CHAPTER # 11
THERMOCHEMISTRY

Q1. Define thermodynamic and thermochemistry.

Ans: Thermodynamic:

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

Thermochemistry:

The branch of thermodynamics that examines the heat involved in chemical reactions is called **thermochemistry**.

Note: 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.

Q2. Explain the role of energy in chemical reactions.

Ans: Role of Energy in Chemical Reactions:

i. The energy in the form of heat is either evolved or absorbed as a result of chemical reaction.

ii. This is because, in a chemical reaction old bonds are broken and new bonds are formed.

iii. Bond breaking always consumes energy and bond making always releases energy.

iv. When the energy released by bond forming is greater than the energy consumed by bond breaking, there is a net release of chemical energy.

v. Whereas energy is absorbed, when the energy of bond breaking is greater than the energy of bond forming.

Thus in chemical reactions energy is exchanged with the surroundings.

Q3. Define the terms system, surrounding, boundary, state function, heat capacity, internal energy, enthalpy of a substance.

Ans: Definitions of Terms Used in Thermodynamics:

1. System:

The part of the universe on which we wish to focus attention is called a system.

Surroundings:

The part of the universe except system is called surroundings.

Boundary:

The real or imaginary surface separating the system from surroundings is called boundary

2. State Function:

A property of a system that is determined by the state of the system regardless of how that condition was achieved is called state function

Examples:

Pressure (P), temperature (T), volume (V) and energy (E)

3. Heat:

Heat is the transfer of thermal energy between two bodies that are at different temperature

4. Heat Capacity:

The amount of heat required to raise the temperature of the given quantity of a substance by one kelvin is called heat capacity

5. Internal Energy:

The sum of all kinds of energies of all the particles of a system is called internal energy

6. Work:

The energy transferred when an object is moved by a force is called work

7. Enthalpy of a Substance (H):

It is defined as the system's internal energy (E) plus the product of its pressure and volume (PV). (for detail see section 11.4.1)

$$H = E + PV$$

Q4. Explain system and surroundings with the help of examples.

Ans: System:

The part of the universe on which we wish to focus attention is called a system. A system in chemistry is usually the substance undergoing physical or chemical change.

Surroundings:

The remaining part of the universe is called surroundings.

Boundary:

The real or imaginary surface separating the system from the surroundings is called the boundary.

Examples:

i. 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.

ii. 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.

Q5. Explain thermochemical reactions and also give its types.

Ans: Thermochemical Reactions:

A balanced chemical equation which also show heat change of a chemical reaction is called reaction is thermochemical equation.

The branch of chemistry which deals with the heat or thermal energy changes in chemical reactions is called thermochemistry.

There are two types of thermochemical reactions: -

(1) Exothermic Reactions:

(2) Endothermic Reactions:

Explanation:

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**.

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.

Solution:

Note: **Lighter** $\longrightarrow$ **Denser**

Energy is given out. Exothermic reaction

ΔH = Negative

Denser $\longrightarrow$ **Lighter**

Energy is taken in. Endothermic reaction

ΔH = Positive

Exothermic process:

These processes are favoured by low temperature and heat is release during this process.

Endothermic process:

These processes are favoured by high temperature and heat is absorbed during this process.

(a) Freezing of water:

Water freezes due to low temperature and it give out heat to its surrounding so it is an exothermic process.

(b) Combustion of methane:

All the combustion processes are exothermic because during these processes heat is released that is why combustion of methane is an exothermic process.

(c) Sublimation of dry ice:

Sublimation is a process in which solid converts directly into its vapours without converting into liquid. As we know gas (vapours) have high energy so energy is required for this process that is why it is an endothermic process.

(d) $H_2O\ (g) \longrightarrow H_2O\ (l)$

Gas molecules have high energy when they convert into liquid energy is released because the liquid molecules have low energy as compare to gas molecules. Thus, it is an exothermic process.

(e) Decomposition of limestone.

Decomposition of any substance requires energy that is why decomposition of limestone is an endothermic process.

Q6. Briefly describe the heat of reaction with the help of example.

Ans: Heat of 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**.

Enthalpy change:

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

Examples:

(i) $C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ = -393.5KJ$

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.

(ii) $H_2(g) + I_2(g) \longrightarrow 2HI(g) \qquad \Delta H^\circ = +53.8KJ$

This equation indicates that when 1 mole of H_2 gas combines with 1 mole of I_2 vapours to give 2 moles of HI(g), 53.8KJ energy is absorbed.

Note: 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.

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

$CO_2(g) \longrightarrow C(s) + O_2(g) \qquad \Delta H^\circ = +393.5KJ$

$2HI(g) \longrightarrow H_2(g) + I_2(g) \qquad \Delta H^\circ = -53.8KJ$

Q7. Briefly explain thermodynamics with the help of examples.

Ans: Thermodynamics:

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

Motion of automobile:

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.

Industrial products:

Chemicals and related industries manufacture products that release, absorb or retain energy.

Fertilizers:

Fertilizers help growing crops absorb solar energy and convert it into the chemical energy of food.

Batteries:

Batteries produce electric energy from chemical reaction.

Conclusion:

Thus the transformation of the energy from one form to another is an important field of science called thermodynamics.

Q8. Define the following terms.

i. State of the system **ii. Initial state final state**

iii. Open system, **iv. Close system and isolated system.**

Ans: i. State of the system

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

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.

Initial state:

The initial state of a system is its state before it undergoes a change.

Final state:

The final state of a system is its state after the change has occurred. In a chemical reaction, the description of the products defines the final state.

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

Open system:

In open system reactants and energy may be exchanged with surroundings.

Close system:

In a close system only energy may be exchanged with surrounding but not material.

Isolated system:

In an isolated system no energy and no material may be exchanged with surroundings. In fact there is no ideally isolated system. It is hypothetical system used for a comparison.

Q9. Write a detail note on state function and also give its examples.

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

OR

A property of a system which is determine by the state of the system and it is independent of the path by which it was achieved is called state function.

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.

Explanation:

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.

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 pressure ΔP are given by the equations.

$$\Delta T = T_2 - T_1$$

$$\Delta P = P_2 - P_1$$

Q10. Differentiate between Spontaneous and non-spontaneous reactions.

Ans:

Spontaneous reactions	Non-spontaneous reactions
i. The reactions which processed on their own and do not need any external energy to proceed are called spontaneous reactions.	**i.** The reactions which required external energy to proceed are called non spontaneous reactions.
ii. For example emission of rays from radioactive elements, burning of methane and coal.	**ii.** For example reaction of nitrogen and oxygen to make nitric oxide, thermal decomposition of P_2O_5

Q11. Define and explain the internal energy of a system.

Ans: Internal Energy:

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.

Mathematically:

$$\Delta E = E_2 - E_1$$

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

Explanation:

i. 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.

ii. 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.

iii. The kinetic energy of the particles is due to the translational, rotational and vibrational motions of particles.

iv. 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's forces.

Q12. How can we relate enthalpy change and heat of reaction or heat of combustion of a reaction?

Ans: Relation between Enthalpy Change and Heat of Reaction or Heat of Combustion of a Reaction:

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).

Mathematically:

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

The enthalpy change of a reaction can be positive or negative depending upon the process.

Exothermic:

Exothermic process, in which heat is released by the system of the surrounding ΔH is negative. Since, combustion is an exothermic process in which heat is released by the system to its surroundings, ΔH is negative.

Examples of exothermic reactions:

(I) $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H^\circ = -393.5KJ$

(ii) $2H_2(g) + O_{2(g)} \longrightarrow H_2O(l)$ $\Delta H^\circ = -571.6KJ$

(iii) $C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$ $\Delta H^\circ = -110.5KJ$

Endothermic:

Endothermic process, in which heat is absorbed by the system from the surroundings ΔH is positive.

Examples of endothermic reactions:

(i) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$ $\Delta H^\circ = +53.8KJ$

(II) $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$ $\Delta H^\circ = +131.4KJ$

(iii) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$ $\Delta H^\circ = +180.5KJ$

Q13. Why we can not measure the value of ΔH for the conversion of graphite to diamond in a calorimeter?

Ans: 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.

The value of ΔH for the conversion of graphite to diamond cannot be measured in a calorimeter because reaction is very slow under normal conditions.

Q14. Calculate the value of *ΔH* for the conversion of graphite to diamond by using following equations.

$C_{graphite}(s) \longrightarrow C_{diamond}(s)$ $\Delta H^\circ = ?$

(I) $C_{graphite}(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H^\circ = -393.5$ KJ

(ii) $C_{diamond}(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H^\circ = -395.4$ KJ

Ans: 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):

$C_{graphite}(s) \longrightarrow C_{diamond}(s)$ $\Delta H^\circ = ?$

(I) $C_{graphite}(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H^\circ = -393.5$ KJ

(II) $C_{diamond}(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H^\circ = -395.4$ KJ

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

(I) $C_{graphite}(s) + \emptyset_2(g) \longrightarrow C\emptyset_2(g)$ $\Delta H^\circ = -393.5$ KJ

(II) $C\emptyset_2(g) \longrightarrow C_{diamond}(s) + \emptyset_2(g)$ $\Delta H^\circ = +395.4$ KJ

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

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Conclusion:

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).

Q15. Explain standard enthalpy of reaction with the help of examples.

Ans: Standard Enthalpy of Reaction $\left(\Delta H_r^o\right)$

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:

(i) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ $\Delta H_r^o = -571.6KJ$

(ii) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ $\Delta H_r^o = -890.4KJ$

(iii) $2Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(s) + 2Fe(s)$ $\Delta H_r^o = -850KJ$

Q16. Define standard enthalpy of formation and how can we write thermochemical equation for enthalpy of reaction.

Ans: Standard Enthalpy of Formation $\left(\Delta H_f^o\right)$

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.

Table: 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
$N_2N_4(l)$	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
$H_2S(g)$	-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

Method to write thermochemical equation for enthalpy of formation:

i. Write elements as reactants and 1mole of the compound as product.

ii. Show standard states of all the substances.

iii. Finally balance the atoms.

Example:

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

Solution:

(i) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O\ (l)\ \Delta H_f^\circ = -285.8\ KJ\ mole^{-1}$

(ii) $S(s) + \frac{3}{2} O_2\ (g) \longrightarrow SO_3\ (g)\ \Delta H_f^\circ = -395.2\ KJ\ mole^{-1}$

(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

Q17. Define standard enthalpy of combustion and how can we write thermochemical equation for standard enthalpy of combustion?

Ans: Standard Enthalpy of Combustion $\left(\Delta H_c^o\right)$

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.

Table: Standard enthalpies of combustion in KJ mole $^{-1}$

H_2 (g)	-285.8	CH_4(g)	-890.4	$C_6H6(l)$	-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

Method to write Thermochemical equation for enthalpy of combustion:

i. Write 1mole of the element of compound and oxygen as reactant.

ii. Write oxides of the given element or oxides of elements present in the compound as products.

iii. Show standard states of all the substances.

iv. Finally, balance the atoms.

Example:

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

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) $H_2(g) + \frac{1}{2} O_2\ (g) \longrightarrow H_2O\ (l)$ $\Delta H_c^\circ = -285.8\ KJ\ mole^{-1}$

Q18. Define standard enthalpy of atomization and also give its examples.

