CHAPTER # 11.

THERMOCHEMISTRY.

INTRODUCTION:-

THERMODYNAMICS:-

The study of all types of energy changes associated with physical and Chemical changes is Known as Thermodynamics.

THERMOCHEMISTRY:-

The branch of chemistry, which deals with the study of heat Changes during the chemical reaction, is called thermochemistry.

ENERGY IN CHEMICAL REACTIONS:

The energy in the form of heat is either evolved or absorbed as a result of Chemical reaction. This is because, in a chemical reaction old bonds are broken and new bonds are formed. Bond breaking always consumes energy and bond making always releases energy.

When the energy released by bond forming is greater than the energy consumed in bond breaking, there is a net release of chemical energy. Whereas energy is absorbed, when the energy of bond breaking is greater than the energy of bond formation. Thus in a chemical reaction, energy is exchanged with the surroundings.

UNITS OF THERMAL ENERGY:-

The SI unit of heat or thermal energy is 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.

Another common unit of heat is calorie.

1 Calorie = 4.18 Joules.

DEFINATIONS OF TERMS USED IN THERMODYNAMICS:

1. SYSTEM:-

The part of universe, which is under observation, is called system.

2. SURROUNDING:-

Part of universe, which is not a part of the system is called surrounding.

→ BOUNDARY:-

Path, which differentiate b/w system and surrounding is called boundary. It may be real or imaginary.

e.g; ice melts in a beaker.
In this case, ice is a system and beaker and other things are surrounding.

3. STATE FUNCTION OR STATE VARIABLE:-

Macroscopic properties, which are used to describe behaviour of gaseous system, are called state functions.

e.g;
Pressure (P), Volume (V), Temperature (T),
Internal Energy (E), Enthalpy (H).

These properties depends upon initial and final state, not a path followed by them.

e.g;

$$\Delta P = P_2 - P_1$$
$$\Delta V = V_2 - V_1$$
$$\Delta T = T_2 - T_1$$
$$\Delta E = E_2 - E_1$$
$$\Delta H = H_2 - H_1$$

4- THERMOCHEMICAL REACTIONS:-

Reactions in which heat is released or absorbed, are called Thermochemical reactions, and equations obtained are called Thermochemical Equations.

Types of Reactions:-

i- EXOTHERMIC REACTIONS:-

A Thermochemical reaction, that proceeds with the evolution of heat is called an exo-thermic reaction.

In this reaction heat transfers from system to surrounding.

e.g;

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H = -393.5 \ KJ/mol.$$

ii- ENDOTHERMIC REACTIONS:-

A chemical reaction that proceeds with the absorption of heat, is called endothermic reaction.

In this reaction, heat transfers from surrounding to system.

e.g;

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO \quad \Delta H = +180.5 \ KJ.$$

Q- Differentiate b/w exothermic & endothermic Reactions.

	EXOTHERMIC REACTIONS.	ENDOTHERMIC REACTIONS.
1-	Reactions in which heat is released are called exothermic reactions.	1- Reactions in which heat is absorbed are called endothermic reactions.
2-	In these reactions, heat transfers from system to surrounding.	2- In these reactions, heat transfers from surrounding to system.
3-	In these reactions, ΔH is -ve. Because enthalpy of reactant is greater than enthalpy of product.	3- In these reactions, ΔH is +ve. Because, enthalpy of product is greater than enthalpy of reactant.
4-	e.g; i- $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = -393.5 \ KJ/mol.$ ii- $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ $\Delta H = -571.6 \ KJ.$	4- e.g; i- $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ $\Delta H = +180.5 \ KJ.$ ii- $2H_2O_{(l)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$ $\Delta H = +571.6 \ KJ$

HEAT OF REACTION:-
OR
ENTHALPY:-

Heat content of the system is Known as enthalpy. It is defined as;

"Sum of internal energy and product of Pressure, volume is Known as Enthalpy."

