11

THERMOCHEMISTRY

After completing this lesson, you will be able to:

- Define the thermodynamics.
- Define the terms system, surrounding, boundary, state function, heat, heat capacity, internal energy, work done and enthalpy of a substance.
- Name and define the units of thermal energy.
- Define bond dissociation energy.
- Classify reaction as exothermic or endothermic.
- Apply Hess's Law to construct simple energy cycles.
- Relate change in internal energy of a system with thermal energy at constant temperature and constant pressure.
- Use the experimental data to calculate the heat of reaction using a calorimeter.
- Specify conditions for the standard heat of reaction.
- Explain reaction pathway diagram in terms of enthalpy changes of the reaction. (Born Haber's Cycle).
- Describe how heat of combustion can be used to estimate the energy available form foods.

Reading

INTRODUCTION

Every process in this universe whether it occurs in living cells, or in test tubes, or in the atmosphere or in water etc. is accompanied by an energy change. Some processes release energy, other require energy. However, in all these cases total amount of energy in the universe remains constant. The branch of thermodynamics that examines the heat involved in chemical reactions is called **thermochemistry**. In this chapter we will discuss the principles that govern energy changes. We will examine the role of energy in chemical reactions. We will also discuss how heat of a chemical reaction is measured in order to focus on the central topic of the chapter i.e., the amount of heat released or absorbed in a reaction. **The study of all types of energy changes associated with physical and chemical changes is known as thermodynamics.**

11.1 ENERGY IN CHEMICAL REACTIONS

When you burn a fuel such as Sui gas, LPG, wood or oil, energy is released, where this energy come from?

The energy in the form of heat is either evolved or absorbed as a result of chemical reaction. This is because, in a chemical reaction old bonds are broken and new bonds are formed. Bond breaking always consumes energy and bond making always releases energy. When the energy released by bond forming is greater than the energy consumed by bond breaking, there is a net release of chemical energy. Whereas energy is absorbed, when the

11.1.3 System and Surroundings

The part of the universe on which we wish to focus our attention is called a system. The remaining part of the universe is called surroundings. The real or imaginary surface separating the system from its surroundings is called the boundary.

A system in chemistry is usually the substance undergoing physical or chemical change.

For example, in the study of reaction between limestone and hydrochloric acid solution in a test tube, limestone and hydrochloric acid solution form a system. The test tube and everything around the test tube is surroundings. Similarly in the study of thermal decomposition of a compound, the sample of the compound would be the system. Whereas the beaker, the source of heat and everything else would be surroundings.

11.1.4 Thermochemical Reactions

When a chemical change takes place, energy is exchanged between system and its surroundings. Energy has many forms such as heat, light, work etc. A chemical reaction which proceeds with the evolution or absorption of heat is called a thermochemical reaction. **A balanced chemical equation which also shows heat change of a chemical reaction is called thermochemical equation. The branch of chemistry which deals with the heat or thermal energy changes in chemical reactions is called thermochemistry.**

Which of the following chemical equations is a thermochemical equation?

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\quad \Delta H^\circ = -393.5kJ$

$2H_2 + O_{2(g)} \longrightarrow 2H_{2(g)}$

There are two types of thermochemical reactions: -

(1) Exothermic Reactions

A chemical reaction that proceeds with the evolution of heat is called an exothermic reaction. In an exothermic reaction the chemical system transfers energy to the surroundings as the reactants are converted to products e.g. burning of fuels is a highly exothermic reaction. The energy released can be used to heat a room, or to drive an engine or to cook food. Examples of exothermic reactions are given below:

(i) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\quad \Delta H^\circ = -393.5kJ$

(ii) $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ $\quad \Delta H^\circ = -571.6kJ$

(iii) $C_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{(g)}$ $\quad \Delta H^\circ = -110.5kJ$

(2) Endothermic Reactions:

A chemical reaction that proceeds with the absorption of heat is called an endothermic reaction. In these reactions heat is transferred from surrounding to the system. Examples of exothermic reactions are given below:

(i) $H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$ $\quad \Delta H^\circ = +53.8kJ$

(ii) $C_{(s)} + H_2O_{(g)} \longrightarrow CO_{(g)} + H_{2(g)}$ $\quad \Delta H^\circ = +131.4kJ$

The student should be guided to differentiate between the different parts of the topic

(iii) $N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$ $\Delta H^\circ = +180.5kJ$

Self Check Exercise 11.1

Classify the following processes as exothermic or endothermic.

(a) Freezing of water (b) Combustion of methane

(c) Sublimation of dry ice (d) $H_2O_{(g)} \longrightarrow H_2O_{(l)}$

(e) decomposition of limestone.

11.1.4 Heat of Reaction

The amount of energy released or absorbed depends on the amount of substances that react. For example, as more fuel burns, more energy is released. Thus when we report an energy change we must also report the amounts of the chemical substances that generate the energy change. For this purpose energy changes are expressed in terms of molar quantities of reactants and products.

Do You Know

Chemical reactions support our lives and assist us at home and at work. For instance cellular respiration is a series of chemical reactions that releases energy from the food we eat to "Power"all the functions and activites inside our body. Combustion reactions help release energy to heat our homes and move our vehicles.

The amount of heat evolved or absorbed in a chemical reaction, when molar quantities of reactants and product are same as shown in a chemical reaction is called heat of reaction.

Heat of reaction measured at 25°C (or 298K) and one atmospheric pressure is known as enthalpy change. It is denoted by ΔH° .(for detail see section 11.5.1)

(i) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H^\circ = -393.5kJ$

This equation shows that 1 mole of solid carbon (12g) reacts with 1 mole of oxygen gas (32g) to give 1 mole of CO_2 gas (44g) at 25°C and 1 atmospheric pressure and 393.5 KJ heat is evolved. What does the following equation show?

(ii) $H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$ $\Delta H^\circ = +53.8kJ$

If a reaction is exothermic when going in one direction, it will be endothermic in the reverse direction. When a reaction is reversed, the magnitude of ΔH° remains the same but its sign changes.

Thus above two thermochemical reactions in the reverse direction would be represented as follows:

$CO_{2(g)} \longrightarrow C_{(s)} + O_{2(g)}$ $\Delta H^\circ = +393.5kJ$

$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$ $\Delta H^\circ = -53.8KJ$

The student should be guided to recall information.

When gasoline burns in an automobile engine energy is released. A part of this energy is converted into heat which heats up the engine. The rest of the energy moves piston which turns a crankshaft and the crankshaft does work to move the automobile. Thus chemical energy released when gasoline burns is converted into heat and work. Chemical and related industries manufacture products that release, absorb or retain energy. Fertilizers help growing crops absorb solar energy and convert it into the chemical energy of food. Batteries produce electric energy from chemical reaction (we will discuss it in chapter 12). Thus the transformation of the energy from one form to another is an important field of science called thermodynamics.

The study of all types of energy changes associated with chemical and physical changes is known as thermodynamics.

11.2.1 State Function

A complete description of a system, which includes its quantity, temperature, pressure and volume describe the state of the system.

There are three types of systems, open system, closed system and isolated system.

In an open system reactants and energy may be exchanged with its surroundings. In a closed system only energy may be exchanged with surroundings but not material. Whereas in an isolated system no energy and no material may be exchanged with its surroundings. In fact there is no ideally isolated system. It is hypothetical system used for a comparison.

The condition of a system when various properties like temperature, pressure, volume, number of moles etc of system have definite values is called state of the system. The initial state of a system is its state before it undergoes a change. Whereas the final state is its state after the change has occurred. In a chemical reaction, the description of the products defines the final state.

Variables such as pressure, temperature, volume and energy depend only on the state of the system. A change in any of these variables depends only on the difference between initial and final conditions, but does not depend on the path followed. Such variables are called state functions or state variables.

The properties that are determined by the state of the system regardless of how that condition was achieved are called state functions.

Change in any property of a system is determined by the difference in the value of that property in the final state and the value of the same property in the initial state.

For example

Let V_1 is the initial volume of H_2 gas confined in a cylinder at temperature T_1, and pressure P_1. When temperature is increased from T_1 to T_2, its volume becomes V_2 and pressure changes to P_2. The changes in volume (ΔV) is given by the following equation.

$$\Delta V = V_2 - V_1$$

Similarly change in temperature ΔT and change in pressure ΔP are given by the equations.

$$\Delta T = T_2 - T_1$$

$$\Delta P = P_2 - P_1$$

Spontaneous and non-spontaneous reactions:

The reactions which processed on their own and do not need any external energy to procced are called spontaneous reactions. For example emission of rays from radioactive elements, burning of methane and coal. On the other hand the reations which require external energy to procced are called non-spontaneous reactions. For example reaction of nitrogen and oxygen to make nitric oxide, thermal decomposition of P_2O_5 etc.