Ans: Standard Enthalpy of Atomization $\left(\Delta H_{at}^o\right)$

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) $\frac{1}{2}H_2(g) \longrightarrow H(g)$ $\quad \Delta H^{o}_{at} = +218\ KJ\ mole^{-1}$

(ii) $\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$ $\quad \Delta H^{o}_{at} = +121\ KJ\ mole^{-1}$

Q19. Define standard enthalpy of neutralization with the help of example.

Ans: 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.,

$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H2O(l) \quad \Delta H^{o}_{n} = -57.4KJ\ mole^{-1}$

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

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

$Na^+(aq) + Cl^-(aq) + H_2O(l) \quad \Delta H^{o}_{n} = -57.4KJ\ mole^{-1}$

or $\quad H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)\ \Delta H^{o}_{n} = -57.4KJ\ mole^{-1}$

Q20. Define standard enthalpy of solution and also give its examples.

Ans: 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 solvent that further dilution results in no detectable heat change, under standard conditions. e.g.,

$NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq) \quad \Delta H^{o}_{sol} = +15.1KJ\ mole^{-1}$

$HCl(g) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq) \quad \Delta H^{o}_{sol} = +75KJ\ mole^{-1}$

SELF-CHECK EXERCISE 11.2

1. **Write thermochemical equation form the given information.**
   - **(I) Standard enthalpy of formation of benzene (*l*) is +49.0 kjmole^{-1}**
   - **(II) Standard enthalpy of formation of ethanol (*l*) is -277.7 kjmole^{-1}**
   - **(III) Standard enthalpy of combustion of acetic acid(*l*) is -876 kjmole^{-1}**
   - **(IV) When ethanol is burned in air –1367 KJmole^{-1} energy is released at 1 atm and 25^{o}c.**

Solution:

$(i)\ 6C\,(s) + 3H_2(g) \longrightarrow C_6H_6\,(l) \qquad \Delta H_f^o = +49.0\ KJ\ mole^{-1}$

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

$\Delta H_f^o = -277.7\ KJ\ mole^{-1}$

$(iii)\ CH_3COOH\,(l) + 2O_2(g) \longrightarrow 2CO_2 + 2H_2O\,(l)$

$\Delta H_f^o = -876\ KJ\ mole^{-1}$

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

$\Delta H_f^o = -1367\ KJ\ mole^{-1}$

2. Which of the following equations describe a reaction for which ΔH° is equal to the enthalpy of formation of a compound, ΔH_f°

(A) $4Al\,(s) + 2O_2\,(g) \longrightarrow 2Al_2O_3\,(s)$

(B) $2Al\,(s) + 3/2O_2\,(g) \longrightarrow Al_2O_3\,(s)$

(C) $CO\,(g) + 1/2O_2\,(g) \longrightarrow CO_2\,(g)$

Solution:

Condition:

i. Write elements as reactants and 1mole of the compound as product.

ii. Show standard states of all the substances.

iii. Finally balance the atoms.

(A) $4Al\,(s) + 2O_2\,(g) \longrightarrow 2Al_2O_3\,(s)$

As 2 moles of product ($2Al_2O_3$) produce, that is why this reaction does not represent the enthalpy of formation.

(B) $2Al\,(s) + 3/2\,O_2\,(g) \longrightarrow Al_2O_3\,(s)$

As 1 mole of product (Al_2O_3) produce from its elements under standard states, that is why this reaction represents the enthalpy of formation of Al_2O_3.

(C) $CO\,(g) + ½\,O_2\,(g) \longrightarrow CO_2\,(g)$

As the reactant (CO) is not an element, thus this reaction does not represent the enthalpy of formation of CO_2.

Q21. Explain bond dissociation energy and bond energy with the help of example.

Ans: Bond Dissociation Energy:

The amount of energy required to break one mole of a particular bond to form neutral atoms is called **bond dissociation energy.**

Bond Energy:

The amount of energy released when one mole of a particular bond form from neutral atoms is called bond energy.

Nature of reaction:

When a chemical reaction occurs, old bonds break and new bonds form. Bond breaking always requires energy and bond formation always releases energy.

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

Mathematically:

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.

$$\Delta H_{reaction} = \sum B.D.E_{\ reactants} - \sum B.E_{\ Products}$$

For reaction between H_2 and O_2 to produce H_2O:

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (l) \quad \Delta H^\circ = ?$$

ΔH_r° = 2 × B.D.E of $H_2(g)$ + B.D.E of $O_2(g)$ - 4 × B.E of O-H bonds

= 2 × (+436KJ) + 493.6KJ - 4 (460KJ)

= 1365 KJ - 1840KJ

ΔH_r° = - 474.4 KJ.

Conclusion:

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

Q22. Differentiate between Heat and temperature.

Ans:

Heat	Temperature.
i. Heat involves the transfer of energy between two objects due to temperature difference. It is the degree of hotness or coldness of a system.	**i.** Temperature is defined as the measure of average kinetic energy of the molecules of a substance.
ii. We use calorimeter for its measurement.	**ii.** We use thermometer for its measurement.
iii. It is not a state function.	**iii.** It is a state function.
iv. Its unit is kJ.	**iv.** Its units are °C, K, °F
v. It is mass dependent.	**v.** It is independent of mass.

Q23. Define heat capacity.

Ans: Heat Capacity:

The amount of heat required to raise the temperature of given amount of a substance by 1Kelvin is called heat capacity.

Unit:

It is expressed in joules per gram or joules per mole of the substance.

Explanation:

The amount of heat absorbed by a substance is proportional to the temperature change.

$$q \propto \Delta T$$

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

Where 'C' is constant of proportionality and is known as the heat capacity of the substance.

Mathematically:

$$\text{Heat Capacity} = \frac{\text{Heat}}{\Delta T}$$

Q24. Define specific heat capacity.

Ans: Heat capacity:

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

Unit:

It is expressed in Joules per gram per Kelvin.

Mathematically:

$$\text{Specific heat Capacity} = \frac{\text{Heat}}{\text{gram x } \Delta T}$$

Q25. Define molar heat capacity.

Ans: Molar heat capacity:

The amount of heat required to raise the temperature of one mole of a substance by one Kelvin is called its molar heat capacity.

Unit:

S.I. unit for molar heat capacity is $J.K^{-1}$ $mole^{-1}$.

Mathematically:

$$\text{Molar heat Capacity} = \frac{\text{Heat}}{\text{moles x } \Delta T}$$

Q26. How can you explain molar heat capacity of a substance at constant pressure?

Ans:

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.

$q_p = \Delta H$

$$C_P = \frac{q_P}{n(\Delta T)}$$

$$C_P = \frac{\Delta H}{n \Delta T}$$

or $\Delta H = nC_P\Delta T$

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

Q27. How can you explain molar heat capacity of a substance at constant volume?

Ans: 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.

Example:

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

∴ Molar heat Capacity of Cu = 0.387 x 63.54

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

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.

Note:

Re-arranging equation (i) we get,

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

Similarly, if we know mole of the substance then:

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

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

SELF-CHECK EXERCISE 11.3

1. Describe the difference between heat capacity and molar heat capacity.

Heat capacity	Molar heat capacity
i. The amount of heat required to raise the temperature of given amount of a substance by 1Kelvin is called heat capacity.	**i.** The amount of heat required to raise the temperature of one mole of a substance by one Kelvin is called its molar heat capacity.
ii. It is expressed in joules per gram or joules per mole of the substance.	**ii.** S.I. unit for molar heat.capacity is $J.K^{-1}$ $mole^{-1}$.
iii. $\text{Heat Capacity} = \frac{\text{Heat}}{\Delta T}$	**iii.** $\text{Molar heat Capacity} = \frac{\text{Heat}}{\text{moles} \times \Delta T}$

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)**

Solution:

$Mass\ of\ Al\ pan = 200\ g$

$C = 0.9\ Jg^{-1}K^{-1}$

$T_1 = 100\ ^\circ C$

$T_2 = 25\ ^\circ C$

$Change\ in\ temperature = \Delta T = T_1 - T_2$

$\Delta T = 100 - 25 = 75\ ^\circ C$

As the temperature difference on °C and K scale is same, therefore

$\Delta T = 75\ ^\circ C$

$q = ?$

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

$q = 200 \times 0.9 \times 75$

$q = 13500\ J$

Q28. Explain calorimetry and also give its types.

Ans: Calorimetry:

Calorimetry is the science of measuring heat of a chemical reaction by measuring the temperature change.

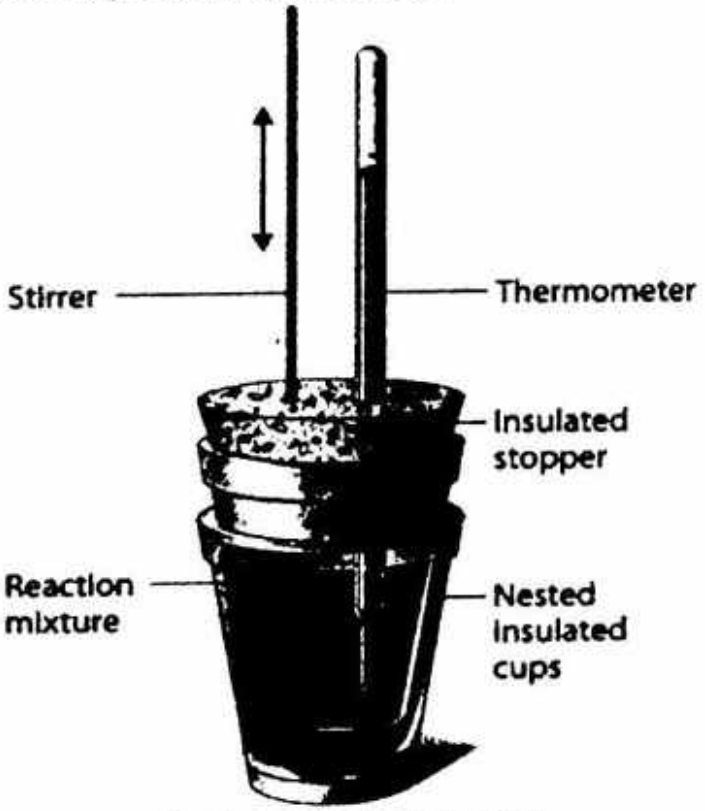
A device that measures heat flow is called calorimeter.

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.

i. 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.



Coffee cup calorimeter

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

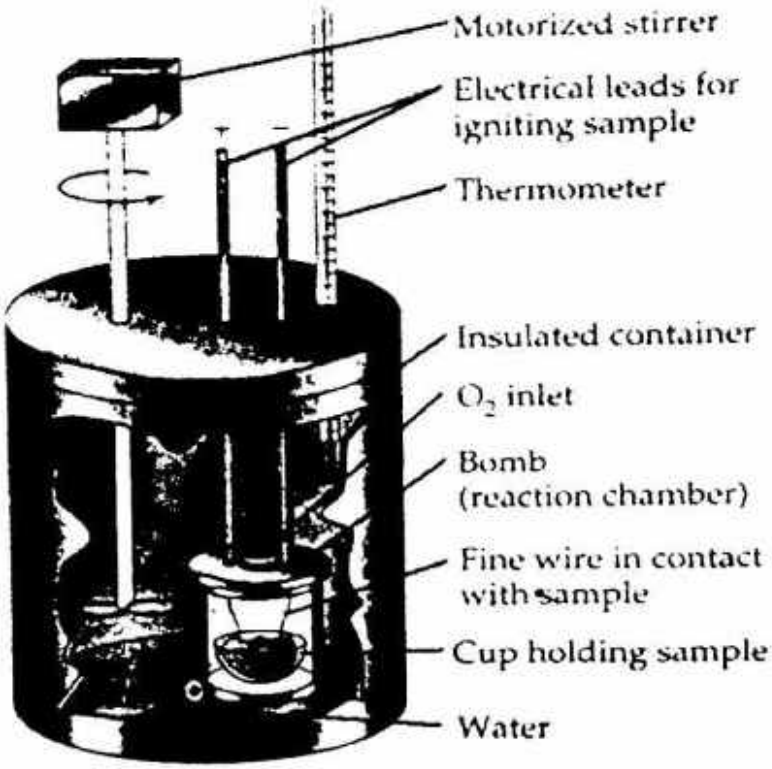
Where m = mass of reactants
C = specific heat of reaction mixture
ΔT = change in temperature.

ii. Constant Volume Calorimetry:

i. Constant volume calorimetry is used for accurate determination of the enthalpy of combustion for food, fuel and other compounds.

ii. 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.

iii. It consists of a strong closed vessel (the bomb) immersed in an insulated water bath.



