(graphite)}$ and $H_2(g)$ are –2878.5 kJ mol^{-1}, –393.5 kJ mol^{-1} and –285.8 kJ mol^{-1} respectively.

Answer. –124.5 kJ mol^{-1} (*Delhi BSc, 2003*)

23. The enthalpy of formation of methane at constant volume at 25°C is –72.3 kJ. What will be the heat of formation at constant pressure? ($R = 8.314$ J K^{-1} mol^{-1})

Answer. –74.777 kJ mol^{-1} (*Arunachal BSc, 2003*)

24. $\Delta G°$ for the formation of CO, H_2O, CO_2 and H_2 gases are –32.81, –54.64, –94.26 and zero kcal mol^{-1} respectively. Calculate $\Delta G°$ and K_p for the forward reaction in the following equilibrium :

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

Answer. 28.49 kJ mol^{-1} (*Delhi BSc, 2003*)

25. The heat of combustion of carbon, hydrogen and sucrose are –393.5, –286.2 and –5644.2 kJ mol^{-1} respectively. Calculate the heat of formation of sucrose.

Answer. 1566.0 kJ mol^{-1} (*Jamia Millia BSc, 2003*)

26. Calculate enthalpy of formation of ethane from the following data :

(*i*) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.4$ kJ

(*ii*) $H_2(g) + ½O_2(g) \rightarrow H_2O(\ell)$ $\Delta H = -284.61$ kJ (*iii*) $C_2H_6(g) + 7/2\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$ $\Delta H = -1561.0$ kJ

Answer. –79.63 kJ (*Sambalpur BSc, 2003*)

27. Define bond energy. Explain how it can be used to calculate the heat of a reaction. Calculate the heat of reaction between propene and chlorine to give 1, 2-dichloropropane from the values of bond energies :

$$E_{C-C} = 347.3 \text{ kJ mol}^{-1}$$
$$E_{C=C} = 615 \text{ kJ mol}^{-1}$$
$$E_{C-H} = 413 \text{ kJ mol}^{-1}$$
$$E_{C-Cl} = 330.5 \text{ kJ mol}^{-1}$$
$$E_{Cl-Cl} = 242.7 \text{ kJ mol}^{-1}$$

Answer. –150.6 kJ mol^{-1} (*Nagpur BSc, 2003*)

28. (*a*) Derive Kirchoff's equation when C_P values are

(*i*) independent on temperature; and

(*ii*) dependent on temperature

(*b*) Calculate the enthalpy of vapourisation of SO_2 at –25°C if the same at its boiling point (i.e. –10°C) be 5950 cal mol^{-1}. Given for SO_2, molar heat capacities in liquid and vapour phase are 206 cal K^{-1} mol^{-1} and 9.3 cal K^{-1} mol^{-1} respectively.

Answer. (*b*) 6119.5 cal mol^{-1} (*Delhi BSc, 2003*)

29. The standard enthalpy of formation (ΔH_f°) of $NH_3(g)$ as indicated by the chemical equation is – 46.19 kJ.

$$1/2\ N_2(g) + 3/2\ H_2(g) \rightarrow NH_3(g)$$

Standard entropies of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are 191.62, 130.60 and 192.46 JK^{-1} mol^{-1} respectively. Calculate the standard free energy of formation of $NH_3(g)$.

Answer. –16.613 kJ mol^{-1} (*Kalyani BSc, 2003*)

30. The heat of combustion of benzoic acid at constant pressure is –771400 calories at 25°C. Calculate the heat of combustion at constant volume.

Answer. –771103.937 cal (*Madurai BSc, 2004*)

31. Heats of combustion of hydrated copper sulphate and anhydrous copper sulphate are –2.80 and 15.89 kcals respectively. Calculate the heat of hydration of copper sulphate.

Answer. –18.69 kcal (*Delhi BSc, 2004*)

32. (*a*) Derive thermodynamically Kirchoff's equation.