11.3 INTERNAL ENERGY

In every chemical process energy is transformed from one form to another. The amount of energy transformed depends upon the energy contents of reactants and products. Every system has definite amount of energy present in it. This energy is due to kinetic as well as potential energies of the particles present in the system. The kinetic energy of the particles is due to the translational, rotational and vibrational motions of particles. The potential energy is due to all types of attractive forces present between the particles. These attractive forces include all types of bonds and Van der Waal'sforces. **The sum of all kinds of energies of the particles of the system is called as internal energy.** It is denoted by E. Absolute value of internal energy of a system cannot be measured. However change in internal energy (ΔE) of a system can be measured. The internal energy is a state function and depends only on the initial and final states of the system. Thus:

$$\Delta E = E_2 - E_1$$

Where E_1 and E_2 are internal energies in the initial and final states of the system respectively.

11.4 FIRST LAW OF THERMODYNAMICS

A system can exchange energy with its surroundings in two distinct ways. Energy can be transferred as heat or work. Heat and work can be transferred into or out of the system. Because energy must be conserved, the energy change of the system is linked to the flow of heat and work.

$$\Delta E = q + w$$

This equation is the mathematical form of first law of thermodynamics. Where ΔE represents the change in the system's internal energy, q represents heat and w represents work. W has positive sign when work is done on the system and negative when work is done by the system. q is positive when system absorbs heat and negative when loses heat.

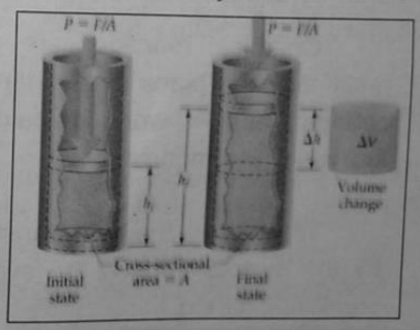

Figure. 11.1: Pressure – volume work

The student should be guided to interpret the information.

Consider a gas confined to a cylinder having a movable piston as shown in Fig: 11.1.

Suppose system absorbs ΔE energy from a source. On absorbing energy gas expands inside the cylinder and pushes the piston through a distance Δh. A part of ΔE absorbed becomes thermal energy q and remaining energy is consumed in doing work w on the piston. Therefore:

$$\Delta E = q + w$$

Since pressure is defined as force per unit area, the pressure of the gas (P) is:

$$P = \frac{F}{A}$$

$$F = P \times A \text{ ---------- (1)}$$

Work done on the piston is:

$$\text{Work} = \text{force} \times \text{distance}$$

$$W = F \times \Delta h \text{ ---------- (2)}$$

From equations 1 and 2, we get.

$$W = P \times A \times \Delta h \text{ ---------- (3)}$$

During expansion, the gas changes its volume. This volume change ΔV is equal to the product of area (A) and displacement (Δh).

$$\Delta V = A.\ \Delta h$$

Therefore equation 3 becomes.

$$W = P \times \Delta V$$

The gas (the system) is expanding, pushing back the piston against the pressure. Therefore, the system is doing work on the surroundings, so the sign of work should be negative.

$$W = - P\Delta V$$

Such type of work is done in an automobile engine. Heat from the combustion of the fuel expands the gases in the cylinder to push back the piston. The piston turns a crankshaft which does work to move the automobile. This type of work is called as pressure-volume work. Under these conditions:

$$\Delta E = q - P\Delta V$$

11.4.1 Relationship between Internal Energy of a System and Thermal Energy at Constant Temperature and Pressure

Chemical reactions are generally carried out in open containers. Therefore, these reactions take place at constant pressure. This means that volume of reaction mixture can change. Thus, PV work can be done and heat can flow to or from the system. According to the first law of thermodynamics,

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

Where q_p is the heat transferred to the system from the surroundings. $P\Delta V$ is work done by the surrounding on the system at constant pressure. If the system does work on the surrounding then,

$$\Delta E = q_p - P\Delta V$$

The student must be guided to employ this knowledge to illustrate the information.

Rearranging this equation,

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

If a chemical reaction involves only PV work at constant pressure, q_p becomes an important quantity. In this case, q_p represents the heat absorbed or evolved by the reaction at constant pressure and is known as enthalpy change, ΔH. Thus, the thermal energy for a reaction is equal to change in internal energy (ΔE) of the system plus PV work done by the system at constant pressure. This thermal energy change is called enthalpy change (ΔH) of the system. Therefore,

$$q_p = \Delta H = \Delta E + P\Delta V \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Thus, enthalpy of a substance is defined as the system's internal energy plus the product of its pressure and volume (H = E + PV). Absolute value of enthalpy of a system cannot be measured. However, change in enthalpy of a system (ΔH) can be measured.

Since enthalpy change (ΔH) for a reaction is measured as thermal energy or heat (q_p), therefore it is also known as heat of reaction. For a combustion reaction, ΔH is also called as heat of combustion. Solid or liquid :-

Since, there is no appreciable volume change in reactions involving solids or liquids, so $\Delta V = 0$. Therefore, equation (1) becomes,

$$\Delta H = \Delta E + P(0)$$

Thus $\Delta H = \Delta E$

Standard enthalpy change is enthalpy change at constant pressure (1 atm) and constant temperature (25°C) and is denoted by ΔH°. Superscript zero indicates that the reaction has been carried out under standard conditions. Under these conditions reactants and products are in their standard states. (For detail see section 11.5)

Equation (1) can be written as

$$q_p = \Delta H^\circ = \Delta E^\circ + P\Delta V$$

Thus thermal energy change for a reaction is equal to the change in the internal energy of a system plus PV work done by the system at constant temperature and pressure.

11.4.2 Relation between Enthalpy Change and Heat of Reaction or Heat of Combustion of A Reaction

Because most chemical reactions occur at constant pressure, we can equate the heat change in these reactions to the change in enthalpy. This means we can define heat of a reaction as the change in enthalpy (ΔH), as the difference between the enthalpies of the products (final estate) and the enthalpies of the reactants (initial state).

$$\Delta H = H_{products}^{final} - H_{reactants}^{initial}$$

The enthalpy change of a reaction can be positive or negative depending upon the process. For an exothermic process, in which heat is released by the system of the surrounding ΔH is negative (see examples in section 11.1.4). For an endothermic process, in which heat is absorbed by the system from the surroundings ΔH is positive (see examples in section 11.1.4). Since, combustion is an exothermic process in which heat is released by the system to its surroundings, ΔH is negative (see examples in section 11.5).

11.5 STANDARD STATES AND STANDARD ENTHALPY CHANGES

We can measure enthalpy change for a chemical reaction at constant pressure using a calorimeter. However, it is not only very difficult but also impossible in many cases. This is because some reactions are too slow. For example value of ΔH for the conversion of graphite to diamond cannot be measured in a calorimeter because reaction is very slow under normal conditions. However ΔH for this conversion can be calculated from heats of combustions of graphite and diamond measured at the same temperature (25°C) and pressure (1 atm):

$$C_{graphite(s)} \longrightarrow C_{diamond(s)} = ?$$

(i) $C_{graphite(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^\circ = -393.5\ kJ$

(ii) $C_{diamond(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^\circ = -395.4\ kJ$

Notice if we reverse the second equation and add it in first equation, we get the desired reaction.

(i) $C_{graphite(s)} + \not{O}_{2(g)} \longrightarrow C\not{O}_{2(g)} \qquad \Delta H^\circ = -393.5kJ$

(ii) $C\not{O}_{2(g)} \longrightarrow C_{diamond(s)} + \not{O}_{2(g)} \qquad \Delta H^\circ = +395.4kJ$

$$C_{graphite(s)} \longrightarrow C_{diamond(s)} \qquad \Delta H^\circ = +1.9kJ/mole$$

Thus the enthalpy of diamond is 1.9 kJ/mole greater than graphite at 25°C and one atm pressure. Therefore, thermodynamic properties of two substances can be properly compared by using a common reference state (standard state).

11.5.1 Conditions for Standard Heat of Reaction

As ΔH varies with conditions, we use standardized ΔH values. These values are calculated when all the substances are in their standard state. Conditions for the standard states are as follows:

1. Standard state for a gas is 1 atm.
2. Standard state for an element or a compound is the most stable physical state at 1 atm and 25°C (298 K).
3. Standard state for a substance in aqueous solution is 1M concentration.

Now we will define important enthalpies.