Bomb calorimeter

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

Now

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

$q = 100g \times 4.2 J.g^{-1} K^{-1} \times 6.9K$

$q = 2.9 \times 10^3 J$

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

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

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

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 = 2.9×10^3 J

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

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

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

Since heat is evolved at constant pressure,

$q_p = \Delta H^\circ_n = -58.0\ KJ\ mole^{-1}$

SELF-CHECK EXERCISE 11.4

Experimental data shows that when 87.5 cm^3 of a 0.10M HCl solution is mixed with 25.0 cm^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:-47.8KJ)

Solution:

$Volume\ of\ NaOH = 25\ cm^3$

$Volume\ of\ HCl = 87.5\ cm^3$

$Total\ Volume\ of\ reaction\ mixture = 25\ cm^3 + 87.5\ cm^3 = 112.5\ cm^3$

$Density\ of\ water = 1\ g\ cm^3$

$Total\ mass\ of\ reaction\ mixture\ (m) = 112.5\ cm^3 \quad 1g\ cm^3 = 112.5\ g$

$Rise\ in\ temperature = \Delta T \quad 26.07^\circ C - 25^\circ C = 1.07^\circ C$

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

$q = 112.5 \times 4.2 \times 1.07 = 505.575\ J$

$Number\ of\ moles\ of\ NaOH = \dfrac{M \times Volume\ of\ solution}{1000} = \dfrac{0.35 \times 25}{1000}$

$= 0.00875\ moles$

$$Number\ of\ moles\ of\ HCl = \frac{0.1 \times 87.5}{1000} = 0.00875\ moles$$

Chemical reaction:

$$\underset{1\ mole}{NaOH\,(aq)} + \underset{1\ mole}{HCl\,(aq)} \longrightarrow \underset{1\ mole}{NaCl\,(aq)} + H_2O\,(l)$$

$$0.00875\ mole \qquad 0.00875\ mole \qquad 0.00875\ mole$$

$$Heat\ release\ during\ the\ formation\ of\ 0.00875\ moles\ of\ water = 505.575\ J$$

$$Heat\ release\ during\ the\ formation\ of\ 1\ moles\ of\ water = \frac{505.575}{0.00875}$$

$$= 5.78 \times 10^4\ J mole^{-1} = 57.8\ kJ\ mole^{-1}$$

At constant pressure

$$\Delta H_n^o = -57.8\ kJ\ mole^{-1}$$

Q29. How can we measure energy available from food?

Ans: 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 is used for measuring the energy available from food, which is just the enthalpy of combustion.

Activity

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. 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 = Δt = 31.52°c - 25°C

= 6.52 °C

Heat evolved = Δt × total heat capacity of calorimeter

= 6.52 × 4.321KJK^{-1}

= 28.1729 KJ

$$\text{Numer of moles of glucose burnt} = \frac{1.8g}{180g.mole^{-1}}$$

= 0.01 moles

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

Solution:

$Mass\ of\ glycerayl\ trioleate = 1.0\ g$

$Molecular\ mass\ of\ glycerayl\ trioleate\ (C_{57}H_{104}O_6)$

$= 12 \times 57 + 1 \times 104 + 16 \times 6 = 884\ g\ mole^{-1}$

$Rise\ in\ temperature = \Delta T = 8.77\ °C = 877K$

$Total\ heat\ capacity\ of\ calorimeter = 4.321\ kJ\ K^{-1}$

$Heat\ evolved = ?$

$Heat\ evolved = \Delta T \times total\ heat\ capacity\ of\ calorimeter$

$= 8.77 \times 4.321\ kJ\ K^{-1} = 37.895\ kJ$

$$Number\ of\ moles\ of\ glyceryl\ trioleate\ burnt = \frac{1\ g}{884\ g.mole^{-1}}$$

$$= 0.001131\ moles$$

$Heat\ produce\ by\ 0.0011\ moles\ of\ glyceryl\ trioleate = 37.895\ kJ$

$$Heat\ produce\ by\ 1\ moles\ of\ glyceryl\ trioleate = \frac{37.895\ g}{0.001131\ mole}$$

$= 3.35 \times 10^4\ kJ\ mole^{-1}$

Amount of heat available from this fat = $3.35 \times 10^4\ kJ\ mole^{-1}$

Q30. Explain HESS'S law apply HESS'S law to construct simple energy cycle. Also give the applications of HESS'S law.

Ans: 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.

Explanation:

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.

Mathematically:

$$\sum \Delta H \text{ (Cycle)} = 0$$

Example:

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:

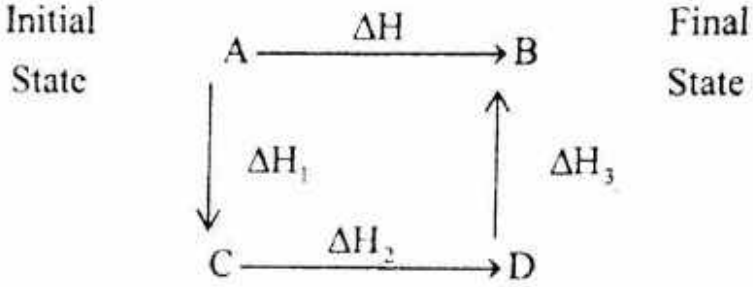


Fig. 11.4

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

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

HESS'S law to construct simple energy cycle:

Example:

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

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H^\circ = 68KJ$$

This reaction can be carried out in two steps.

$$N_2(g) + O_2(g) \longrightarrow 2NO(g) \qquad \Delta H_1^\circ = 180KJ$$

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H_2^\circ = -112KJ$$

Net reaction:

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H_1^\circ + \Delta H_2^\circ = 68KJ$$

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

$\Delta H^\circ = \Delta H_1^\circ + \Delta H_2^\circ = 68KJ$

For energy cycle see fig. 11.4.

Example:

Combustion of C to CO_2 evolves 393.5 KJ of energy.

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ = -393.5KJ$$

This reaction may takes place in two steps.

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H_1^\circ = -110.52KJ$$

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_2^\circ = -282.98KJ$$

Net reaction $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\qquad \Delta H_1^\circ + H_2^\circ = -393.51KJ$

Energy cycles:

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

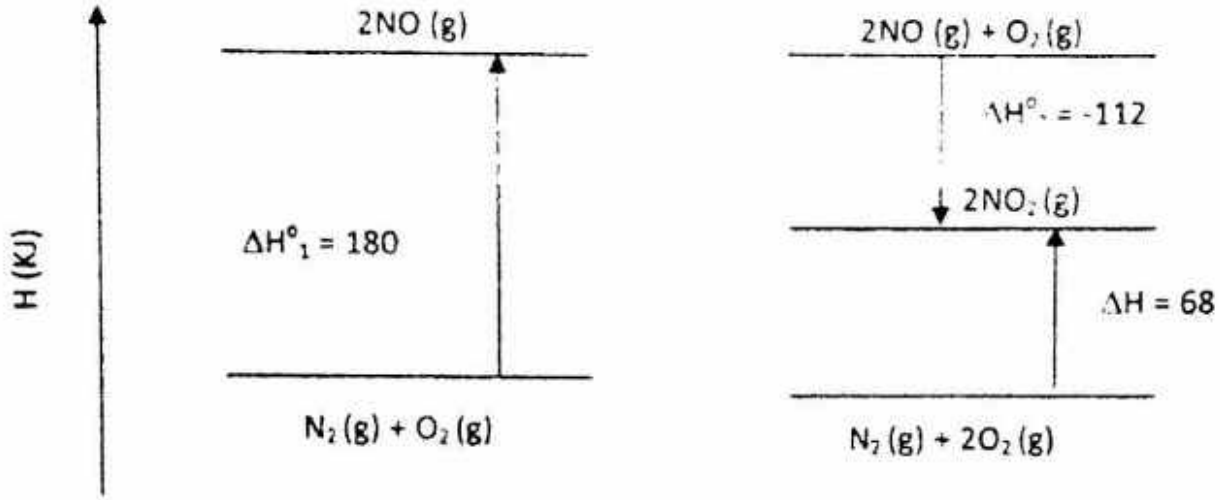


Fig: Energy cycle for the reaction between $N_2(g)$ and $O_2(g)$ to produce NO_2 (g)

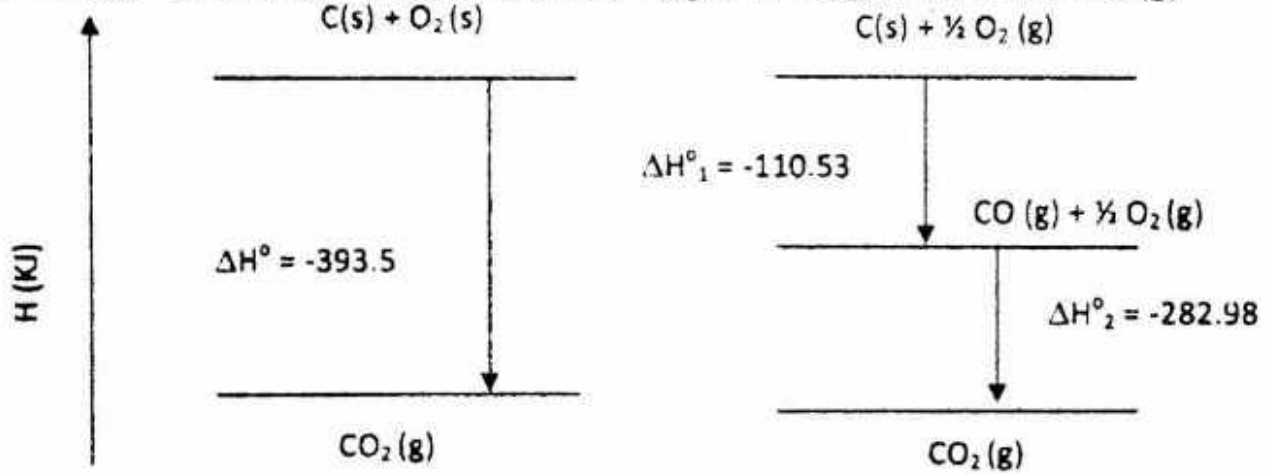


Fig: Energy cycle for the reaction between C(s) and O_2(g) to produce CO_2 (g)

Applications:

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 calorimeter.