(*b*) Calculate the heat of formation of acetic acid its heat of combustion is –869.0 kJ mol^{-1}. The heats of formation of $CO_2(g)$ and $H_2O(\ell)$ are –390.0 kJ mol^{-1} and –285.0 kJ mol^{-1} respectively.

Answer. (*b*) – 481 kJ mol^{-1} (*Agra BSc, 2004*)

33. (*a*) State and Explain Hess's Law.

(*b*) The heat of formation of methane at 27°C is –19.3 kcal when the measurements are made at constant pressure. What will be the heat of formation at constant volume?

Answer. (*b*) –18.70 kcal (*Guru Nanak Dev BSc, 2005*)

34. The heat of combustion of $C_2H_4(g)$, $C_2H_6(g)$ and $H_2(g)$ are –1409 kJ, –1558.3 kJ and – 285.645 respectively. Calculate the heat of hydrogenation of ethylene.

Answer. 136.8 kJ (*Assam BSc, 2005*)

35. When 2 moles of ethane are completely burnt 3129 kJ of heat is liberated. Calculate the heat of formation, ΔH_f for C_2H_6. ΔH_f for $CO_2(g)$ and $H_2O(l)$ are – 395 and – 286 kJ respectively.

Answer. – 83.5 kJ (*Purvanchal BSc, 2005*)

36. The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. Calculate the enthalpy of formation of HCl.

Answer. – 22.0 kcal (*Madras BSc, 2005*)

37. In an experiment 5.48 g of formic acid, HCOOH, was burnt and the amount of heat evolved was 30.3 kJ. Calculate ΔH per mole of formic acid.

Answer. 42.79 kJ (*Nehu BSc, 2006*)

38. Calculate the heat of formation of ammonia from the heats of combustion of ammonia and hydrogen which are 9.06 and 68.9 kcals respectively.

Answer. – 94.29 kcals (*Madurai BSc, 2006*)

39. Calculate the standard heat of formation of carbon disulphide (*l*). Given that the standard heat of combustion of carbon(*s*), sulphur(*s*) and carbon disulphide(*l*) are –393.3, – 293.72 and – 1108.76 kJ mol^{-1} respectively.

Answer. + 128.02 kJ (*Kerala BSc, 2006*)

40. The standard heat of formation of $CH_4(g)$, $CO_2(g)$ and $H_2O(g)$ are – 76.2, – 394.8 and –241.6 kJ mol^{-1} respectively. Calculate the amount of heat evolved by burning 1 m^3 of methane measured under normal condition.

Answer. 3.58×10^4 kJ (*Delhi BSc, 2006*)

41. The heat of combustion of methane is – 890.65 kJ mol^{-1} and heats of formation of CO_2 and H_2O are – 393.5 and –286.0 kJ mol^{-1} respectively. Calculate the heat of formation of methane.

Answer. –74.85 kJ mol^{-1} (*Lucknow BSc, 2006*)

MULTIPLE CHOICE QUESTIONS

1. The branch of chemistry which deals with the heat changes caused by chemical reactions is called

(*a*) thermodynamics (*b*) thermal chemistry
(*c*) thermochemistry (*d*) none of these

Answer. (*c*)

2. In an exothermic reaction, the internal energy of the products is _______ internal energy of the reactants

(*a*) greater than (*b*) lesser than
(*c*) equal to (*d*) none of these

Answer. (*a*)

3. In an endothermic reaction

(*a*) $E_R > E_P$ (*b*) $E_R < E_P$
(*c*) $E_R = E_P$ (*d*) None of these

Answer. (*a*)

4. The enthalpy of a system is defined by the relation

(*a*) $H = E + P V$ (*b*) $H = E - P V$
(*c*) $E = H + P V$ (*d*) $P V + E - H$

Answer. (*a*)

5. For exothermic reactions, ΔH is _______ while for endothermic reactions it is _______.

(*a*) positive, negative (*b*) positive, positive
(*c*) negative, negative (*d*) negative, positive

Answer. (*d*)