1. STANDARD ENTHALPY OF REACTION $\left(\Delta H_r^0\right)$

The enthalpy change in a chemical reaction, when reactants and products are in their standard states and their molar quantities are same as shown by the balanced chemical equation is called standard enthalpy of reaction. Examples are given below:

(i) $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} \qquad \Delta H_r^\circ = -571.6kJ$

(ii) $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H_r^\circ = -890.4kJ$

The student should be guided to remember the information.

(iii) $2Al_{(s)} + Fe_2O_{3(s)} \longrightarrow Al_2O_{3(s)} + 2Fe_{(s)} \quad \Delta H_r^\circ = -850kJ$

STANDARD ENTHALPY OF FORMATION $\left(\Delta H_f^0\right)$ · Element · 1 mole

It is defined as the enthalpy change that accompanies the formation of one mole of a compound from its elements with all substances in their standard states. Standard enthalpies of formation of some compounds are shown in table 11.1.

Table 11.1: Standard enthalpies of formation of some compounds in kJ mole^{-1}

$H_2O_{(g)}$	-245.1	$Fe_2O_{3(s)}$	-824.2	$Na^+_{(aq)}$	-240.1
$H_2O_{(l)}$	-285.8	$Fe_2O_{3(s)}$	-824.2	$Na^+_{(aq)}$	-240.1
$H_2O_{2(l)}$	-187.8	$SiO_{2(s)}$	-910.9	$K^+_{(aq)}$	-252.4
$NH_{3(g)}$	-46.1	$CaCO_{3(s)}$	-1207	$Mg^{2+}_{(aq)}$	-466.9
$NH_{3(aq)}$	-80.3	$BaCO_{3(S)}$	-1219	$Ca^{2+}_{(aq)}$	-542.8
$N_2H_{4(l)}$	50.6	$NaOH_{(s)}$	-425.6	$Al^{3+}_{(aq)}$	-524.7
$HF_{(g)}$	-271.1	$KOH_{(s)}$	-424.8	C(s, diamond)	1.9
$HCl_{(g)}$	-92.3	$HONO_{2(l)}$	174.1	$CH_{4\ (g)}$	-74.8
$HCl_{(aq)}$	167.2	$HONO_{2(aq)}$	-207.4	$C_2H_{2(g)}$	226.7
$HBr_{(g)}$	-36.4	$(HO)_2SO_{2(l)}$	-814.0	$C_2H_{4(g)}$	52.3
$HI_{(g)}$	26.5	$(HO)_2SO_{2(aq)}$	-909.3	$C_2H_{6(g)}$	-84.7
$NH_4Cl_{(s)}$	-20.6	$NH_4Cl_{(s)}$	-314.4	$C_3H_{8(g)}$	-103.9
$CO_{(g)}$	-110.5	$NaCl_{(s)}$	-411.2	$C_4H_{10(g)}$	-126.2
$CO_{2(g)}$	-393.5	$NaBr_{(s)}$	-361.1	$C_6H_{6(l)}$	49.0
$NO_{(g)}$	90.3	$NaI_{(s)}$	-287.8	$C_6H_5CH_{3(l)}$	12.1
$NO_{2(g)}$	33.2	$KCl_{(s)}$	-436.8	$C_8H_{18(l)}$	-249.9
$N_2O_{4(g)}$	9.2	$KBr_{(s)}$	-393.8	$CH_3OH_{(l)}$	-238.7
$SO_{2(g)}$	-296.8	$KI_{(s)}$	327.9	$C_2H_5OH_{(l)}$	-277.7
$SO_{3(g)}$	-395.7	$AgCl_{(s)}$	-127.1	$CH_3CHO_{(l)}$	-192.3
$MgO_{(s)}$	-601.7	$CaCl_{2(s)}$	-795.8	$CH_3COCH_{3(l)}$	-248.1
$CaO_{(s)}$	-635.1	$AlCl_{3(s)}$	-704.2	$CH_3COOH_{(l)}$	-484.5

For writing thermochemical equation for enthalpy of formation, write elements as reactants and 1mole of the compound as product. Show standard states of all the substances. Finally balance the atoms.

Example 11.1

Write thermochemical equation for the formation of H_2O, SO_3 and H_2O_2. Use data given in table 11.1

SOLUTION:

(i) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)} \quad \Delta H_f^\circ = -285.8 \text{ kJ mole}^{-1}$

(ii) $S_{(s)} + \frac{3}{2}O_{2(g)} \longrightarrow SO_{3(g)} \quad \Delta H_f^\circ = -395.2 \text{ kJ mole}^{-1}$

(iii) $H_{2(g)} + O_{2(g)} \longrightarrow H_2O_{2(l)}$ $\Delta H_f^\circ = -191.2$ kJ mole^{-1}

Standard enthalpies of formation of some substances are shown in table 11.1.

3. STANDARD ENTHALPY OF COMBUSTION $\left(\Delta H_c^\circ\right)$

The enthalpy change when one mole of a substance is completely burnt in excess of oxygen under standard conditions is called standard enthalpy of combustion. Standard enthalpies of combustion of some substances are shown in table 11.2.

Table 11.2 Standard enthalpies of combustion in kJ mole $^{-1}$

$H_{2\ (g)}$	-285.8	$CH_{4(g)}$	-890.4	$C_6H_{6(l)}$	-3268
$C_{(graphite)}$	-393.5	$C_2H_{6(g)}$	-1560	$C_2H_5OH_{(l)}$	-1367
$C_{(diamond)}$	-395.4	$C_8H_{18(l)}$	-5512	$CH_3CHO_{(l)}$	-1167
$S_{(rhombic)}$	-296.9	$C_2H_{4(g)}$	-1411	$CH_3COOH_{(l)}$	-875
$S_{(monoclinic)}$	-297.2	$C_2H_{2(g)}$	-1300	$C_6H_{12}O_{6(s)}$ (glucose)	-2802

For writing thermochemical equation for enthalpy of combustion, write 1mole of the element or compound and oxygen as reactant. Write oxides of the given element or oxides of elements present in the compound as products. Show standard states of all the substances. Finally, balance the atoms.

Example 11.2

Write thermochemical equation for the combustion of, C, CH_4 and H_2. Use data given in 11.2.

Solution:

(i) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H_c^\circ = -393.5$ kJ mole^{-1}

(ii) $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$ $\Delta H_c^\circ = -890.4$ kJ mole^{-1}

(iii) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$ $\Delta H_c^\circ = -285.8$ kJ mole^{-1}

4. STANDARD ENTHALPY OF ATOMIZATION $\left(\Delta H_{at}^\circ\right)$

The enthalpy change when one mole of gaseous atoms are formed from its element under standard conditions is called standard enthalpy of atomization. e.g.,

(i) $\frac{1}{2}H_{2(g)} \longrightarrow H_{(g)}$ $\Delta H_{at}^\circ = +218$ kJ mole^{-1}

(ii) $\frac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)}$ $\Delta H_{at}^\circ = +121$ kJ mole^{-1}

The student should be guided to explain and interpret information.

STANDARD ENTHALPY OF NEUTRALIZATION $\left(\Delta H^{o}_{n}\right)$

It is defined as the amount of heat evolved when one mole of H^+ ions from an acid combine with one mole of OH^- ions from a base to form one mole of water under standard conditions. e.g.

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)} \quad \Delta H^{o}_{n} = -57.4 kJ\ mole^{-1}$$

Strong acids and bases ionize completely in their aqueous solutions. Thus, when solutions NaOH and HCl are mixed together, the only change which occurs is the formation of water. $^+$ and Cl^- ions remain in solution. Thus heat of neutralization is due to the formation of water m H^+ and OH^- ions.

$$Na^+_{(aq)} + OH^-_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)} \longrightarrow$$

$$Na^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)} \qquad \Delta H^{o}_{n} = -57.4 kJ\ mole^{-1}$$

or $$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)} \qquad \Delta H^{o}_{n} = -57.4 kJ\ mole^{-1}$$

STANDARD ENTHALPY OF SOLUTION $\left(\Delta H^{o}_{sol}\right)$

It is the enthalpy change when one mole of a substance is dissolved in so much olvent that further dilution results in no detectable heat change, under standard onditions. e.g.,

$$NH_4Cl_{(s)} \xrightarrow{H_2O} NH^+_{4(aq)} + Cl^-_{(aq)} \qquad \Delta H^{o}_{sol} = +15.1 kJmole^{-1}$$

$$HCl_{(g)} \xrightarrow{H_2O} H^+_{(aq)} + Cl^-_{(aq)} \qquad \Delta H^{o}_{sol} = +75\ kJmole^{-1}$$

Self Check Exercise 11.2

Write thermochemical equation form the given information:

Standard enthalpy of formation of benzene (l) is +49.0 kJ mole^{-1}

Standard enthalpy of formation of ethanol (l) is -277.7 kJ mole^{-1}

Standard enthalpy of combustion of acetic acid(l) is -876 kJ mole^{-1}

When ethanol is burned in air –1367 kJ mole^{-1}energy is released at 1 atm and 25°c.