Mathematically;

$$H = E + PV.$$

Enthalpy is a state function. For change in enthalpy, we can write;

$$\Delta H = \Delta E + \Delta(P.V)$$

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

at constant pressure;

$$\Delta P = 0$$

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

in case of solid and liquid; $\Delta V = 0$

so;

$$\Delta H = \Delta E + 0.P$$

$$\boxed{\Delta H = \Delta E}$$

Heat of reaction can be defined as;

"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."

e.g;

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^\circ = -393.5\ KJ/mol.$$

$$H_{2(g)} + I_{2(g)} \longrightarrow 2HI \qquad \Delta H^\circ = +53.8\ KJ.$$

Heat of reaction measured at 25°C (or 298K) and 1 atm pressure, is called enthalpy change. It is denoted by ΔH°.

Q. Differentiate b/w Spontaneous and Non-Spontaneous reactions.

ANS:

	SPONTANEOUS REACTION	NON-SPONTANEOUS REACTION
1.	Reaction, which proceeds on its own, without any outside assistance, is spontaneous.	1. Reaction, which needs an outside assistance to proceed, is non-spontaneous.
2.	It is uni-directional.	2. It is bi-directional.
3.	It always proceeds from Non equilibrium to Equilibrium state.	3. It always proceeds from Equilibrium to Non equilibrium state.
4.	Due to spontaneous reaction, Entrapy .	4. Due to non-spontaneous reaction, Entrapy .
5.	e.g; Flow of water from higher level to lower.	5. e.g; Pumping of water from ground to a certain height.
6.	Heat transfers from hot body to cold body is spontaneous.	6. Heat transfers from cold body to hot body is non-spontaneous.
7.	The emission of rays from radio-active elements, burning of coal and methane, are spontaneous.	7. The reaction of nitrogen & oxygen to make nitric oxide, Thermal decomposition of P_2O_5, are non-spontaneous.

INTERNAL ENERGY:-

Total energy within a chemical system is called internal energy.

OR

Sum of all types of energies of the particles of a system is called internal energy.

It is the sum of K.E and P.E. It is denoted by "E".

$$E = K.E + P.E.$$

Kinetic Energy:-

Energy due to motion of particles is called Kinetic energy. These motions may be translational, rotational or vibrational.

Potential Energy:-

Attractive forces b/w the particles is called P.E. These attractive forces may be chemical bonding or vander waal forces.

Internal energy is a state function. It depends upon initial and final state, not on path followed by it. Absolute value of "E" can't be measured, but change in internal energy can be measured.

$$\Delta E = E_2 - E_1.$$

where; E_1 = initial internal Energy.
E_2 = Final " "

TRANSFER OF ENERGY:-

There are two possible ways of transfer of energy:

1. Heat
2. WORK.

1. HEAT :-

Total Kinetic energy of the molecule is called heat. It is the form of energy. It transfers b/w system and surrounding as a result of temperature difference. It is denoted by "q".

i- when heat is given to the system, "q" is +ve. (Means heat absorption).

ii- when heat is given by the system, "q" is -ve. (Means heat is released).

2. WORK :-

Work is the form of energy. It is defined as;
"Force into displacement is called work."

$$W = F \cdot d.$$

But, in term of Pressure-volume work, it is defined as;
"Product of Pressure and change in volume is called work."

$$W = P \cdot \Delta V.$$

i- when work is done on the system, W is +ve.
ii- " " " " by the " , W is −ve.

*Q.- STATE AND EXPLAIN FIRST LAW OF THERMODYNAMICS.

Ans. This law is also called law of conservation of energy. According to this law;

"Energy can neither be created, nor destroyed, but one form of energy converted into another form."

A system can exchange energy with its surroundings in two distinct ways. Energy can be transfered as heat or work.

EXPLANATION:-

Consider a cylinder having moveable piston. Given amount of gas is enclosed in it. When heat is given to the system (cylinder) and is done on it, internal energy of the gas increases from E_1 to E_2.

$$\Delta E = E_2 - E_1$$

$$\boxed{\Delta E = q + W}.$$

SIGNS :-

i- when internal energy of the system increases, $\Delta E = +ve$.
ii- " " " " " " decreases, $\Delta E = -ve$.
iii- when heat is given to the system, q is $+ve$.
iv- " " " " by the system, q is $-ve$.
v- when work is done on the system, w is $+ve$.
vi- " " " " by the system, w is $-ve$.

APPLICATIONS :-

1- PROCESS AT CONSTANT VOLUME:
OR
PROVE THAT $\Delta E = q_v$.