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) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ $\Delta H^\circ = -890.4 KJ\ mole^{-1}$

(ii) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$ $\Delta H = -285.5 KJ\ mole^{-1}$

(iii) $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -393.5 KJ\ mole^{-1}$

(iv) $C(s) + 2H_2(g) \longrightarrow CH_4(g)$ $\Delta H^\circ = ?$

To obtain ΔH° for the required reaction we must somehow 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 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.

$CO_2(g) + 2H_2O(l)$	$\longrightarrow$	$CH_4(g) + 2O_2(g)$	$\Delta H^\circ = +890.4$ KJ
$2H_2(g) + O_2(g)$	$\longrightarrow$	$2H_2O(l)$	$\Delta H^\circ = -571.6$ KJ
$C(s) + O_2(g)$	$\longrightarrow$	$CO_2(g)$	$\Delta H^\circ = -393.5$ KJ
$C(s) + 2H_2(g)$	$\longrightarrow$	$CH_4(g)$	$\Delta H^\circ = -74.6\ KJ\ mole^{-1}$

This gives the required equation and its enthalpy.

Q31. How we can calculate standard enthalpies of reactions with the help of enthalpies of formation.

Ans: Enthalpies of Reactions from Enthalpies of Formation:

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

Mathematically:

$\Delta H^\circ = \sum$ coeff. ΔH_f° (products) - $\sum$ Coeff. ΔH_f° (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 1:

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, 0Kj, -393.5Kj and -285Kj 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:

$\Delta H^\circ_{reaction} = \sum coeff_p \Delta H_f^\circ$ (products) - $\sum coeff_r \Delta H_f^\circ$ (reactants)

= [16 × ΔH_f° for $CO_2(g)$ + 18 × ΔH_f° for $H_2O(l)$] –

[2 × ΔH_f° for C_8H_{18} (*l*) + 25 × ΔH_f° for $O_2(g)$]

= 16(-393.5KJ) + 18 (-285.8KJ) - 2 (-269KJ) - 25(0)

= -6296 KJ - 5144.4KJ + 538KJ + 0

= -11440.4 KJ + 538KJ

= -10902.4 KJ

= -1.09×10^4 KJ

Example 2:

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 -1258.18Kj, 0Kj, -393.5Kj and -285Kj for $C_6H_{12}O_6(s)$, $O_2(g)$, $CO_2(g)$ and $H_2O(l)$ respectively

Solution:

$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$ $\Delta H^\circ_{reaction} = ?$

$\Delta H^\circ_{reaction} = \sum Coeff_p \Delta H_f^\circ$ (products) - $\sum coeff_r (\Delta H_f^\circ$ (reactants)

ΔH° reaction = [6 ΔH_f° $CO_2(g)$ + 6 ΔH_f° ($H_2O(l)$]

– [ΔH_f° $C_6H_{12}O_6$ + 6 ΔH_f° $O_2(g)$]

= [6(-393.5KJ) + 6(–285.8KJ] – [–1258.18KJ + 6×0]

= [–2361.0KJ – 1714.8KJ] – [–1258.18KJ]

= –4075.8KJ + 1258.18KJ

= –2817.62KJ

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

Q32. Explain Born Haber cycle for the formation of NaCl Draw a complete Born Haber Cycle for the formation of NaCl. Calculate the lattice energy for NaCl.

Ans: Born Haber Cycle:

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

Lattice energy:

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 $mole^{-1}$

Cycle:

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 **108 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.

$Na(g) \longrightarrow Na^{+}(g) + 1e^{-} \quad \Delta H^{\circ}_{IE} = +496$ KJ/mole

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.

$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g) \quad \Delta H^{\circ}_{at} = +121$ KJ/mole

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

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

$Cl(g) + 1e^{-} \longrightarrow Cl^{-}(g) \qquad \Delta H^{\circ}_{EA} = -349$ 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.

$Na^{+}(g) + Cl^{-}(g) \longrightarrow NaCl(s) \qquad \Delta H^{\circ}_{l} = ?$

Calculation of lattice energy of NaCl:

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

$$\Delta H^{\circ}_{f} = \Delta H^{\circ}_{s} + \Delta H^{\circ}_{IE} + \Delta H^{\circ}_{at} + \Delta H^{\circ}_{EA} + \Delta H^{\circ}_{l}$$

$$-411KJ = +108KJ + 496KJ + 121KJ + (-349KJ) + \Delta H^{\circ}_{l}$$

$$\Delta H^{\circ}_{l} = -411KJ - (108\ KJ + 4961KJ + 121KJ - 349KJ)$$

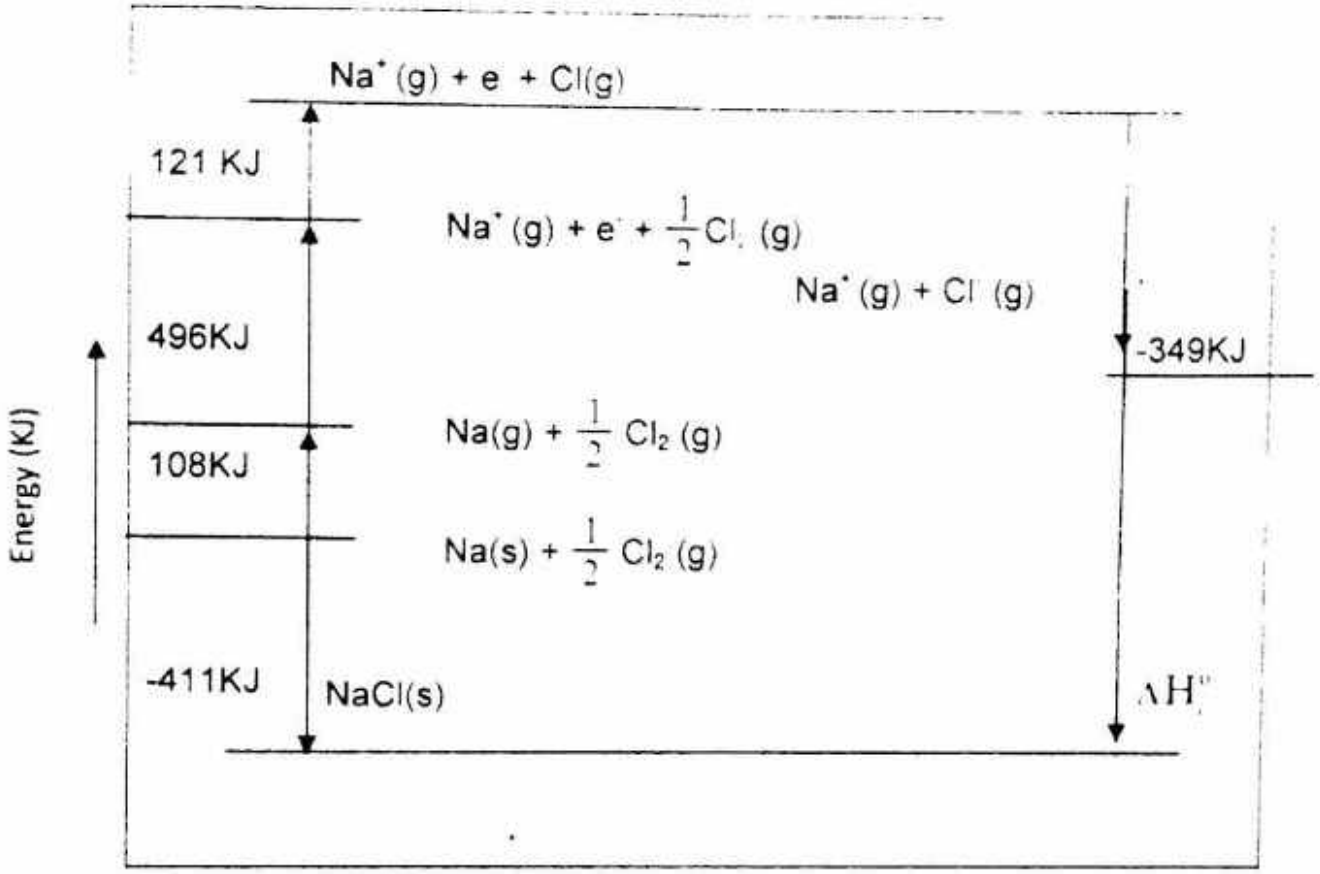
$$\Delta H^{\circ}_{l} = -787KJ\ mole^{-1}$$

Thus lattice energy of NaCl is 787 KJ/mole.

$Na(s)$	$\longrightarrow$	$Na(g)$	1st Step
$Na(g)$	$\longrightarrow$	$Na^{+}(g) + 1e^{-}$	2nd Step
$\frac{1}{2}Cl_2(g)$	$\longrightarrow$	$Cl(g)$	3rd Step
$Cl(g) + 1e^{-}$	$\longrightarrow$	$Cl^{-}(g)$	4th Step
$Na^{+}(g) + Cl^{-}(g)$	$\longrightarrow$	$NaCl(s)$	5th Step
$Na(s) + \frac{1}{2}Cl_2(g)$	$\longrightarrow$	$NaCl(s)$	Net reaction

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

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.

i) **Standard enthalpy of formation of MgO = -602 KJmole^{-1}**
ii) **Standard enthalpy of sublimation of Mg = 150KJmole^{-1}**
iii) **Ionization energy of Mg(g) to form Mg^{+2}(g) is 2180 KJ mole^{-1}**
iv) **Standard enthalpy of atomization of O_2 = 247 KJ mole^{-1}**
v) **Electron affinity of O (g) to form O^{-1} (g) = -141 KJ mole^{-1}**
vi) **Electron affinity of O^{-1}(g) to form O^{-2} (g) = 878 KJ mole^{-1}**

(Ans: -1367.4KJ)

Solution: $\Delta H_f^o = \Delta H_s^o + \Delta H_{I.E}^o + \Delta H_{at}^o + \Delta H_{E.A\,(I)}^o + \Delta H_{E.A\,(II)}^o + \Delta H_l^o$