Which of the following equations describe a reaction for which ΔH^o is equal to the nthalpy of formation of a compound, ΔH^{o}_{f}

$$4\ Al_{(s)} + 2\ O_{2(g)} \longrightarrow 2\ Al_2O_{3(s)}$$

$$4Al_{(s)} + \tfrac{3}{2}\ O_{2(g)} \longrightarrow Al_2O_3 \quad \text{(correct)}$$

$$CO_{(g)} + \tfrac{1}{2}\ O_{2(g)} \longrightarrow CO_{2(g)}$$

The student should be guided to choose useful information to solve various problems.

11.5.1 Bond Dissociation Energy

When a chemical reaction occurs, old bonds break and new bonds form. Bond breaking always require energy and bond formation always releases energy. **The amount of energy required to break one mole of a particular bond to form neutral atoms is called bond dissociation energy.** Whereas the amount of energy released when one mole of a particular bond form from neutral atoms is called bond energy.

The difference between bond dissociation energy and bond energy determines whether the reaction absorbs or releases energy overall.

For any chemical reaction, the enthalpy change is the sum of bond dissociation energies of the reactants minus the sum of bond energies of products.

$$\Delta H_{reaction} = \sum \text{B.D.E}_{\text{ reactants}} - \sum \text{B.E}_{\text{ Products}}.$$

For reaction between H_2 and O_2 to produce H_2O:

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} \quad \Delta H^{\circ} = ?$$

$$\Delta H_r^{\circ} = 2 \times \text{B.D.E of } H_{2(g)} + \text{B.D.E of } O_{2(g)} - 4 \times \text{B.E of O-H bonds}$$

$$= 2 \text{ x } (+436\text{kJ}) + 493.6\text{kJ} - 4\ (460\text{kJ})$$

$$= 1365.6 \text{ kJ} - 1840\text{kJ}$$

$$\Delta H_r^{\circ} = -474.4 \text{ kJ}.$$

Thus the reaction between hydrogen and oxygen to form water is exothermic.

11.6 HEAT CAPACITY

When you rub your hands, what happens?

The different forms of energy can be converted into one another. Any other form of energy can be completely transformed into heat energy. But at constant temperature heat cannot be completely converted into another form of energy. Temperature is not the same as heat. Temperature is a property that reflects the random motions of the particles in a substance. Temperature is defined as the measure of average kinetic energy of the molecules of a substance. Heat on the other hand, involves the transfer of energy between two objects due to temperature difference. Temperature difference determines the direction in which heat flows spontaneously. Temperature of a substance does not depend on its mass. But quantity of heat within a substance at a given temperature is directly proportional to its mass. Therefore, amount of heat absorbed by a substance is proportional to the temperature change.

$$q \propto \Delta T$$

$$q = \text{Heat capacity} \times \Delta T$$

Where heat capacity is constant of proportionality. substance.

$$\text{Heat Capacity} = \frac{\text{Heat}}{\Delta T} \qquad \text{.....(1)}$$

The amount of heat required to raise the temperature of given amount of a substance by 1Kelvin is called heat capacity. It is expressed in joules per Kelvin.

The amount of heat required to raise the temperature of one gram of a substance by 1Kelvin is called specific heat capacity. It is expressed in Joules per gram per Kelvin.

Do You Know

Water is a major component of living organisms and plants on earth. Its specific heat capacity is very important property for all living beings. Thanks to its high heat capacity, even on very hot days, the heat is generally not high enough to raise the temperature of the internal fluids in animals and plants significantly.

$$\text{Specific heat capacity (c)} = \frac{\text{Heat}}{\text{gram} \times \Delta T} \qquad \text{----------(2)}$$

The amount of heat required to raise the temperature of one mole of a substance by one Kelvin is called its molar heat capacity. S.I. unit for molar heat capacity is $J.K^{-1}$ $mole^{-1}$.

$$\text{Molar heat Capacity (C)} = \frac{\text{Heat}}{\text{moles} \times \Delta T} \qquad \text{.....(3)}$$

If the quantity of heat q is absorbed by n moles of the substance and its temperature raises from T_1 to T_2, its molar heat capacity C is give by the expression.

$$C = \frac{q}{n\,(T_2 - T_1)}$$

Since heat absorbed by a substance at constant pressure is equal to ΔH.

$$q_p = \Delta H$$

$$\therefore \quad C_p = \frac{q_p}{n(\Delta T)}$$

$$C_p = \frac{\Delta H}{n\,\Delta T}$$

or $$\Delta H = nC_P\Delta T$$

Where C_p is molar heat capacity of the substance at constant pressure.

When heat is absorbed by a substance at constant volume, then $q_v = \Delta E$.

and $$C_V = \frac{q_V}{n\,\Delta T}$$

$$C_V = \frac{\Delta E}{n\,\Delta T}$$

$$\Delta E = nC_V\Delta T$$

Where C_v is molar heat capacity of the substance at constant volume.

For Example,

Specific heat capacity of Cu = $0.387\ J.g^{-1}K^{-1}$

\ Molar heat Capacity of Cu = 0.387×63.54

$= 24.59\ Jmole^{-1}K^{-1}$

Science Titbits

We select materials based on heat capacity to make everyday items such as pots and pans, table ware etc. that are subjected to heat during use. For example it is generally better to use materials with low heat capacity such as metals for cooking utensils, pots or frying pan's to ensure that the heat passes to food faster and to speed up the cooking process.

Knowing specific heat capacity of a substance, its mass and temperature change of substance being heated or cooled, we can determine heat absorb or released.

Re-arranging equation (2) we get,

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

Similarly, if we know mole of the substance then:

$$q = C \times n \times \Delta T$$

Self Check Exercise 11.3:

1. Describe the difference between heat capacity and molar heat capacity.
2. Calculate the heat involved when an Al pan weighing 200g is cooled from 100°C to 25°C at constant pressure. Specific heat capacity of Al is 0.9 $Jg^{-1}.K^{-1}$ (**Ans**: 13500J)

11.7 CALORIMETRY

Calorimetry is the science of measuring heat of a chemical reaction by measuring the temperature change. **A device that measures heat flow is called calorimeter.** Calorimeters measure the heat released from a system either at constant pressure ($q_p = \Delta H$) or at constant volume ($q_v = \Delta E$). Thus there are two types of calorimetry.

Constant Pressure Calorimetry

In constant pressure calorimetry pressure of the system is fixed. For this purpose we need a thermally insulated container with a thermometer and stirrer. For most purposes a coffee cup calorimeter is used (Fig 11.2).

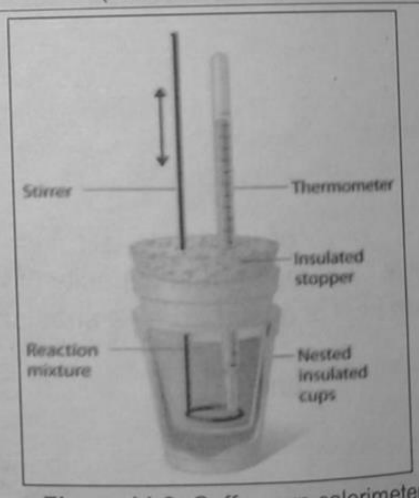

Figure 11.2: Coffee cup calorimeter

$$q = m \times c \times \Delta T$$

Where m = mass of reactants
C = specific heat of reaction mixture
ΔT = change in temperature.

11.7.1 ESTIMATION OF HEAT OF REACTION FROM EXPERIMENTAL DATA

This process can be understood by the following example.

In a reaction $50cm^3$ of 1.0M NaOH neutralizes $50cm^3$ of 1.0M HCl at 25°C. Use this experimental data to calculate the heat of reaction (neutralization) using a calorimeter. Specific heat of water is $4.2\ Jg^{-1}K^{-1}$.