According to 1st law of thermodynamics;

$$\Delta E = q + w \longrightarrow ①$$

By the defination of work;

$$w = P \cdot \Delta V \longrightarrow ②$$

put ② in ①;

$$\Delta E = q + P \cdot \Delta V$$

At constant volume;

$$\Delta V = 0$$

$$\Delta E = q + P \cdot 0$$

$$\boxed{\Delta E = q_v.}$$

2- PROCESS AT CONSTANT PRESSURE OR PROVE THAT $\Delta H = q_p$.

According to 1st law of Thermodynamics;

$$\Delta E = q + w \longrightarrow ①$$

At constant pressure; system performs work,
Therefore; $w = -ve$

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

equation ① becomes;

$$\Delta E = q - P \cdot \Delta V \longrightarrow ②$$

At constant pressure, Enthalpy is given by;

$$\Delta H = \Delta E + P \cdot \Delta V \longrightarrow ③$$

from ② & ③; $\Delta H = q - \cancel{P \cdot \Delta V} + \cancel{P \cdot \Delta V} \Rightarrow \boxed{\Delta H = q_p.}$

STANDARD ENTHALPY CHANGE:-

Enthalpy change at constant pressure (1 atm) and constant temperature (25°C), is called standard enthalpy change.

It 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.

STANDARD STATES AND STANDARD ENTHALPY CHANGES:-

We can measure enthalpy change for a chemical reaction at constant pressure using a calorimeter. However, it is not only very difficult but also impossible in many cases. This is because, Some reactions are too slow.

For example, value of ΔH for the conversion of graphite to diamond can't be measured in a calorimeter because reaction is very slow under normal conditions. However, ΔH for this conversion can be calculated from heats of combustions of graphite and diamond measured at same temp. (25°C) and pressure (1 atm).

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

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

ii- $C_{Diamond(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^\circ = -395.4\ KJ/mole.$

By reversing eqs (ii) & adding it with eqs. (i), we get;

i- $C_{graphite(s)} + \cancel{O}_{2(g)} \longrightarrow C\cancel{O}_{2(g)} \qquad \Delta H^\circ = -393.5\ KJ/mole.$

ii- $\cancel{CO}_{2(g)} \longrightarrow C_{Diamond(s)} + \cancel{O}_{2(g)} \qquad \Delta H^\circ = +395.4\ KJ/mole.$

$$C_{Graphite(s)} \longrightarrow C_{Diamond(s)} \qquad \Delta H^\circ = +1.9\ KJ/mole.$$

CONDITION FOR STANDARD HEAT OF REACTION :-

As ΔH varies with conditions, we use standardized ΔH values. The 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 mm and 25°C (298 K).
3. Standard state for a substance in aqueous solution is 1 M Concentration.

Q. Define the following terms.

1. STANDARD ENTHALPY OF REACTION :- (ΔH_r°)

Amount of heat, released or absorbed, when no. of moles of reactant react with each other and form product, under standard conditions is called standard enthalpy of reaction.

All the reactants and product must be in their standard physical state.

e.g;

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

2. STANDARD ENTHALPY OF FORMATION :- (ΔH_f°)

Amount of heat, released or absorbed, when no. of moles of reactant react with each other and form one mole of product, under standard conditions, is called standard enthalpy of formation.

All the reactants and product must be in their standard Physical state.

e.g;

$$Mg_{(s)} + \frac{1}{2}O_{2\,(g)} \longrightarrow MgO_{(s)} \qquad \Delta H_f^\circ = -601.4\ KJ/mol.$$

3. STANDARD ENTHALPY OF ATOMIZATION :- ($\Delta H^\circ_{at.}$)

Amount of heat absorbed when one mole gaseous atom is formed from its elements, under standard conditions, is called enthalpy of atomization.

e.g;

$$\frac{1}{2}H_{2(g)} \longrightarrow H_{(g)} \qquad \Delta H^\circ_{at} = 218\ KJ/mol.$$

$$\frac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)} \qquad \Delta H^\circ_{at} = 121\ KJ/mol.$$

4. STANDARD ENTHALPY OF COMBUSTION :- (ΔH°_c)

Amount of heat released, when one mole compound is burn in free supply of air (O_2), under standard conditions, is called standard enthalpy of combustion.

e.g;

$$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)} \qquad \Delta H^\circ_c = -1365\ KJ/mol.$$