6. In an exothermic reaction the heat energy is _______ while in endothermic reaction it is _______.

(*a*) released, released (*b*) released, absorbed
(*c*) absorbed, released (*d*) absorbed, absorbed

Answer. (*b*)

7. Which one of the following is correct for a reaction aA + bB $\rightarrow$ cC + dD where $\Delta n = (c + d) - (a + b)$

(*a*) $P\Delta V = \Delta H - \Delta E$
(*b*) $\Delta H = \Delta E + \Delta n\,R\,T$
(*c*) $\Delta n\,R\,T = \Delta H - \Delta E$
(*d*) all of these

Answer. (*d*)

8. For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the change in enthalpy is given by

(*a*) $\Delta H = \Delta E - 2\,R\,T$
(*b*) $\Delta H = \Delta E + 2\,R\,T$
(*c*) $\Delta H = \Delta E + 3\,R\,T$
(*d*) $\Delta H = \Delta E + R\,T$

Answer. (*a*)

9. $\Delta H = \Delta E$ is true for the reaction

(*a*) $H_2 + Cl_2 \rightleftharpoons 2HCl$
(*b*) $2NO \rightleftharpoons N_2 + O_2$
(*c*) $2HI \rightleftharpoons H_2 + I_2$
(*d*) all of these

Answer. (*d*)

10. Which of the following relations holds good for the reaction

$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g)$$

(*a*) $\Delta H = \Delta E$
(*b*) $\Delta H = \Delta E + R\,T$
(*c*) $\Delta H = \Delta E + \tfrac{1}{2}\,R\,T$
(*d*) $\Delta\,H = \Delta\,E - \tfrac{1}{2}\,R\,T$

Answer. (*d*)

11. The change in internal energy with temperature at a constant volume is given by the relation

(*a*) $\Delta E = \Delta C_v\,(T_1 - T_2)$
(*b*) $\Delta E = \Delta C_p\,(T_2 - T_1)$
(*c*) $\Delta E = \Delta C_v\,(T_2 - T_1)$
(*d*) $\Delta E = \Delta C_p\,(T_1 - T_2)$

Answer. (*c*)

12. The Kirchoff's equation is

(*a*) $\Delta H_2 - \Delta H_1 = \Delta C_p\,(T_2 - T_1)$
(*b*) $\Delta E_2 - \Delta E_1 = \Delta C_v\,(T_2 - T_1)$
(*c*) both
(*d*) neither (*a*) nor (*b*)

Answer. (*c*)

13. The change in enthalpy that takes place when one mole of the compound is formed form its elements is called

(*a*) heat of formation of compound
(*b*) heat of synthesis
(*c*) heat of combustion
(*d*) standard heat of formation

Answer. (*a*)

14. By convention, the standard heat of formation of all elements is assumed to be

(*a*) zero
(*b*) negative
(*c*) positive
(*d*) infinity

Answer. (*a*)

15. The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen is called

(*a*) heat of reaction
(*b*) heat of formation
(*c*) heat of oxidation
(*d*) heat of combustion

Answer. (*d*)

16. The calorific value is defined as the amount of heat produced in calories when _______ of a substance is completely burnt.

(*a*) one gram
(*b*) one mole
(*c*) 100 grams
(*d*) 1 kg

Answer. (*a*)

17. The fuel efficiency of methane (mol mass = 16) is _______ that of ethane (mol mass = 30).

(*a*) lesser than
(*b*) greater than

(*c*) equal to (*d*) none of these

Answer. (*b*)

18. Which of the following always has a negative value?

(*a*) heat of formation (*b*) heat of reaction

(*c*) heat of combustion (*d*) heat of solution

Answer. (*c*)

19. The change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent at a given temperature is called

(*a*) heat of reaction (*b*) heat of combustion

(*c*) heat of solvation (*d*) heat of solution

Answer. (*d*)

20. The change in enthalpy of the system when one _________ of an acid is neutralised by one _______ of a base or *vice versa* in dilute solution is called heat of neutralisation.