ACTIVITY:

Since neutralization reaction is carried out at constant pressure. We will use coffee cup calorimeter (shown in figure 11.2) to calculate the heat of neutralization in the above example. For this purpose take two nested styrofom cups. The outer cup will provide extra thermal insulation. Place $50cm^3$ of 1.0M NaOH in the inner styrofom cup and $50cm^3$ of 1.0M HCl in a beaker. Keep the two solutions for some time to let them to acquire room temperature. Suppose room temperature is 25°C. Now add slowly the acid solution into the NaOH in the inner cup. The temperature of the solution will rise due to the evolution of heat during the neutralization process. Note down this temperature (suppose it is 31.9°C). Calculate the amount of heat evolved by the following equation.

$$q = m \times c \times \Delta T$$

Volume of NaOH	=	$50cm^3$
Volume of HCl	=	$50cm^3$
Total Volume of reaction mixture	=	$50cm^3 + 50cm^3 = 100cm^3$
Density of water	=	$1\ g.cm^{-3}$
Total mass of reaction mixture(m)	=	$100cm^3 \times 1g.cm^{-3} = 100g$
Raise in temperature ΔT	=	31.9°C – 25°C
	=	6.9°C
or	=	6.9K

$$q = m \times c \times \Delta T$$
$$q = 100g \times 4.2J.g^{-1}K^{-1} \times 6.9K$$
$$q = 2.9 \times 10^3 J$$

$$\text{No. of moles of NaOH} = \frac{M \times \text{Vol of solution } cm^3}{1000}$$

$$= \frac{1 \times 50}{1000} = 0.05$$

$$\text{Similarly, No of moles of HCl} = \frac{1 \times 50}{1000} = 0.05$$

Considering, chemical equation.

$$NaOH\ (aq) + HCl\ (aq) \longrightarrow NaCl\ (aq) + H_2O\ (l)$$

1 mole 1 mole 1 mole

0.05 mole 0.05 mole 0.05 mole

Thus formation of 0.05 moles of water release heat $= 2.9 \times 10^3$ J

The student should be guided to examine and discuss different parts of the information.

Formation of 1 mole of water will release heat = $\frac{2.9 \times 10^3}{0.05}$

$= 5.8 \times 10^4 J\ mole^{-1}$

$= 58.0\ kJ\ mole^{-1}$

Since heat is evolved at constant pressure,

$q_p = \Delta H_n^\circ = -58.0\ kJ\ mole^{-1}$

Self Check Exercise 11.4:

Experimental data shows that when 87.5 cm^3 of a 0.10M HCl solution is mixed with 25.0cm^3 of 0.35M NaOH in a calorimeter, complete neutralization occurs. The temperature of the calorimeter changes from 25°C to 26.07°C. Use this data to determine heat of neutralization for the reaction. (**Ans**:-57.78kJ)

Constant Volume Calorimetry

Constant volume calorimetry is used for accurate determination of the enthalpy of combustion for food, fuel and other compounds. A bomb calorimeter is used for this purpose. Chemical reaction in a bomb calorimeter takes place under constant volume conditions. A bomb calorimeter is shown in fig 11.3. It consists of a strong closed vessel (the bomb) immersed in an insulated water bath.

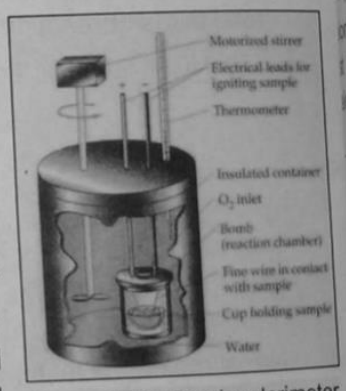

Figure 11.3: Bomb calorimeter

11.7.2 Estimation of Energy Available from Food

Human beings require three major classes of food (1) carbohydrates (2) fats (3) proteins. Most human energy is derived from carbohydrates and fats. Carbohydrates are the source of quickest energy. Glucose is the simpler carbohydrate, also known as blood sugar. It is soluble in blood and is transported by the blood to all the tissues. In tissues it is oxidized to form CO_2 and H_2O and energy. We can measure energy available from glucose by determining its heat of combustion. The bomb calorimeter shown in figure 11.3 is used for measuring the energy available from food, which is just the enthalpy of combustion .we can understand this by the following activity.

Activity 1.2

Weigh 1.8 g of glucose and place it in the holder cup of bomb calorimeter and seal it. Adjust the pressure of oxygen in the calorimeter to about 25 atm. Immerse calorimeter in an insulated water bath fitted with a motorized stirrer and a thermometer. Record the temperature of water.

The student must be guided to analyze data.

Suppose it is 25°C. Ignite glucose electrically when it will burn energy will flow from the chemicals to the calorimeter and water. Record the temperature of water again. Thermometer will show 31.52°c. If calorimeter has a total heat capacity of 4.321 kJK^{-1}. We can calculate energy available from glucose as follows:

Increase in temperature = $\Delta T = 31.52°C - 25°C$

$= 6.52\ °C$

Heat evolved = ΔT x total heat capacity of calorimeter

$= 6.52 \times 4.321 kJK^{-1}$

$= 28.1729\ kJ$

No. Of moles of glucose burnt = $\frac{1.8g}{180\ g.mole^{-1}}$

$= 0.01$ moles

Since 28.1729 kJof heat was evolved for 0.01 moles of glucose the heat of combustion of glucose per mole $= \frac{28.1729g}{0.01 mole^{-1}}$

$= 2817.29\ kJmole^{-1}$

Thus energy available from glucose is 2817.29 $kJmole^{-1}$.

Self Check Exercise 11.5

Fats and oils are a rich source of energy. They provide more energy as compares to carbohydrates and proteins. When 1.0g of a typical fat glyceral trioleate, $C_{57}H_{104}O_6$ is burnt completely in a bomb calorimeter at 25°C raises its temperature by 8.77°C. Total specific heat of calorimeter is 4.321 kJK^{-1}. List important steps you will use in the determination of heat content of this fat calorimetrically. Calculate also amount of heat available from this fat.

(**Ans**:33535.3 kJ $mole^{-1}$)

11.8 HESS'S LAW

Enthalpy is a state function; therefore, enthalpy change in a chemical reaction in going from some initial state to some final state is independent of the path followed by the reaction. Thus in going from a particular set of reactant to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in many steps. This principle is known as Hess's law.

G.H. Hess stated this law in 1840. **It states that the enthalpy change in a chemical reaction is same whether the reaction takes place in a single step or in several steps.**

Mathematically $\Sigma\Delta H\ (Cycle) = 0$

Suppose a reactant A changes into the product B in one step and enthalpy change in this step is ΔH. Now suppose this change takes place in three steps, involving a change from A to C, C to D, and finally D to B as shown below:

of this activity.

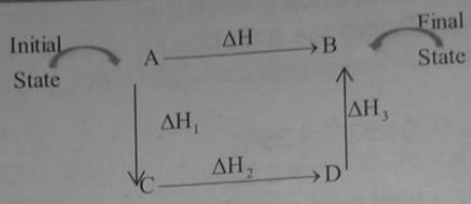

Fig. 11.4

If ΔH_1, ΔH_2 and ΔH_3 are enthalpy changes in these steps, as shown in the figure (11.4). Then according to the Hess's Law.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Example 11.3

Oxidation of nitrogen to produce nitrogen dioxide absorbs 68kJ of energy.

$$N_{2(g)} + 2O_{2(g)} \longrightarrow 2NO_{2(g)} \qquad \Delta H^\circ = 68\,kJ$$

This reaction can be carried out in two steps.

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)} \qquad \Delta H_1^\circ = 180\,kJ$$

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)} \qquad \Delta H_2^\circ = -112\,kJ$$

Net reaction:

$$N_{2(g)} + 2O_{2(g)} \longrightarrow 2NO_{2(g)} \qquad \Delta H_1^\circ + \Delta H_2^\circ = 68\,kJ$$

Notice that the sum of two steps gives the net reaction and

$$\Delta H^\circ = \Delta H_1^\circ + \Delta H_2^\circ = 68\,kJ$$

For energy cycle see fig. 11.4.

Example 11.4

Combustion of C to CO_2 evolves 393.5 KJ of energy.

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_1^\circ = -393.5\,kJ$$

This reaction may takes place in two steps.

$$C_{(s)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \qquad \Delta H^\circ = -110.52\,kJ$$

$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_2^\circ = -282.98\,kJ$$

Net reaction $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_1^\circ + H_2^\circ = -393.51\,kJ$

Thus the enthalpy change in a chemical reaction is independent of the path followed. Fig. 11.5 shows energy cycle for this reaction.

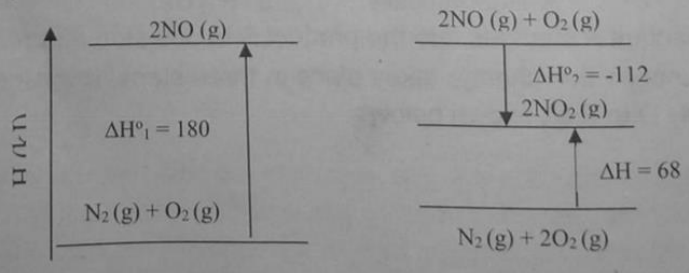

Fig.11.5 (a): Energy cycle for the reaction between $N_2(g)$ and $O_2(g)$ to produce NO_2 (g) which steps in this cycle is/are exother mic?