5. STANDARD ENTHALPY OF NEUTRALIZATION :- (ΔH°_n)

Amount of heat released when one mole of hydrogen ion from acid react with one mole of hydroxyl ion from base and form one mole of water, under standard conditions is called standard enthalpy of neutralization.

e.g;

$$NaOH_{(aq)} + HCl_{(aq)} \rightleftharpoons NaCl_{(aq)} + H_2O_{(l)} \qquad \Delta H^\circ_n = -57.4\ KJ/mol.$$

6. STANDARD ENTHALPY OF SOLUTION :- ($\Delta H^\circ_{sol.}$)

Amount of heat released or absorbed, when one mole of compound is dissolved in so much solvent, there is no heat change on further dilution, under standard conditions, is called standard enthalpy of solution.

e.g;

$$NH_4Cl_{(s)} \rightleftharpoons NH^+_{4(aq)} + Cl^-_{(aq)} \qquad \Delta H^\circ_{sol.} = +15.1\ KJ/mol.$$

BOND DISSOCIATION ENERGY:-

when chemical reaction occurs, old bonds break and new bonds form. Bond breaking always require energy and bond formation always releases energy.

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

whereas;

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

The difference b/w bond dissociation energy and bond energy determines whether the reaction absorbs or releases energy overall.

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

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

EXAMPLE:-

For reaction b/w H_2 and O_2 to produce H_2O:

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

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

$$= 2\times(+436\ KJ) + 493.6\ KJ - 4(460\ KJ).$$

$$= 1365\ KJ - 1840\ KJ.$$

$$\Delta H_r^\circ = -474.4\ KJ.$$

It means, the formation of water is exothermic.

HEAT CAPACITY:-

It is defined as;

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

The different forms of energies can be converted into one another. Any other form of energy can be completely transformed into heat energy. But at constant temp., heat can't be completely converted into another form of energy. Temp. is not same as heat.

Temperature of a substance doesn't depends upon its mass. But quantity of heat within a substance at a given temp. is directly proportional to its mass. Therefore; amount of heat absorbed by a substance is proportional to temp. change.

$$q \propto \Delta T$$

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

where; "C" is constant of proportionality and is Known as heat capacity of a substance.

Specific heat capacity:-

"The amount of heat required to raise the temp. of one gram of a substance by 1 K is called specific heat capacity.

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

Molar heat capacity:-

The amount of heat required to raise the temperature of one mole of a substance by one Kelvin is called Molar heat Capacity.