$-602\ kJ = +150\ kJ + 2180\ kJ + 247\ kJ + (-141\ kJ) + 878\ kJ + \Delta H_l^o$

$\Delta H_l^o = -602\ kJ - (+150kJ + 2180\ kJ + 247\ kJ - 141\ kJ + 878\ kJ)$

$\Delta H_l^o = -602\ kJ - 3314\ kJ = -3916\ kJ\ mole^{-1}$

To calculate the lattice energy of MgO following steps must be addopted

$Mg(s) \longrightarrow Mg(g)$ *Step − 1*

$Mg(g) \longrightarrow Mg^{2+}(g) + 2e^{-1}$ *Step − 2*

$\frac{1}{2}O_2(g) \longrightarrow O(g)$ *Step – 3*

$O(g) + 1e^- \longrightarrow O^-(g)$ *Step – 4*

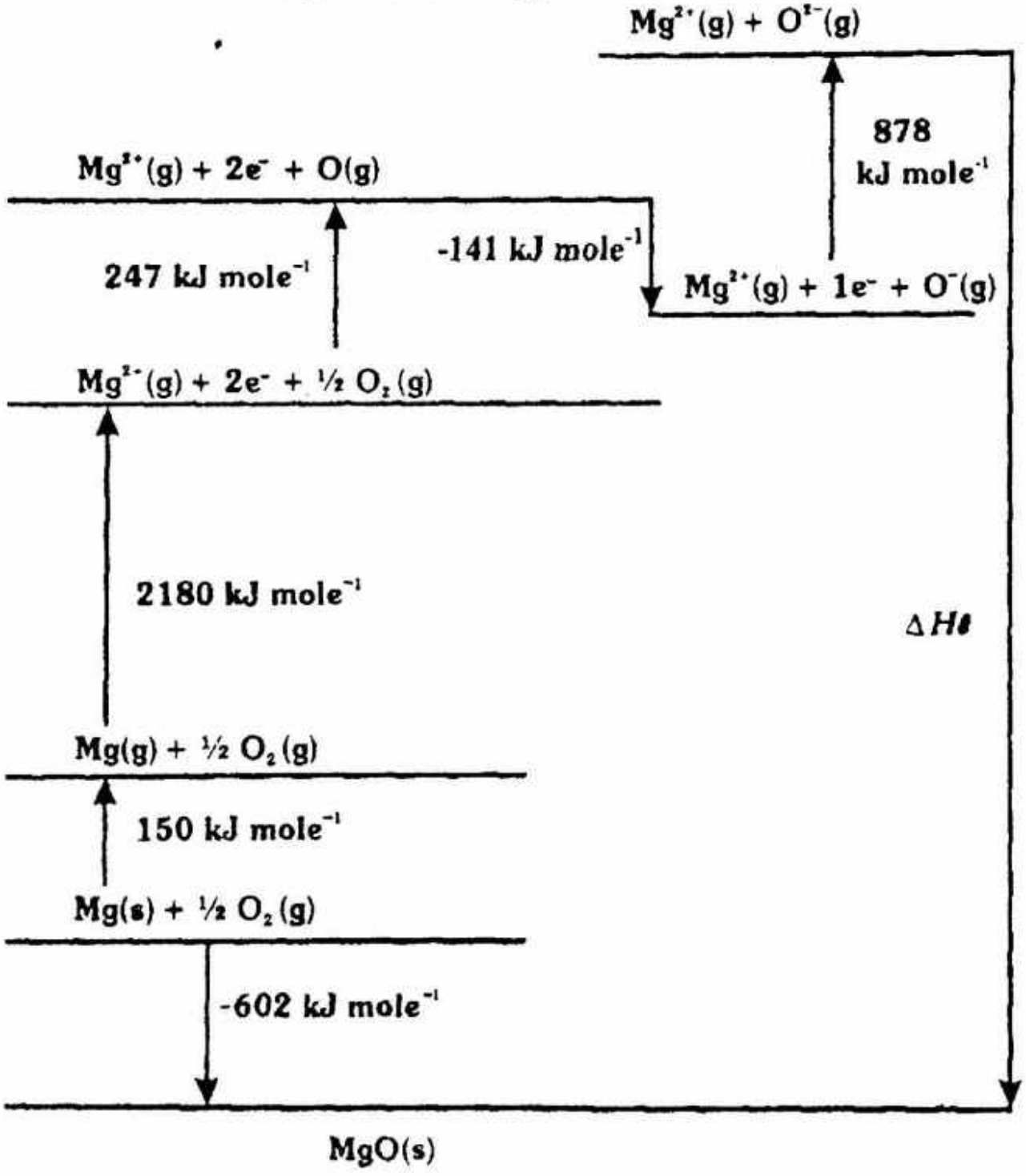
$O^-(g) + 1e^- \longrightarrow O^{2-}(g)$ *Step – 5*

$Mg^{2+}(g) + O^{2-}(g) \longrightarrow MgO(s)$ *Step – 6*

$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$

The sum of these steps gives the overall desired reaction.

The Born-Haber for MgO lattice energy is



SUMMARY OF 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 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.

EXERCISE

MULTIPLE CHOICE QUESTIONS

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.

SUMMARY OF KEY TERMS

- The branch of chemistry which deals with the heat or thermal energy changes in chemical reactions is called thermochemistry
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- 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.
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EXERCISE

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(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}

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^\circ_{Combustion} = -393.5$ 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

Answers

i. d	**ii. a**	**iii. c**	**iv. a**	**v. b**	**vi. b**	**vii. a**
viii. b	**ix. b**	**x. b**	**xi. d**	**xii. 3**		

2. Name and define units of thermal energy.

Ans: Units of Thermal Energy:

SI Unit:

Unit of heat or thermal energy used in SI system is the Joule (J).

Joule (J):

It is defined as the energy required to move an object or a particle through a distance of one meter by a force of one Newton.

Common Unit of Heat:

Common unit of heat is the calorie.

Calorie:

It is defined as the heat or thermal energy required to raise the temperature of one gram of water from 14.5 to 15.5°C.

Relationship:

1 Calorie = 4.18 Joules

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

Ans: System:

The part of the universe on which we wish to focus attention is called a system.

Surroundings:

The part of the universe except system is called surroundings.

Boundary:

The real or imaginary surface separating the system from surroundings is called boundary

State Function:

A property of a system that is determined by the state of the system regardless of how that condition was achieved is called state function

Examples:

Pressure (P), temperature (T), volume (V) and energy (E)

Heat Capacity:

The amount of heat required to raise the temperature of the given quantity of a substance by one kelvin is called heat capacity

Internal Energy:

The sum of all kinds of energies of all the particles of a system is called internal energy

Enthalpy of a Substance (H):

It is defined as the system's internal energy (E) plus the product of its pressure and volume (PV). (for detail see section 11.4.1)

$$H = E + PV$$

4. Classify reactions as exothermic or endothermic.

Ans: (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 derive an engine or to cook food.

Examples of exothermic reactions:

(i) $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H^\circ = -393.5KJ$

(ii) $2H_2(g) + O_2(g) \longrightarrow H_2O(l)$ $\Delta H^\circ = -571.6KJ$

(iii) $C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$ $\Delta H^\circ = -110.5KJ$

(2) Endothermic Reactions:

A chemical reaction that proceeds with the absorption of heat is called an endothermic reaction In these reaction heat is transferred from surrounding to the system.

Examples of endothermic reactions:

(i) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$ $\Delta H^\circ = +53.8KJ$

(ii) $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$ $\Delta H^\circ = +131.4KJ$

(iii) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$ $\Delta H^\circ = +180.5KJ$

5. Define bond dissociation energy.

Ans: Bond Dissociation Energy:

The amount of energy required to break one mole of a particular bond to form neutral atoms is called bond dissociation energy.

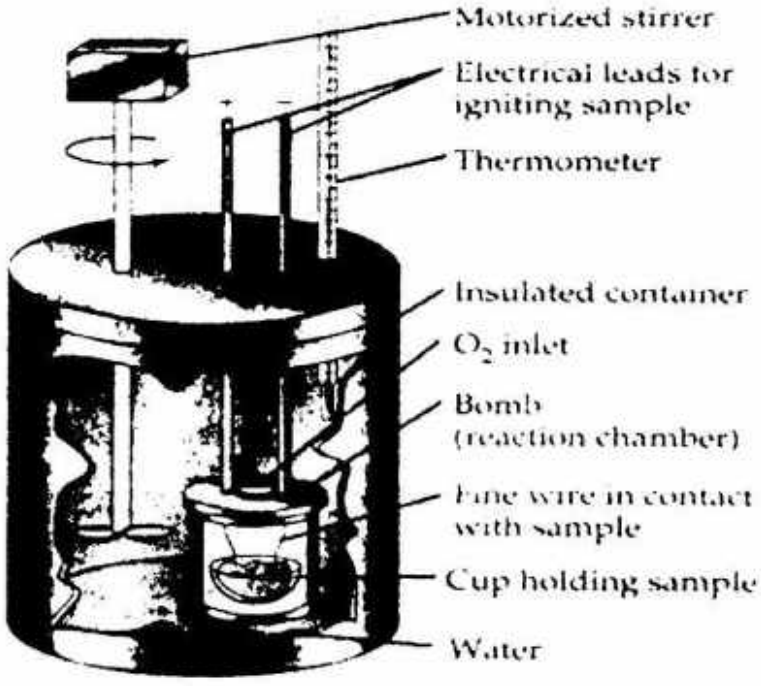
6. Describe how heat of combustion can be used to estimate the energy available from foods.

Ans: Constant Volume Calorimetry:

i. Constant volume calorimetry is used for accurate determination of the enthalpy of combustion for food, fuel and other compounds.

ii. 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

iii. It consists of a strong closed vessel (the bomb) immersed in an insulated water bath



Bomb calorimeter

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 is used for measuring the energy available from food, which is just the enthalpy of combustion.

Activity

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. 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 = Δt = 31.52°c - 25°C = 6.52 °C

Heat evolved = Δt × total heat capacity of calorimeter

= 6.52 × 4.321KJK^{-1} = 28.1729 KJ

Number of moles of glucose burnt = $\frac{1.8g}{180g.mole^{-1}}$ = 0.01 moles

Since 28.1729 KJ of 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 $KJmole^{-1}$.

7. Apply Hess's law to construct simple energy cycles.

Ans: HESS'S law to construct simple energy cycle:

HESS'S law can be use to construct energy cycles.

Example: **Oxidation of nitrogen to produce nitrogen dioxide absorbs 68KJ of energy.**

$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g)$ $\quad \Delta H^\circ = 68KJ$

This reaction can be carried out in two steps.

$N_2(g) + O_2(g) \longrightarrow 2NO(g)$ $\quad \Delta H_1^\circ = 180KJ$

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $\quad \Delta H_2^\circ = -112KJ$

Net reaction:

$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g)$ $\quad \Delta H_1^\circ + \Delta H_2^\circ = 68KJ$

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

$\Delta H^\circ = \Delta H_1^\circ + \Delta H_2^\circ = 68KJ$

For energy cycle see fig. 11 4.

Example:

Combustion of C to CO_2 evolves 393.5 KJ of energy.

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\quad \Delta H^\circ = -393.5KJ$

This reaction may takes place in two steps.

$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$ $\quad \Delta H_1^\circ = -110.52KJ$

$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ $\quad \Delta H_2^\circ = -282.98KJ$

Net reaction $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\quad \Delta H_1^\circ + H_2^\circ = -393.51KJ$

Energy cycles:

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

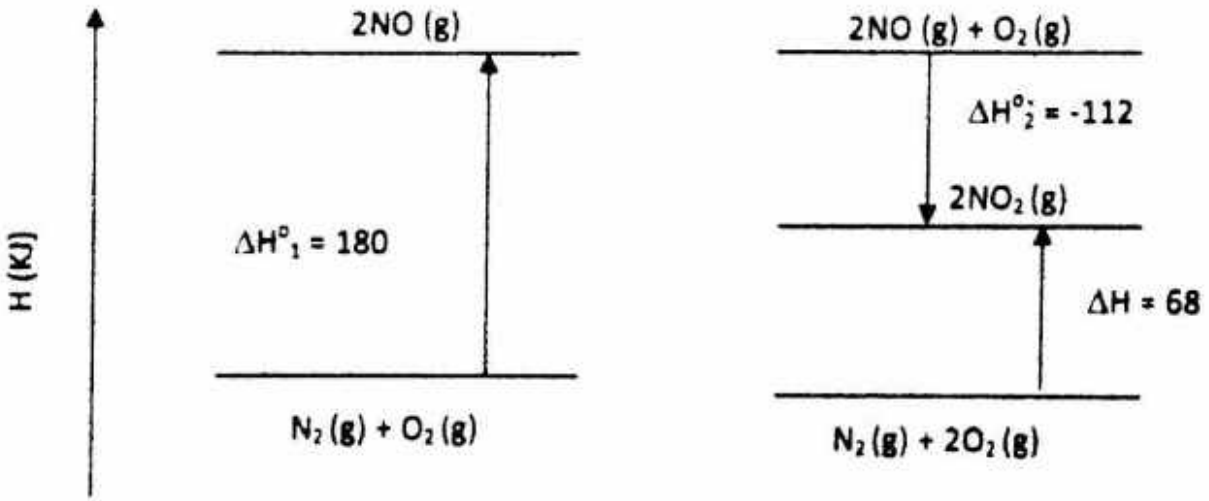


Fig: Energy cycle for the reaction between $N_2(g)$ and $O_2(g)$ to produce NO_2 (g)