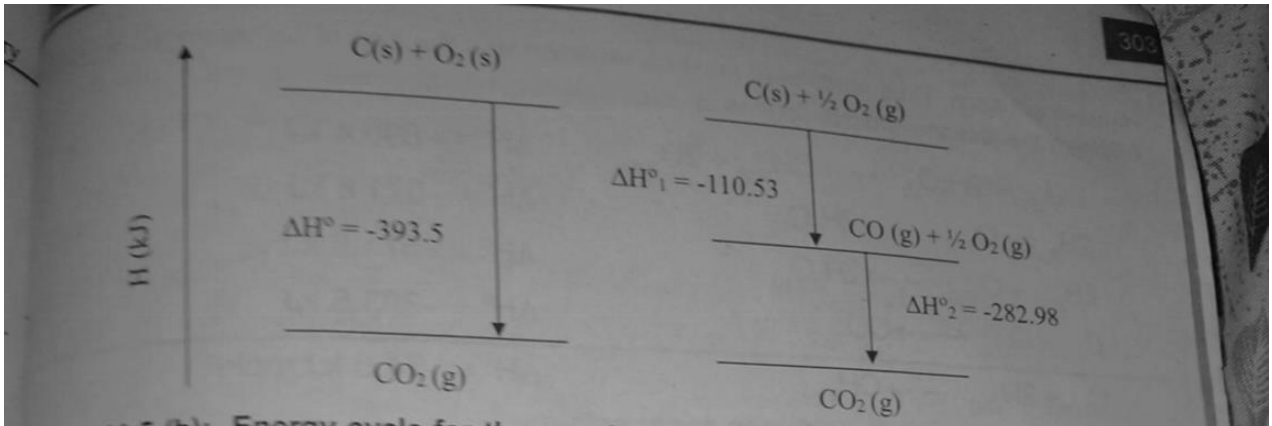

Figure11.5 (b): Energy cycle for the reaction between C(s) and $O_{2(g)}$ to produce CO_2 (g) which steps in this cycle is/are exothermic?

There are many compounds which cannot be prepared directly from their elements. Some of these compounds cannot be decomposed into their constituent elements. e.g. CCl_4. Some elements do not burn completely due to the formation of a protective covering on their surface. Such as Al, B etc. Thus enthalpies of formation of CCl_4, Al_2O_3, B_2O_3 etc cannot be determined directly by calorimetery, Hess's law is particularly useful for determining enthalpies of formation of such compounds.

Example 11.5

Enthalpy of formation of methane cannot be measured directly. By the application of Hess's law it can be determined indirectly from the enthalpies of combustion for CH_4, H_2 and C.

(i) $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$ $\quad \Delta H^\circ = -890.4\,kJ\ mole^{-1}$

(ii) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$ $\quad \Delta H^\circ = -285.5\,kJ\ mole^{-1}$

(iii) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\quad \Delta H^\circ = -393.5\,kJ\ mole^{-1}$

(iv) $C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)}$ $\quad \Delta H^\circ = ?$

To obtain ΔH° for the required reaction we must some how combine equations i, ii, and iii to produce that reaction and add the corresponding ΔH° values. This can be done by focusing on reactants and products of the required reaction. The reactants are $C_{(s)}$ and $2H_{2(g)}$ and the product is $CH_{4(g)}$. How can we obtain the correct equation? Reaction (iii) has $C_{(s)}$ as reactant which is needed in the required equation. Thus equation (iii) will be used as such. Equation (ii) has $H_{2(g)}$ as reactant but the required equation needs $2H_{2(g)}$, thus equation (ii) will be used after multiplying by 2. Equation (i) has $CH_{4(g)}$ as reactant, but this is needed as product in the

The student must be guided to to interpret given information.

required equation. Thus reaction (i) must be reversed and the sign of ΔH° changed according. Adding the equations and deleting the species that occur on both sides we get.

$$CO_{2(g)} + 2H_2O_{(l)} \longrightarrow CH_{4(g)} + 2O_{2(g)} \qquad \Delta H^\circ = +890.4 \text{ kJ}$$
$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} \qquad \Delta H^\circ = -571.6 \text{ kJ}$$
$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} \qquad \Delta H^\circ = -571.6 \text{ kJ}$$
$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^\circ = -393.5 \text{ kJ}$$
$$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)} \qquad \Delta H^\circ = -74.6 \text{ kJ mole}^{-1}$$

This gives the required equation and its enthalpy.

11.8.1 Enthalpies of Reactions from Enthalpies of Formation

It is often convenient to calculate the ΔH° values for a reaction from values of the standard enthalpies of formation, ΔH_f° of the reactants and products. For a given reaction:

$\Delta H^\circ = \sum \text{coeff}_P \Delta H_f^\circ$ (products) - $\sum \text{Coeff}_r \Delta H_f^\circ$ (reactants)

Where coeff = Coefficient

Elements in their standard states are not included in the ΔH° reaction calculation i.e. ΔH_f° for an element in its standard state is zero. When balanced equation for a reaction is multiplied by an integer, the value of ΔH° for that reaction should be multiplied by the same integer.

Example 11.6

Calculate ΔH of reaction for the following reaction, which take place when gasoline burns in internal combustion engines. Where the values of ΔH_f° are -269Kj, 0 kJ, -393.5 kJ and -285 kJ for $C_8H_{18(l)}$, $O_{2(g)}$, $CO_{2(g)}$ and $H_2O_{(l)}$ respectively

$$2C_8H_{18(l)} + 25O_{2(g)} \longrightarrow 16CO_{2(g)} + 18H_2O_{(l)}$$

Solution:

$$DH^\circ_{reaction} = \sum \text{coeff}_P \Delta H_f^\circ (\text{products}) - \sum \text{coeff}_r \Delta H_f^\circ (\text{reactants})$$

$= [16 \times \Delta H_f^\circ \text{ for } CO_{2(g)} + 18 \times \Delta H_f^\circ \text{ for } H_2O_{(l)}] -$
$[2 \times \Delta H_f^\circ \text{ for } C_8H_{18(l)} + 25 \times \Delta H_f^\circ \text{ for } O_{2(g)}]$

$= 16(-393.5 \text{ kJ}) + 18 (-285.8 \text{ kJ}) - 2 (-269 \text{ kJ}) - 25(0)$

$= -6296 \text{ kJ} - 5144.4 \text{ kJ} + 538 \text{ kJ} + 0$

$= -11440.4 \text{ kJ} + 538 \text{ kJ}$

$= -10902.4 \text{ kJ}$

$= -1.09 \times 10^4 \text{ kJ}$

The student must be guided to evaluate the expression.

Example 11.7

Calculate $\Delta H^\circ_{reaction}$ for the following reaction. This reaction takes place in the tissues of the living organisms. Where the values of ΔH°_f are -1258.18 kJ, 0 kJ, -393.5 kJ and -285 kJ for $C_6H_{12}O_{6(s)}$, $O_{2(g)}$, $CO_{2(g)}$ and $H_2O_{(l)}$ respectively

Solution:

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(l)} \qquad \Delta H^\circ_{reaction} = ?$$

$$\Delta H^\circ_{reaction} = \sum Coeff_P \Delta H^\circ_f (products) - \sum coeff_r (\Delta H^\circ_f (reactants)$$

$$\Delta H^\circ_{reaction} = \left[6\Delta H^\circ_f CO_{2(g)} + 6\Delta H^\circ_f (H_2O_{(l)})\right] - [\Delta H^0_f C_6H_{12}O_6 + 6\Delta H^0_f O_{2(g)}]$$

$$= [6(-393.5kJ)+6(-285.8kJ] - [-1258.18kJ + 6\times 0]$$
$$= [-2361.0kJ - 1714.8kJ] - [-1258.18kJ]$$
$$= -4075.8kJ + 1258.18kJ$$
$$= -2817.62kJ$$

This means one mole (180g) of glucose provides 2818.82 kJ energy. Therefore energy [illegible] by one gram of glucose will be $\frac{2817.62\,kJ\,mole^{-1}}{180\,g\,mole^{-1}} = 15.65\,kJ$.

11.9 BORN HABER CYCLE

This is special application of Hess's law to binary ionic compounds. It helps us to calculate lattice energies of binary ionic compounds (M^+X^-).