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

CALORIMETERY:-

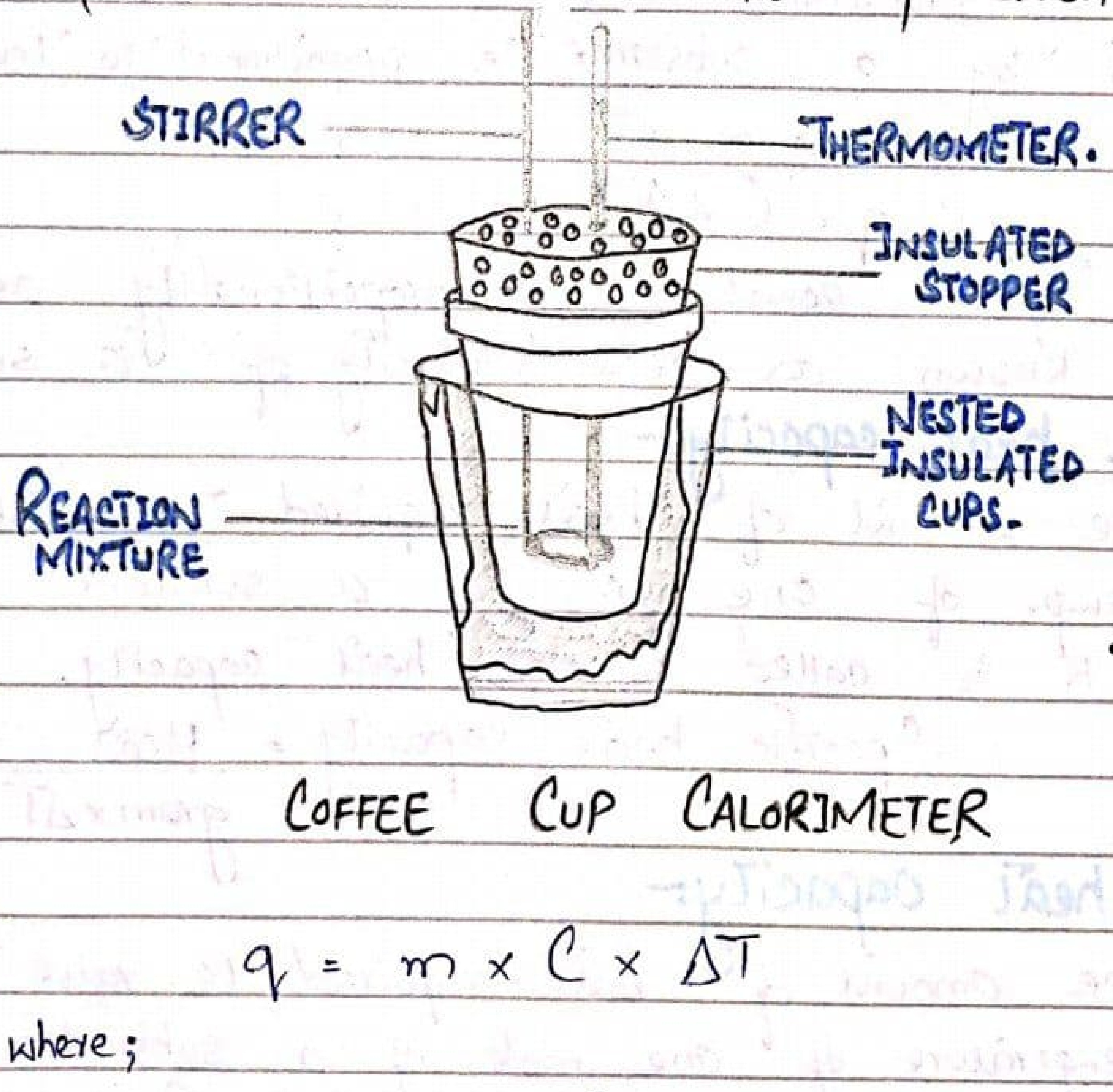
It is the science of measuring heat of a chemical reaction by measuring the temperature change. A device that measures heat flow is called Calorimeter. Calorimeters measures the heat released from a system either at constant pressure or at constant volume.

There are two types of Calorimetery:

1. CONSTANT PRESSURE CALORIMETERY:-

In this type of calorimetery, pressure is fixed. For this purpose, we need a thermally insulated container with a thermometer and stirrer. For most purposes, Coffee cup calorimeter is used.

(Also See Book For Explanation.)