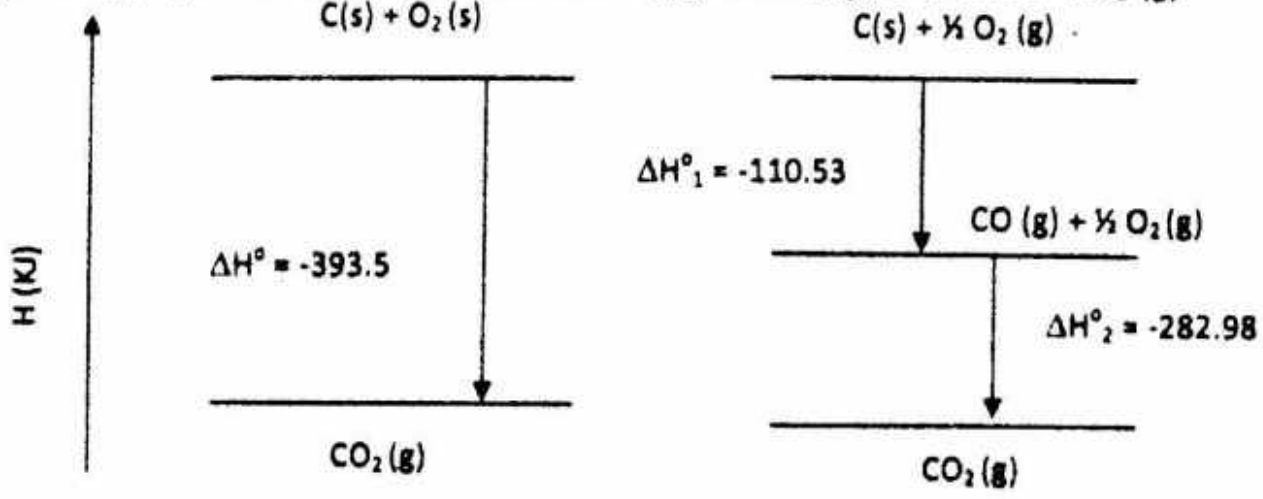


Fig: Energy cycle for the reaction between C(s) and O_2(g) to produce CO_2 (g)

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

Ans: 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,

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

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,

$$q_p = \Delta H = \Delta E + P\Delta V \quad \text{.....(1)}$$

Enthalpy:

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.

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:

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.

Equation (1) can be written as

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

Conclusion:

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.

9. 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}

Solution:

(a) $C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ ΔH_c° = -1367 kJ mole^{-1}

(b) Required equation:

Heat of combustion of liquid $C_2H_5OH_{(l)}$

$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ ΔH° = ?

Given equations:

ΔH_f° liquid ethanol ($C_2H_5OH_{(l)}$)

$$2C_{(s)} + 3H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow C_2H_5OH_{(l)} \quad \Delta H_f^o = -277.0 \text{ kJ mole}^{-1} \ldots\ldots\ldots\ldots \text{(i)}$$

ΔH_f° of gaseous $CO_{2(g)}$

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H_f^o = -393.5 \text{ kJ mole}^{-1} \ldots\ldots\ldots\ldots \text{(ii)}$$

ΔH_f° of liquid $H_2O_{(l)}$

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

To get the require equation following steps should be adopted

Step 1: Multiply equation (ii) by 2,
Step 2: Multiply equation (iii) by 3,
Step 3: Reverse equation (i),
Step 4: Then add all the resulting equations, we get the required the enthalpy of combustion for ethanol C_2H_5OH.

$$2C_{(s)} + 2O_{2(g)} \longrightarrow 2CO_{2(g)} \quad \Delta H = -787.0 \text{ kJ mole}^{-1}$$

$$3H_{2(g)} + \frac{3}{2}O_{2(g)} \longrightarrow 3H_2O_{(l)} \quad \Delta H = -857.4 \text{ kJ mole}^{-1}$$

$$C_2H_5OH_{(l)} \longrightarrow 2C_{(s)} + 3H_{2(g)} + \tfrac{1}{2}O_{2(g)} \quad \Delta H = +277.0 \text{ kJ mole}^{-1}$$

$$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)} \quad \Delta H_c^o = -1367.4 \text{ kJ mole}^{-1}$$

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

(a) $C_6H_6(l) \rightarrow 6C(s) + 3H_2(g)$ **(Ans: -49.6 KJ/mole)**

(b) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2O(g) \rightarrow NH_3(g) + \frac{3}{4}O_2(g)$ **(Ans: 321.55 KJ)**

Solution:

(a) $C_6H_6(l) \rightarrow 6C(s) + 3H_2(g)$

Required equation:

Heat of decomposition of liquid $C_6H_{6(l)}$

$C_6H_{6(l)} \longrightarrow 6C_{(s)} + 3H_{2(g)}$ $\Delta H°=?$

Give equations:

Heat of combustion of liquid benzene $C_6H_{6(l)}$

$C_6H_{6\ (l)} + \frac{15}{2} O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)}$ $\Delta H° = -3268$ kJ mole^{-1} .....(i)

Heat of formation of gaseous $CO_{2(g)}$

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H° = -393.5$ kJ mole^{-1} .....(ii)

Heat of formation of liquid $H_2O_{(l)}$

$H_{2(g)} + ½\ O_{2(g)} \longrightarrow H_2O_{(l)}$ $\Delta H° = -285.8$ kJ mole^{-1} .....(iii)

To get the require equation following steps should be adopted.

Step 1: Multiply equation (ii) by 6 and reverse the equation.

Step 2: Multiply equation (iii) by 3 and reverse the equation.

Step 3: Take equation (i) without any change.

Step 4: Then add all the resulting equations, we get required enthalpy changes.

$6CO_{2(g)} \longrightarrow 6C_{(s)} + 6O_{2(g)}$ $\Delta H° = +2361.0$ kJ mole^{-1}

$3H_2O_{(l)} \longrightarrow 3H_{2(g)} + 3/2\ O_{2(g)}$ $\Delta H° = +857.4$ kJ mole^{-1}

$C_6H_{6(l)} + \frac{15}{2} O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)}$ $\Delta H° = -3268$ kJ mole^{-1}

$C_6H_{6(l)} \longrightarrow 6C_{(s)} + 3H_{2(g)}$ $\Delta H° = -49.6$ kJ mole^{-1}

(b) $\frac{1}{2}\mathbf{N_2(g)} + \frac{3}{2}\mathbf{H_2O(g)} \rightarrow \mathbf{NH_3(g)} + \frac{3}{4}\mathbf{O_2(g)}$

Required equation:

$\frac{1}{2} N_{2(g)} + \frac{3}{2} H_2O_{(g)} \longrightarrow NH_{3(g)} + \frac{3}{4} O_{2(g)}$ $\Delta H° = ?$

Given equations:

Heat of formation of gaseous $NH_{3(g)}$

$\frac{1}{2} N_{2(s)} + \frac{3}{2} H_{2(g)} \longrightarrow NH_{3(g)}$ $\Delta H° = -46.1$ kJ mole^{-1} .....(i)

Heat of formation of gaseous $H_2O_{(g)}$

$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(g)}$ $\Delta H° = -245.1$ kJ mole^{-1} .....(ii)

To get the require equation following steps should be adopted.

Step 1: Multiply equation (ii) by $\frac{3}{2}$ and reverse the equation.

Step 1: Take equation (i) as such.

Step 1: Then add all the resulting equations, we get

$\frac{1}{2} N_{2(s)} + \frac{3}{4} H_{2(g)} \longrightarrow NH_{3(g)}$ $\Delta H° = -46.1$kJ

$\frac{1}{2} H_2O_{(g)} \longrightarrow \frac{3}{2} H_{2(g)} + \frac{3}{4} O_{2(g)}$ $\Delta H° = +367.65$ kJ

$\frac{1}{2} N_{2(g)} + \frac{3}{2} H_2O_{(g)} \longrightarrow NH_{3(g)} + \frac{3}{4} O_{2(g)}$ $\Delta H° = +321.55$ 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)**

Solution: **Required equation:** Heat of formation of $C_6H_{6(l)}$

$$6C_{(S)} + 3H_{2(g)} \longrightarrow C_6H_{6(l)} \quad \Delta H^\circ = ?$$

Given equations: Heat of combustion of liquid benzene $C_6H_{6(l)}$

$$C_6H_{6(l)} + \frac{15}{2} O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)} \quad \Delta H^\circ = -3268 kJ\ mole^{-1} \quad (i)$$

Heat of formation of gaseous $CO_{2(g)}$

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

Heat of formation of liquid $H_2O_{(l)}$

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

To get the require equation following steps should be adopted.

Step 1: Multiply equation (ii) by 6. **Step 2:** Multiply equation (iii) by 3.

Step 3: Reverse equation (i).

Step 4: Then add all the resulting equation, we get

$$6C_{(S)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} \quad \Delta H^\circ = -2361.0\ kJ\ mole^{-1}$$

$$3H_{2(g)} + \frac{3}{2} O_{2(g)} \longrightarrow 3H_2O_{(l)} \quad \Delta H^\circ = -857.4\ kJ\ mole^{-1}$$

$$6CO_{2(g)} + 3H_2O_{(l)} \longrightarrow C_6H_{6(l)} + \frac{15}{2} O_{2(g)} \quad \Delta H^\circ = +3268.0\ kJ\ mole^{-1}$$

$$6C_{(S)} + 3H_{2(g)} \longrightarrow C_6H_{6(l)} \quad \Delta H^\circ = +49.6\ kJ\ mole^{-1}$$

12. Specify conditions for the standard heats of reactions.

Ans: Condition for Standard Heat of Reaction:

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.

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

Ans: HESS'S law to construct simple energy cycle:

HESS'S law can be use to construct energy cycles.

Example: Oxidation of nitrogen to produce nitrogen dioxide absorbs 68KJ of energy.

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \quad \Delta H^\circ = 68KJ$$

This reaction can be carried out in two steps.

$$N_2(g) + O_2(g) \longrightarrow 2NO(g) \quad \Delta H_1^\circ = 180KJ$$

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \quad \Delta H_2^\circ = -112KJ$$

Net reaction: $N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \quad \Delta H_1^\circ + \Delta H_2^\circ = 68KJ$

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

$\Delta H^\circ = \Delta H_1^\circ + \Delta H_2^\circ = 68KJ$

For energy cycle see fig. 11.4.

Example: Combustion of C to CO_2 evolves 393.5 KJ of energy.

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ = -393.5KJ$$

This reaction may takes place in two steps.