(*a*) g-equivalent, mole (*b*) mole, g-equivalent

(*c*) g-equivalent, g-equivalent (*d*) mole, mole

Answer. (*c*)

21. The heat of neutralisation of a strong acid and a strong base is always

(*a*) zero (*b*) constant

(*c*) positive (*d*) changing

Answer. (*b*)

22. The heat of neutralisation is of a weak acid by a strong base is _______ that of a strong acid by a strong base.

(*a*) lesser than (*b*) greater than

(*c*) equal to (*d*) none of these

Answer. (*a*)

23. The heat change in equations $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$ $\Delta H = -13.7$ kcal represents

(*a*) heat of neutralisation (*b*) heat of formation of water

(*c*) heat of dissociation of water (*d*) heat of solution

Answer. (*a*)

24. The heat change (or enthalpy change) when one mole of a solid substance is converted into the liquid state at its _______ is called heat of fusion.

(*a*) boiling point (*b*) melting point

(*c*) freezing point (*d*) evaporation point

Answer. (*b*)

25. The process depicted by the equation

$$H_2O(s) \rightarrow H_2O(\ell) \quad \Delta H = +\ 1.43 \text{ kcal represents}$$

(*a*) melting (*b*) boiling

(*c*) evaporation (*d*) fusion

Answer. (*d*)

26. Greater the heat of fusion of a substance ______ is the magnitude of intermolecular forces

(*a*) higher (*b*) lower

(*c*) zero (*d*) infinite

Answer. (*a*)

27. The heat change when one mole of a liquid is converted into vapour or gaseous state at its boiling point is called

(*a*) heat of liquefaction (*b*) heat of fusion (*c*) heat of vaporisation (*d*) heat of sublimation

Answer. (*c*)

28. The process of sublimation for a solid occurs

(*a*) at the melting point (*b*) at a temperature below its melting point

(*c*) at a temperature above its melting point (*d*) none of these

Answer. (*b*)

29. The change in enthalpy which occurs when one mole of an element changes from one allotropic form to another is called.

(*a*) heat of allotropy (*b*) heat of transition

(*c*) heat of transformation (*d*) heat of sublimation

Answer. (*b*)

30. The thermochemical equations may be

(*a*) multiplied (*b*) added

(*c*) subtracted (*d*) all of these

Answer. (*d*)

31. In a chemical process, the amount of total heat change is same no matter by which method the change is brought about. This is statement of

(*a*) law of thermochemistry (*b*) Hess's law

(*c*) thermodynamic law (*d*) law of heat of reaction

Answer. (*b*)

32. The average amount of energy required to break all bonds of a particular type in one mole of the substance is called

(*a*) heat of reaction (*b*) bond energy

(*c*) heat of transition (*d*) heat of bond formation

Answer. (*b*)

33. The bond energy depends upon

(*a*) size of the atom (*b*) electronegativity

(*c*) bond length (*d*) all of these

Answer. (*d*)

34. When a bond is broken, the bond energy is positive because heat _______

(*a*) is evolved (*b*) is absorbed

(*c*) remains unchanged (*d*) none of these

Answer. (*b*)

35. For an endothermic reaction

(*a*) ΔH is –ve (*b*) ΔH is +ve

(*c*) ΔE is –ve (*d*) ΔH is zero

Answer. (*b*)

36. The enthalpy change in the reaction

$$2\,CO + O_2 \rightarrow 2CO_2$$

is termed as

(*a*) enthalpy of reaction (*b*) enthalpy of fusion

(*c*) enthalpy of formation (*d*) enthalpy of combustion

Answer. (*a*)

37. For a reaction

$$A_2(g) + B_2(g) \rightarrow 2AB(g) \quad \Delta H = x \text{ kcal}$$

According to this reaction, the heat of formation of AB will be

(*a*) x kcal (*b*) –x kcal

(*c*) x/2 kcal (*d*) –x/2 kcal

Answer. (*c*)