The change in energy that takes place when separated gaseous ions are packed together to form one mole of an ionic solid is called lattice energy.

$$M^+_{(g)} + X^-_{(g)} \longrightarrow MX_{(s)}$$

Lattice energy cannot be determined directly. However it can be determined indirectly by means of Born Haber cycle. Consider the case of NaCl. Its standard enthalpy of formation (ΔH°_f) is -411kJ mole^{-1}. The formation reaction can be considered as taking place in several steps, one of which is the formation of lattice. This complete sequence of reaction is called a cycle (Fig.11.6)

Step-I: Sublimation of solid sodium. The energy of sublimation for Na(s) is 161 kJ mole^{-1}

$$Na_{(s)} \longrightarrow Na_{(g)} \qquad \Delta H^\circ_s = +108\ kJ/mole$$

Step-II: Ionization of $Na_{(g)}$ atom to form $Na^+_{(g)}$ ion. This process corresponds to the first ionization energy for Na.

$$Na_{(g)} \longrightarrow Na^+_{(g)} + Ie^- \quad \Delta H^\circ_{LE} = +496\ kJ/mole$$

The student must be guided to choose useful information to solve various problems.

Step-III: Dissociation of Cl_2 molecules. We need to form one mole of Cl atoms by breaking the Cl-Cl bond in $\frac{1}{2}$ mole of Cl_2 molecules. The energy required to break this bond is 121 kJ/mole and is known as enthalpy of atomization for Cl_2.

$$\frac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)} \qquad \Delta H^{\circ}_{at} = +121\ kJ/mole$$

All these three steps are endothermic and are drawn upward in the figure (11.6).

Step-4: Formation of $Cl^-(g)$ ion. Energy is released in this step equal to the electron affinity for Cl.

$$Cl_{(g)} + 1e^- \longrightarrow Cl^-_{(g)} \qquad \Delta H^{\circ}_{E.A} = -349\ kJ/mole$$

Step-5: Formation of solid NaCl from the gaseous Na^+ and Cl^- ions. This corresponds to the lattice energy (ΔH_l) for NaCl(s) which is to be calculated.

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)} \qquad \Delta H_{\ell}$$

Since the sum of these five steps gives the overall reaction desired, the sum of the individual energy changes give the overall energy change. Thus

$$\Delta H^{\circ}_f = \Delta H^{\circ}_s + \Delta H^{\circ}_{I.E} + \Delta H^{\circ}_{at} + \Delta H^{\circ}_{E.A} + \Delta H^{\circ}_l$$

$$-411kJ = +108kJ + 496kJ + 121kJ + (-349kJ) + \Delta H^{\circ}_l$$

$$\Delta H^{\circ}_l = -411kJ - (108\ kJ + 496kJ + 121kJ - 349kJ)$$

$$\Delta H^{\circ}_l = -787kJ\ mole^{-1}$$

Thus lattice energy of NaCl is 787 kJ/mole.

$$Na_{(s)} \longrightarrow Na_{(g)} \qquad 1^{st}\ Step$$

$$Na_{(g)} \longrightarrow Na^+_{(g)} + 1e^- \qquad 2^{nd}\ Step$$

$$\frac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)} \qquad 3^{rd}\ Step$$

$$Cl_{(g)} + 1e^- \longrightarrow Cl^-_{(g)} \qquad 4^{th}\ Step$$

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)} \qquad 5^{th}\ Step$$

$$Na_{(s)} + Cl_{2(g)} \longrightarrow NaCl_{(s)} \qquad \text{Net reaction}$$

Electron affinities of atoms are usually calculated from Born-Haber cycle because it is difficult to determine electron affinities directly.

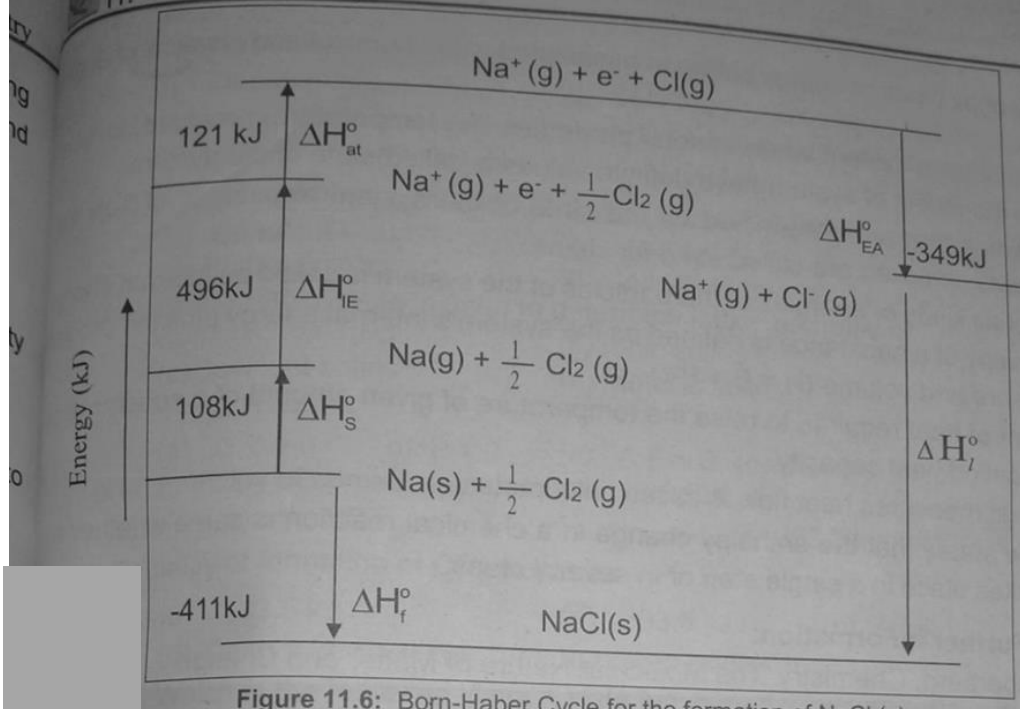

Figure 11.6: Born-Haber Cycle for the formation of NaCl (s)

Self Check Exercise 11.6:

Draw a complete Born Haber Cycle for the formation of MgO (s). Calculate the lattice energy for MgO from the following data.

Standard enthalpy of formation of MgO = -602 kJmole^{-1}

Standard enthalpy of sublimation of Mg = 150kJmole^{-1}

Ionization energy of Mg(g) to form Mg^{+2}(g) is 2180 kJ mole^{-1}

Standard enthalpy of atomization of O_2 = 247 kJ mole^{-1}

Electron affinity of O (g) to form O^{-1} (g) = -141 kJ mole^{-1}

Electron affinity of O^{-1}(g) to form O^{-2} (g) = 878 kJ mole^{-1}

(Ans: -3916kJ)

Summary of the Key Terms

- The branch of chemistry which deals with the heat or thermal energy changes in chemical reactions is called thermochemistry.
- A chemical reaction that proceeds with the evolution of heat is called an exothermic reaction.
- A chemical reaction that proceeds with the absorption of heat is called an endothermic reaction.
- The amount of heat evolved or absorbed in a chemical reaction, when molar quantities of reactants and product are same as shown in a chemical reaction is called heat of reaction.

The Student be guided to demonstrate skills to distinguish between different parts of calculations and analyse given data.

- The study of all types of energy changes associated with chemical and physical changes is known as thermodynamics.
- The condition of a system when various properties like temperature, pressure, volume, number of moles etc of system have definite values is called state of the system.
- The properties that are determined by the state of the system regardless of how that condition was achieved are called state functions.
- The sum of all kinds of energies of the particles of the system is called as internal energy.
- Thus, enthalpy of a substance is defined as the system's internal energy plus the product of its pressure and volume (H = E + PV).
- The amount of heat required to raise the temperature of given amount of a substance by 1Kelvin is called heat capacity.
- A device that measures heat flow is called calorimeter.
- Hess's Law states that the enthalpy change in a chemical reaction is same whether the reaction takes place in a single step or in several steps.

References for Further inFormation:

- Martin Silberberg, Chemistry, The Molecular Nature of Matter and Change
- Steven S. Zumdahl, Chemistry
- Olmsted Williams, Chemistry, The Molecular Science
- Bonder Pardue, Chemistry, An experimental Science
- Darrell D. Ebbing, R.A.D Wentworth, Introductory Chemistry.
- Raymond Chang, Essential Chemistry

Graham Hill and John Holman, Chemistry in context

Exercise

1. Choose the Correct Answer

(i) Which of the following substances have zero value for their standard enthalpy of formation.

(a) O_3 (b) H_2O (c) ZnO (d) None of these.

(ii) Calorie is equivalent to

(a) 4.18J (b) 4.18kJ (c) 0.418J (d) 0.418kJ.