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H_1^\circ = -110.52KJ$$

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_2^\circ = -282.98KJ$$

Net reaction $C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_1^\circ + H_2^\circ = -393.51KJ$

Energy cycles:

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

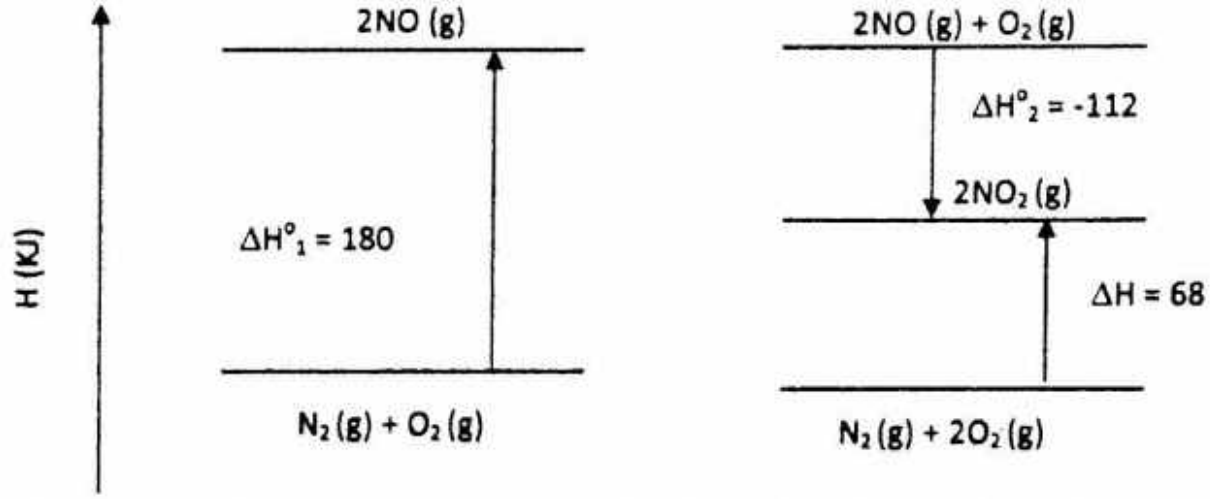


Fig: Energy cycle for the reaction between $N_2(g)$ and $O_2(g)$ to produce NO_2 (g)

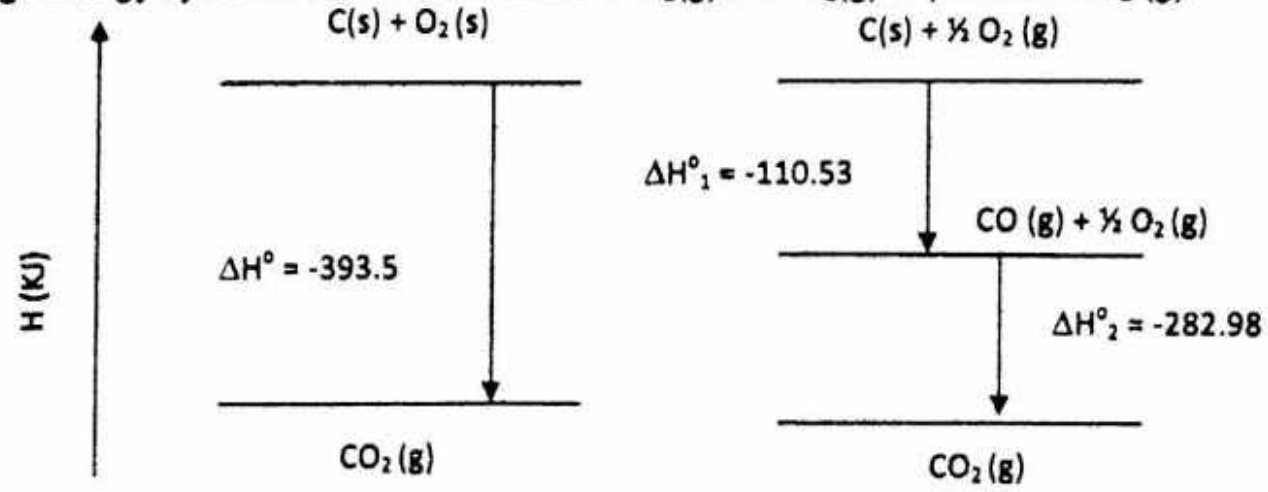


Fig: Energy cycle for the reaction between C(s) and $O_2(g)$ to produce CO_2 (g)

14. State and explain First law of Thermodynamics.

Ans: First Law of Thermodynamics:

Energy can neither be created nor be destroyed during a chemical reaction but it can be transferred from one form to another form.

OR

The total energy of a system and its surroundings always remain conserve.

OR

Total energy of the universe always remain conserve.

Mathematically:

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.

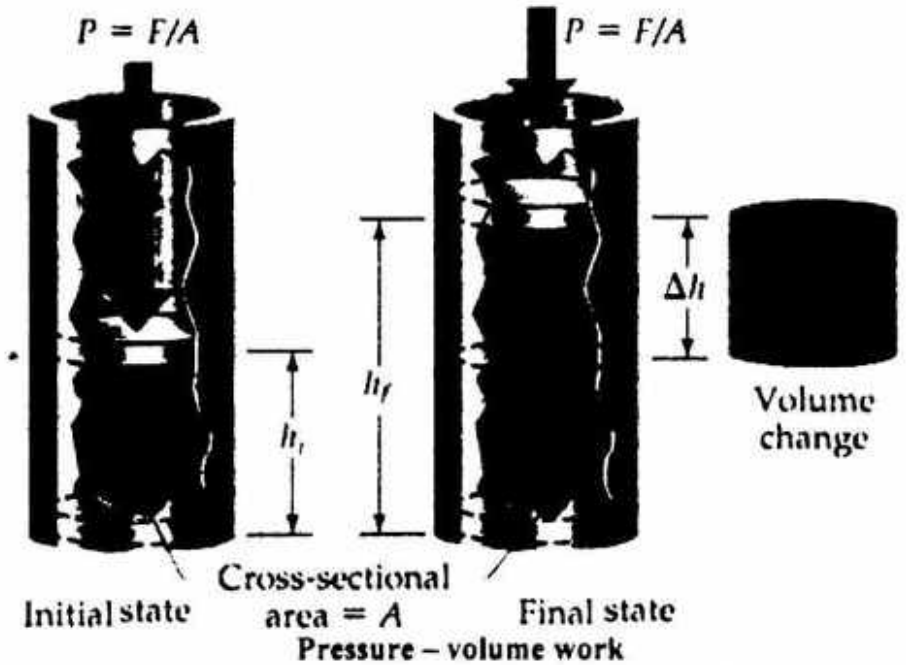
Conversion of signs:

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.

Explanation:

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



Pressure – volume work

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:

Work = force x area $\quad W = F \times \Delta h$ ---------- **(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.

$$W = -P\Delta V$$

Pressure – volume work:

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:

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

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)

Solution: $Here \quad P = 10\ atm$

$$\Delta V = V_2 - V_1 = 68 - 50 = 18\ dm^3$$

$As \quad w = P\Delta V$

$So \quad w = 10 \times 18$

$= 180\ atm.dm^3$

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:3.2798KJ/K/mole)

Solution: Mass of camphor $= m = 0.1204$ g

Increase in temperature $= \Delta T = 2.28°C$ or 2.28 K

Enthalpy of combustion $= \Delta H_c^o = 5903.6$ kJ mole^{-1}

Molar mass of camphor ($C_{10}H_{16}O$) $= 12 \times 10 + 1 \times 16 + 16$

$= 152$ g mole^{-1}

Number of moles of camphor $= \frac{0.1204\ g}{152\ g\ mole^{-1}} = 7.92 \times 10^{-4}$ moles

1 mole of camphor produce heat $= 5903.6$ kJ

7.92×10^{-4} moles of camphor produce heat $= 5903.6 \times 7.92 \times 10^{-4}$

$= 4.675$ kJ

In a constant volume calorimeter

Heat evolved $= \Delta T \times$ Total heat capacity of calorimeter

4.675 kJ = 2.28 × Total heat capacity of calorimeter

$\frac{4.675}{2.28}$ = Total heat capacity of calorimeter

or Total heat capacity of calorimeter = $\frac{4.675}{2.28}$ = 2.05 kJ K^{-1}

17. In a coffee-cup calorimeter 100cm³ of 1.0M HCl and 100 cm³ 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).

Solution:

Volume of HCl = 100 cm^3

Total Volume of reaction mixture = 100 cm^3 + 100 cm^3 = 200cm^3

Volume of NaOH = 100 cm^3

Density of water = 1 g cm^{-3}

Total mass of reaction mixrure (m) = 200 cm^3 × 1g.cm^{-3} = 200g

Rise in temperature = ΔT = 6.9°C

Heat capacity of water = C = 4.18 J g^{-1} $°C^{-1}$

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

$q = 200g \times 4.2\ J\ g^{-1}\ °C^{-1} \times 6.9°C$

$q = 5.796 \times 10^3\ J$

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

$= \frac{1 \times 100}{1000} = 0.10\ moles$

Now. No of moles of HCl = $\frac{1 \times 100}{1000} = 0.10\ moles$

Consider chemical equation.

$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$

1 mole 1 mole 1 mole

0.1 mole 0.1 mole 0.1 mole

Formation of 0.1 moles of water release heat = 5.796×10^3 J

Formation of 1 mole of water will release heat = $\frac{5.796 \times 10^3 J}{0.10}$ = 5.796 x 10^4J $mole^{-1}$

= 57.96 kJ $mole^{-1}$

Thus heat evolved at constant pressure will be,

$q_p = \Delta H_n^o$ = - 57.96 kJ $mole^{-1}$

18. Calculate ΔH° for the reaction

$S(s) + O_2(g) \rightarrow SO_2(g)$

from the following data

$S(s) + \frac{3}{2} O_2(g) \rightarrow SO_3(g)$ ΔH° = -395.2 KJ

$2SO_2(g)\ O_2(g) \rightarrow 2SO_3(g)$ ΔH° = -198.2 KJ (Ans: -296.11 KJ)

Solution:

Required equation:

Heat of formation of $C_6H_{6(l)}$

$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$ ΔH° = ?

Given equations:

Heat of combustion of liquid benzene $C_6H_{6(l)}$

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

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

To get the require equation following steps should be adopted.

Step 1: Divide equation (ii) by 2,

Step 2: Take equation (i) without any change

Step 3: Then add all the resulting equation, we get

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

$$SO_{3(g)} \longrightarrow SO_{2(g)} + \frac{1}{2} O_{2(g)} \qquad \Delta H^\circ = +99.1 \text{ kJ} \ldots\ldots\text{(ii)}$$

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)} \qquad \Delta H^\circ = -296.1 \text{ kJ}$$

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: 120.94 kJ)

Solution:

Mass of Al frying pan = 745 g

Number of moles of Al = $n = \frac{745}{27} = 27.596$ moles

Initial temperature = $T_1 = 25°C$

Final temperature = $T_2 = 205°C$

Change in temperature = $\Delta T = 205°C - 25°C$

= 180 °C

or = 180K

Heat capacity of Al = $C_P = 24.35 \text{ J mole}^{-1}K^{-1}$

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

$= 27.596 \text{ mole} \times 24.35 \text{ J mole}^{-1}K^{-1} \times 180 \text{ K}$

= 120953 J

= 120.953 kJ

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 $(NH_2)_2CO$**

Solution:

(a) C_4H_9OH (Butanol):

$$4C(s) + 5H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_4H_9OH(l)$$

(b) Rust, Fe_3O_4:

$$FeO(s) + Fe_2O_3(g) \longrightarrow Fe_3O_4(s)$$

(c) Acetic acid CH_3CO_2H:

$$2C(s) + 2H_2(g) + O_2(g) \longrightarrow CH_3COOH(l)$$

(d) Urea $(NH_2)_2CO$:

$$C(s) + N_2(g) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow (NH_2)_2CO\,(s)$$

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)**

Ans: (a) $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

(b) $Molar\ Mars\ of\ Glucose\ (C_6H_{12}O_6) = 180$

$Heat\ produced\ by\ burning\ 1\ g\ of\ Glucose = 15.65\ KJ$

$Heat\ produced, by\ burning\ 1\ mole\ (180)\ of\ Glucose = 15.65 \times 180$

$= 2817\ KJ$

$\Delta H_c^o\ for\ Glucose = -2817\ KJ\ mole^{-1}$

(c) Solution:

Required equation:

Heat of combustion of $C_6H_{12}O_{6\,(s)}$

$6C_{(s)} + 6H_{2(g)} + 3O_{2(g)} \longrightarrow C_6H_{12}O_{6(s)}$ $\Delta H° = ?$

Given equations:

Heat of combustion of glucose

$C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(l)}$ $\Delta H° = -2817.28$ kJ mole^{-1} .....(i)

Heat of combustion of C

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H° = -393.5$ kJ mole^{-1} .....(ii)

Heat of combustion of H_2

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

To get the require equation following steps should be adopted.