38. For a gaseous reaction

$$X(g) + Y(g) \rightarrow 4Z(g)$$

ΔE at 300 K is 20 kcal. Taking $R = 2$ cal K^{-1} mol^{-1}, ΔH for the above reaction will be

(*a*) 18.8 kcal (*b*) 19.4 kcal

(*c*) 20.0 kcal (*d*) 21.2 kcal

Answer. (*d*)

39. The heat of neutralization of an acid A with a base B is 13.7 kcal. Which of the following is true

(*a*) A is weak and B is also weak (*b*) A is strong and B is weak

(*c*) A is weak nd B is strong (*d*) A is strong and B is also strong

Answer. (*d*)

40. For which of the following reactions, will ΔH be equal to ΔE?

(*a*) $N_2(g) + 3H_2(g) \rightarrow 2NH_3$ (*b*) $2HI(g) \rightarrow H_2(g) + I_2(g)$

(*c*) $2NO_2 \rightarrow N_2O_4(g)$ (*d*) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

Answer. (*b*)

41. The neutralization of an acid with a base is represented by

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell) \quad \Delta H = -13.7 \text{ kcal}$$

The heat of neutralization of one mole of H_2SO_4 with sodium hydroxide will be

(*a*) –13.7 kcal (*b*) –27.4 kcal

(*c*) +27.4 kcal (*d*) –6.85 kcal

Answer. (*b*)

42. Given that heat neutralization of strong acid and strong base is –13.7 kcal. The heat produced when one mole of HCl is mixed with 0.5 mole of NaOH will be

(*a*) 6.85 kcal (*b*) – 6.85 kcal

(*c*) –27.4 kcal (*d*) –13.7 kcal

Answer. (*b*)

43. The apparatus used to measure heat changes during chemical reactions is called

(*a*) polarimeter (*b*) colorimeter

(*c*) calorimeter (*d*) none of these

Answer. (*c*)

44. Hess's law is used to determine

(*a*) heat of formation of substances which are otherwise difficult to measure

(*b*) heat of transition

(*c*) heats of various other reactions like dimerization

(*d*) all of the above

Answer. (*d*)

45. $\Delta H°$ represent the enthalpy change

(*a*) at 0°C and 1 atm pressure (*b*) at 0 K and 1 atm pressure

(*c*) at 25 K and 1 atm pressure (*d*) none of these

Answer. (*c*)

46. The heats of formation of CO(g) and $CO_2(g)$ are –26.4 kcal and –94.0 kcal respectively. The heat of combustion of carbon monoxide according to Hess's law will be

(*a*) +26.4 kcal (*b*) + 94.0 kcal

(*c*) – 67.6 kcal (*d*) –120.4 kcal

Answer. (*c*)

47. The heat of combustion of ethane (C_2H_6) is –337.0 kcal at 25°C. The heat of the reaction when 3 g of ethane is burnt completely is

(*a*) –3.37 kcal (*b*) +3.37 kcal

(*c*) –33.7 kcal (*d*) +33.7 kcal

Answer. (*c*)

48. For the reaction $CaCO_3(s) \quad CaO(s) + CO_2(g)$ which one of the following is true?

(*a*) $\Delta H = \Delta E$ (*b*) $\Delta H > \Delta E$

(*c*) $\Delta H < \Delta E$ (*d*) $\Delta H = ½\, \Delta E$

Answer. (*b*)

49. Consider the reaction

$$CO(g) + ½O_2(g) \qquad CO_2(g)$$

at constant temperature and pressure. Which one of the following is correct?

(*a*) $\Delta H < \Delta E$ (*b*) $\Delta H > \Delta E$

(*c*) $\Delta H = \Delta E$ (*d*) none of these

Answer. (*a*)

50. The energy required to dissociate 6 g of gaseous hydrogen into free gaseous atoms is 3.12 kcal at 25°C. The bond energy of H–H bond will be

(*a*) 3.12 kcal (*b*) 1.56 kcal

(*c*) 1.04 kcal (*d*) 10.04 kcal

Answer. (*c*)

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