COFFEE CUP CALORIMETER

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

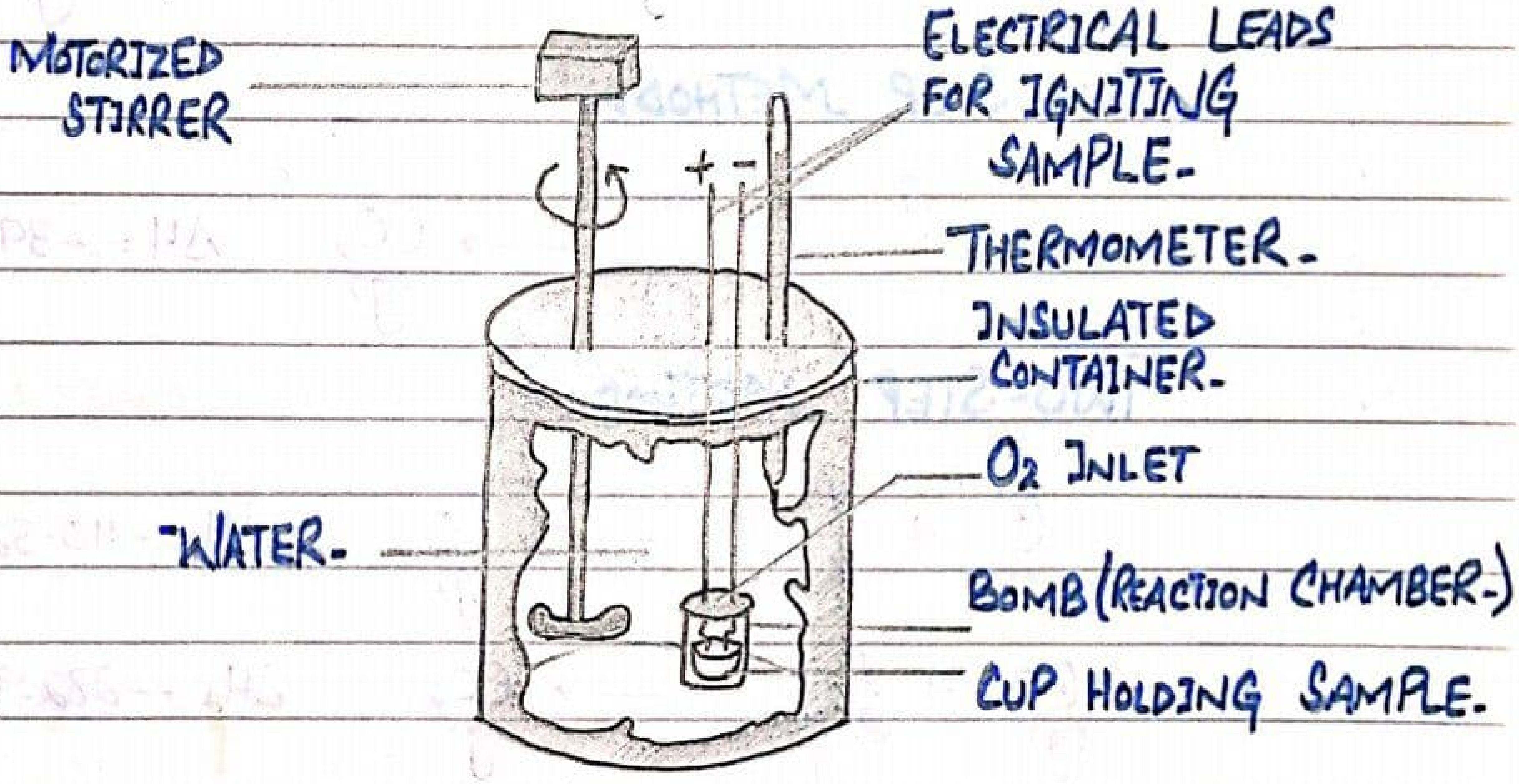
where;

m = mass of reactants.
C = Specific heat of reaction mixture.
ΔT = Change in temperature.

2. CONSTANT VOLUME CALORIMETERY:-

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

(Also See book 237 for Explanation.)



BOMB CALORIMETER-

most important ★

HESS'S LAW OF CONSTANT HEAT SUMMITION:-

G.H Hess stated this law in 1840.

"According to this law, Enthalpy change during the chemical reaction, is same whether the reaction takes place in one step or more than one step."

Mathematically;

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

$$\begin{tikzcd} A \arrow[r, "\Delta H"] \arrow[d, "\Delta H_1"] & B \\ C \arrow[r, "\Delta H_2"'] & D \arrow[u, "\Delta H_3"'] \end{tikzcd}$$

$$\sum \Delta H_{cyclic} = 0$$

Explanation:-

Carbon dioxide can be prepared by two methods;