(iii) Enthalpy of neutralization of all the strong acids and strong basis has the same value due to

(a) The formation of salt and water

(b) The formation of salt

(c) The complete ionization of acids and bases

(d) The combination of H^+ and OH^- ions to form water.

(iv) Total heat content of a system is called

(a) Enthalpy (b) Internal energy (c) Heat (d) State function

(v) Heat of _____ of a substance is always negative
(a) Formation (b) Combustion
(c) Decomposition (d) Solution

(vi) A balloon filled with oxygen is placed in a freezer. Identify system
(a) Balloon (b) Oxygen (c) Freezer (d) All of these

(vii) A bomb calorimeter is used in _____ calorimetry
(a) Constant volume (b) Constant pressure
(c) Both a and b (d) Constant temperature

(viii) Boron Haber cycle is used to determine lattice energies of
(a) Molecular solids (b) Ionic solids
(c) Covalent solids (d) Metallic solids

(ix) $q = \Delta H$ when
(a) $\Delta V = 0$ (b) $P = 0$ (c) $\Delta E = 0$ (d) None of these

(x) Enthalpy of combustion for C is $-393.5\ kJmole^{-1}$

$C_{(s)} + O_2(g) \rightarrow CO_{2(g)}$ $\Delta H^{o}_{Combustion} = -393.5\ kJmole^{-1}$

Enthalpy of formation of CO_2 would be
(a) +393.5 kJ (b) -393.5 kJ (c) Zero
(d) Cannot be predicted form the given equation.

(xi) Which of the following is not a state function of a system.
(a) Thermal energy at constant pressure
(b) Enthalpy
(c) Internal energy
(d) Work done

(xii) For writing a thermochemical equation for enthalpy of combustion of an element requires,
(a) 1 mole of element as reactant
(b) 1 mole of oxide of element as product
(c) Standard states of all the substances
(d) Balanced equation of 1 mole of element

1. a 2. a, b 3. a, c, d 4. a, b, c, d

Name and define units of thermal energy

Define the terms system, surrounding, boundary, state function, heat capacity, internal energy, enthalpy of a substance.

Classify reactions as exothermic or endothermic.

Define bond dissociation energy.

Examine how heat of combustion can be used to estimate the energy available from foods.

Apply Hess's law to construct simple energy cycles.

Relate change in internal energy of a system with thermal energy at constant temperature and constant pressure.

When ethanol burns in oxygen, carbon dioxide and water are formed
(a) Write the equation which describes this reaction.
(b) Using the following data, calculate the enthalpy of combustion for ethanol C_2H_5OH.

ΔH_f° for ethanol(l) = -277.0 kJmole^{-1}

ΔH_f° $CO_{2(g)}$ = -393.5 kJ mole^{-1}, ΔH_f° water(l) = -285.8kJmole^{-1}

10. Calculate from the data in table 11.1 and 11.2 the enthalpy changes of the following reactions at standard conditions.

(a) $C_6H_{6(l)} \longrightarrow 6C_{(s)} + 3H_{2(g)}$ (Ans: -49.6 kJ/mole)

(b) $\frac{1}{2}N_{2(g)} + \frac{3}{4}H_2O_{(g)} \longrightarrow NH_{3(g)} + O_{2(g)}$ (Ans: 382.6 kJ)

11. The heat of combustion of liquid benzene, C_6H_6 to form H_2O and CO_2 at 1 atm and 25°C is –3268 KJmole^{-1} of benzene. What is the heat of formation of liquid benzene under these conditions. (Ans: +49.6 kJ/mole)

12. Specify conditions for the standard heats of reactions.

13. Sketch reaction pathway diagram in term of enthalpy changes of the reaction.

14. State and explain First law of Thermodynamics.

15. Calculate the work associated with the expansion of a gas from 50dm^3 to 68dm^3 at a constant external pressure of 10 atm. (Ans: 180 atm.dm^3)

16. Camphor ($C_{10}H_{16}O$) has a heat of combustion of 5903.6 KJ/mole. A sample of camphor having mass of 0.1204g is burned in a bomb calorimeter. The temperature increases by 2.28°C. Calculate heat capacity of the calorimeter. (Ans: 2.04531kJK^{-1})

17. In a coffee-cup calorimeter 100cm^3 of 1.0M HCl and 100 cm^3 of 1.0M NaOH are mixed at 24.6°C raised temperature by 6.9°C. Calculate the enthalpy of neutralization of HCl by NaOH from the given data. Heat capacity of water is 4.18 J/g°C. (Ans: -57.684 kJ/mole).

18. Calculate ΔH° for the reaction

$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$

from the following data

$S_{(s)} + \frac{3}{2}O_{2(g)} \longrightarrow SO_{3(g)}$ $\Delta H^\circ = -395.2$ kJ

$2SO_{2(g)}O_{2(g)} \longrightarrow 2SO_{3(g)}$ $\Delta H^\circ = -198.2$ kJ

19. An aluminium frying pan weighs 745g is heated on a stove from 25°C to 205°C. What is q for the frying pan? C_P for Al is 24.35 Jmole^{-1}K^{-1} (Ans: 120938.3 J)

20. Write the balanced equation for the formation reaction of each of the following substances

(a) C_4H_9OH (Butanol) (b) Rust, Fe_3O_4

(c) Acetic acid CH_3CO_2H (d) Urea $(NH_2)_2CO$

21. The human body burns glucose for energy. Burning 1.0g of glucose produces 15.65 kJ of heat.

(a) Write the balanced equation for the combustion of glucose.

(b) Determine the molar heat of combustion of glucose. (Ans: -2817kJ mole^{-1})

(c) Heats of combustions of C and H_2 are -393.5kJmole^{-1}and -285.8kJmolre^{-1} respectively. Determine the heat of formation of glucose. (Ans: -1258.8 kJ/mole)

22. Sketch the balanced chemical equation associated with each of the following enthalpy changes.
(a) Heat of sublimation of iodine.
(b) Heat of formation of gaseous atomic iodine.
(c) Heat of formation of $C_2H_5Cl_{(g)}$.
(d) Heat of combustion of benzene $C_6H_{6(l)}$.

23. The standard combustion enthalpies of carbon, hydrogen and acetic acid are -393.5 kJ mole^{-}, -285.8kJmole^{-1} and –875 kJmole^{-1} respectively. Deduce the value of standard enthalpy of formation of acetic acid, CH_3COOH. (Ans: -483.6 kJ/mole)

24. Is the conversion of magnetite, Fe_3O_4 to hematite, Fe_2O_3 by oxygen is endothermic or exothermic? Justify your answer.

$$3Fe(s) + 2O_{2(g)}\,Fe_3O_{4(s)} \longrightarrow Fe_3O_{4(s)} \quad \Delta H^\circ = -1118 \text{ kJ}$$

$$2Fe_{(s)} + O_{2(g)} \longrightarrow Fe_2O_{3(s)} \quad \Delta H^\circ = -824.2 \text{ kJ}$$

25. Which of the following processes would you expect to be endothermic?
(a) $H_2O_{(g)} \longrightarrow H_2O_{(l)}$
(b) $NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$
(c) $Mg^{+}_{(g)} + 2e^{-} \longrightarrow Mg_{(g)}$
(d) $O^{-1}_{(g)} + 1e^{-} \longrightarrow O^{-2}_{(g)}$
(e) $2Mg_{(s)} + O_{2(g)} \longrightarrow MgO_{(s)}$
(f) $NaCl_{(s)} \longrightarrow 2Na_{(s)} + Cl_{2(g)}$

26. Cooling effect is experienced when few drops of ethanol are put on your palm, Justify this statement.

$$C_2H_5OH_{(l)} \longrightarrow C_2H_5OH_{(g)} \quad \Delta H^\circ = 42.2 \text{ kJmole}^{-1}$$

27. In some countries liquid methanol is being used as an alternative fuel in cars and trucks. Industrially ethanol is produced by the following reaction.

$$CO_{(g)} + 2H_{2(g)} \xrightarrow{\text{catalyst}} CH_3OH_{(l)}$$

Standard enthalpies of formation of CH_3OH and CO are –238.7 kJmole^{-1} and -110.5kJmole^{-1} respectively. Will the reverse reaction be exothermic or endothermic. Justify your stand. (Ans: endothermic)

28. Methane is the major substance in natural gas. How much heat is released when 20 g of methane burns in excess of air under standard conditions. The standard enthalpies formation of CO_2, H_2O and CH_4 are -393.5 kJ/mole, -285.8 kJ/mole and -74.6 kJ/mole respectively. (Ans: 1113.125 kJ)

29. Evaluate the importance of Hess's Law.