Step 1: Multiply equation (ii) by 6,

Step 2: Multiply equation (iii) by 6,

Step 3: Reverse equation (i),

Step 4: Then add all the resulting equations, we get

$6C_{(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)}$ $\Delta H° = -2361$ kJ mole^{-1}

$6H_{2(g)} + 3O_{2(g)} \longrightarrow 6H_2O_{(l)}$ $\Delta H° = -1714.8$ kJ mole^{-1}

$6CO_{2(g)} + 6H_2O_{(l)} \longrightarrow C_6H_{12}O_{6(s)} + 6O_{2(g)}$ $\Delta H° = +2817.28$ kJ mole^{-1}

$6C_{(s)} + 6H_{2(g)} + 3O_{2(g)} \longrightarrow C_6H_{12}O_{6(s)}$ $\Delta H° = -1258.52$ kJ mole^{-1}

22. Write 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 $C_2H_3Cl(g)$.

(d) Heat of combustion of benzene $C_6H_6(l)$.

Ans:

(a) Heat of Sublimation of Iodine.

$I_2\ (s) \longrightarrow I_2\ (g) \quad \Delta H = positive$

(b) Heat of Formation of Gaseous Atomic Iodine.

$$\frac{1}{2}I_2\,(g) \longrightarrow I\,(g) \quad \Delta H = positive$$

(c) Heat of Formation of $C_2H_3Cl(g)$.

$$2C(s) + \frac{3}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow C_2H_3Cl(g) \quad \Delta H = positive$$

(d) Heat of Combustion of Benzene $C_6H_6(l)$.

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$$

$$\Delta H = positive = 3268\ KJ\ mole^{-1}$$

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)

Solution:

Required equation:

Heat of combustion of liquid $C_2H_5OH_{(l)}$

$2C_{(s)} + 2H_{2(g)} + O_{2(g)} \longrightarrow CH_3COOH_{(l)} \quad \Delta H° = ?$

Given equations:

Heat of combustion of glucose

$CH_3COOH_{(l)} + 2O_{2(g)} \longrightarrow 2CO_{2(g)} + 2H_2O_{(l)} \quad \Delta H° = -875\ kJ\ mole^{-1}$ .....(i)

Heat of combustion of C

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

Heat of combustion of H_2

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

To get the require equation following steps should be adopted.

Step 1: Multiply equation (ii) by 2.

Step 2: Multiply equation (iii) by 2.

Step 3: Reverse equation (i).

Step 4: Then add all the equations, we get the required equation

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

$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} \quad \Delta H° = -285.8\ kJ\ mole^{-1}$

$2C_{(s)} + 2HO_{2(g)} \longrightarrow CH_3COOH_{(l)} + 2O_{2(g)} \quad \Delta H° = -393.5\ kJ\ mole^{-1}$

$2C_{(s)} + 2H_{(g)} + O_{2(g)} \longrightarrow CH_3COOH_{(l)} \quad \Delta H° = -393.5\ kJ\ mole^{-1}$

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

$3Fe(s) + 2O_2(g) \rightarrow Fe_3O_4(s)$ $\Delta H° = -1118$ KJ

$2Fe(s) + \frac{3}{2}O_2(g) \rightarrow Fe_2O_3(s)$ $\Delta H° = -824.2$ KJ

Solution: Required equation:

The required conversion is

$2Fe_3O_4(s) + O_2 \longrightarrow 3Fe_2O_3(s) \quad \Delta H° = ?$

Given equations:

$3Fe(s) + 2O_2(g) \longrightarrow Fe_3O_4(s)$ $\quad \Delta H^\circ = -1118\ kJ$ ____(i)

$2Fe(s) + \frac{3}{2}O_2(g) \longrightarrow Fe_2O_3(s)$ $\quad \Delta H^\circ = -824.2\ kJ$ ____(ii)

As we know that

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

$= [3 \times (-824.2)] - [2 \times (-1118) + (0)]$

$= (-2472.6) - (-2236) = -2472.6 + 2236 = -236.6\ kJ$

Thus the required conversion is exothermic.

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) $Mg^{+2}\ (g) + 2e^- \longrightarrow Mg\ (g)$

(d) $O^{-1}\ (g) + 1e^- \longrightarrow O^{-2}(g)$

(e) $2Mg\ (s) + O_2\ (g) \longrightarrow MgO\ (s)$

(f) $NaCl\ (s) \longrightarrow 2Na(s) + Cl_2\ (g)$

Ans:

Note:

Lighter ⟶ Denser

Energy is given out. And the reaction will be exothermic.

ΔH = Negative

Denser ⟶ Lighter

Energy is taken in and the reaction will be endothermic.

ΔH = Positive

(a) This is a condensation process and during this process energy releases and also because gas is being converted into liquid so, it is an exothermic process.

(b) This is an exothermic process because gases are being converted into solid. And during the formation of NH_4Cl heat releases so it is an exothermic reaction in this reaction. $\Delta H^o_{reaction} = -101\ kJ$.

(c) When electron is added to a cation (Mg^{+2}) they release energy and form atom so it is an exothermic process.

(d) Energy is required for the addition of electron to overcome the repulsion between O^{-1} ion and the incoming electron therefore it is an endothermic process.

(e) MgO is an ionic compound and during its formation a lot of energy releases due to the formation of ionic bond thus it is an exothermic process.

(f) This is a decomposition reaction and in this reaction NaCl decomposes into Na and Cl_2 therefore energy is required for this decomposition so it is an endothermic reaction.

26. Explain the cooling effect experienced when few drops of ethanol are put on your palm, given that:

$C_2H_5OH(l) \longrightarrow C_2H_5OH(g)$ $\quad \Delta H^\circ = 42.2\ KJmole^{-1}$

Ans:

i. As we know that evaporation is a cooling process and when we put few drops of ethanol on our palm these drops absorb heat from the body and the

surrounding due to which they evaporate and the temperature of the palm decreases and a cooling effect can be experienced.

ii. The given equation shows that the conversion of liquid ethanol to gaseous ethanol is an endothermic process due to which the reaction requires heat to proceed.

iii. As ethanol has hydrogen bonding due to which it has high heat of vaporization that is why its molecules absorb a lot of heat from the surrounding to evaporate.

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 exothermic or endothermic. Explain. (Ans: exothermic)

Solution:

Required equation:

The reverse of the given equation i.e.,

$$CH_3OH_{(l)} \longrightarrow CO_{(g)} + 2H_{2(g)} \quad \Delta H^\circ = ?$$

Given equations:

Heat of formation of $CH_3OH_{(l)}$

$$C_{(s)} + 2H_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CH_3OH_{(l)} \quad \Delta H^\circ = -238.7 \text{ kJ mole}^{-1} \ldots\ldots(i)$$

Heat of formation of combustion of H_2

$$C_{(s)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \quad \Delta H^\circ = -110.5 \text{ kJ mole}^{-1} \ldots\ldots(ii)$$

To get the require equation following steps should be adopted.

Step 1: Reverse equation (i)

Step 2: Add equation (i) to equation (ii).

$$CH_3OH_{(l)} \longrightarrow C_{(s)} + 2H_{2(g)} + \tfrac{1}{2}O_{2(g)} \quad \Delta H^\circ = +238.7 \text{ kJ mole}^{-1}$$

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

$$CH_3OH_{(l)} \longrightarrow CO_{(g)} + 2H_{2(g)} \quad \Delta H^\circ = +128.2 \text{ kJ mole}^{-1}$$

Conclusion:

Hence, the reverse of the given reaction is 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 of CO_2, H_2O and CH_4 are -393.5 KJ/mole, -285.8 KJ/mole and -74.6 KJ/mole respectively. (Ans: 1100.625 KJ)

Solution:

Required equation:

Heat of combustion of $CH_{4(g)}$

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)} \quad \Delta H^\circ = ?$$

Given equations:

Heat of formation of $CH_{4(g)}$

$C_{(s)} + 2H_{2(g)} \longrightarrow CH_4$ $\Delta H^\circ = -74.6$ kJ mole^{-1} .....(i)

Heat of formation of gaseous $CO_{2(g)}$

$C_{(s)} + O_2(g) \longrightarrow CO_{2(g)}$ $\Delta H^\circ = -393.5$ kJ mole^{-1} .....(ii)

Heat of formation of liquid $H_2O_{(l)}$

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

To get the require equation following steps should be adopted.

Step 1: Multiply equation (iii) by 2,

Step 2: Reverse equation (i),

Step 3: Then add all the equations, we get

$C_{(s)} + O_2(g) \longrightarrow CO_{2(g)}$ $\Delta H^\circ = -393.5$ kJ mole^{-1}

$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O$ $\Delta H^\circ = -571.6$ kJ mole^{-1}

$CH_{4(g)} \longrightarrow C_{(s)} + 2H_{2(g)}$ $\Delta H^\circ = +74.6$ kJ mole^{-1}

$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$ $\Delta H^\circ = -890.5$ kJ mole^{-1}

Thus one mole of CH_4 releases 890.5 kJ energy on combustion.

Given mass of CH_4 = 20 g

Molar mass of CH_4 = $12 + 1\times4 = 16$ g mole^{-1}

Number of moles of CH_4 = $\frac{20}{16} = 1.25$ moles

So,

1 mole of CH_4 produce heat = -890.5 kJ

1.25 mole of CH_4 produce heat = $-890.5 \times 1.25 = -1113.125$ kJ

29. Evaluate the importance of Hess's Law.

Ans: i. Determination of heat of formation:

Compounds whose heats of formation cannot be measured directly using calorimetric methods because they cannot be synthesised from their elements easily e.g. methane, carbon monoxide, benzene etc are determined using Hess's Law.

ii. Determination of heat of transition:

The heats of transition of allotropic modification of compounds such as diamond to graphite, rhombic sulphur to monoclinic sulphur, yellow phosphorous to red phosphorous etc. can be determined using Hess's Law.

iii. Determination of heat of hydration:

The heats of hydration of substances is calculated using Hess's law.

iv. Determination of heats of various reactions:

Hess's law is useful in calculating the enthalpies of many reactions whose direct measurement is difficult or impossible.