ONE-STEP METHOD:-

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -393.5\ KJ/mo$$

TWO-STEP METHOD:-

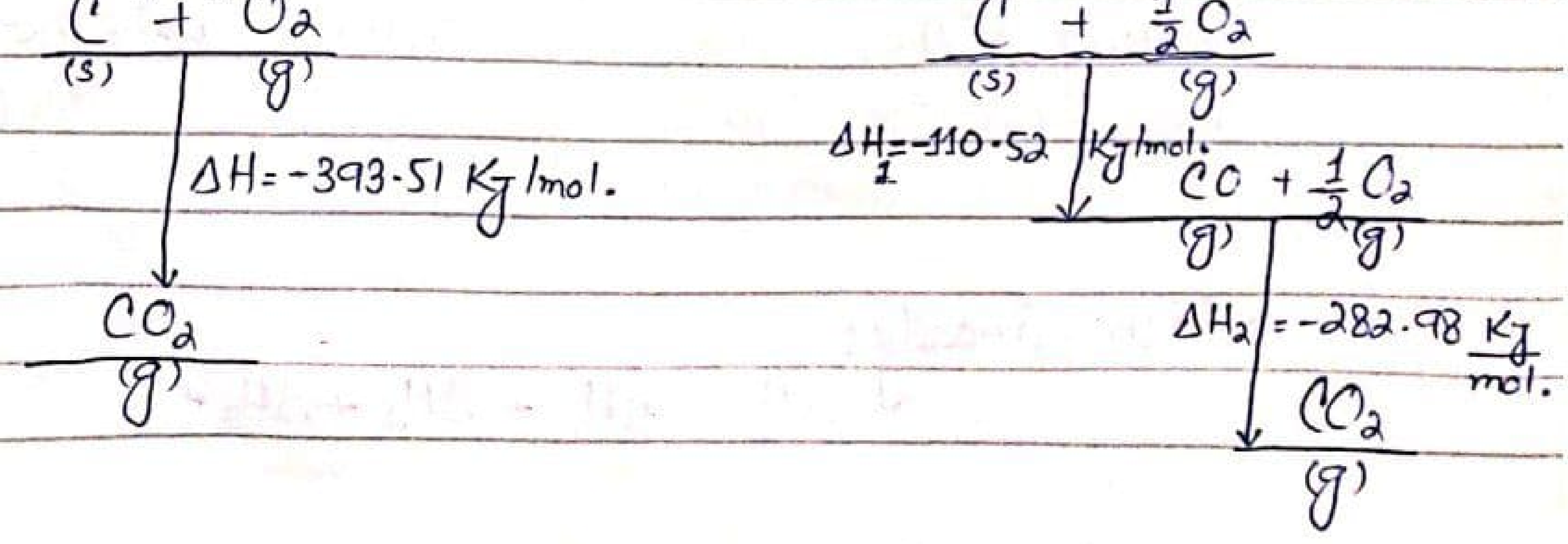
$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \qquad \Delta H_1 = -110.52\ KJ/mol.$$

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_2 = -282.98\ KJ/mol.$$

Acc. to Hess's law;

$$\Delta H = \Delta H_1 + \Delta H_2$$
$$= -110.52 - 282.98$$
$$\Delta H = -393.51\ KJ/mol.$$

Energy cycle of these reactions



IMPORTANCE OF HESS'S LAW:-

There are many reactions for which ΔH can't be calculated directly by Calorimeteric method. For such reactions, Hess's law is used.

For example;

- ⇒ Formation of CCl_4 can't be measured directly by calorimeteric method.
- → Formation of B_2O_3 and Al_2O_3 Can not be measured directly

APPLICATION OF HESS'S LAW:-

BORN HABER CYCLE:-

It is an application of Hess's law. It is defined as;

"ENERGY CHANGE IN A CYCLIC PROCESS IS ALWAYS ZERO".

It is used to find the lattic energy of binary ionic compound.

LATTICE ENERGY:-

It is defined as;

"Amount of energy released when one mole ionic Compound is formed from its opposite Charged ions in gaseous state."

e.g;

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)} \quad \Delta H_x = -787 \text{ KJ/mol.}$$

lattice energy depends upon size of cation and Anion. As the size of cation or anion increases, lattice energy decreases.

ENERGY TRIANGLE OF NaCl :-

$$\begin{tikzcd}
Na_{(s)} + \frac{1}{2}Cl_{2(g)} \arrow[rr, "\Delta H_x"] \arrow[dr, "\Delta H_f = -411\ Kj/mol"'] & & Na^+_{(g)} + Cl^-_{(g)} \arrow[dl, "\Delta H_l = ?"] \\
& NaCl_{(s)} &
\end{tikzcd}$$

$Na_{(s)} \longrightarrow Na_{(g)}$ $\Delta H^\circ_{at.} = 108$ Kj/mol.

$Na_{(g)} \longrightarrow Na^+_{(g)} + e^-$ $\Delta H^\circ_{I.E} = 496$ Kj/mol.

$\frac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)}$ $\Delta H^\circ_{at.} = 121$ Kj/mol.

$Cl_{(g)} + e^- \longrightarrow Cl^-_{(g)}$ $\Delta H^\circ_{E.A} = -349$ Kj/mol.

$$\Delta H^\circ_x = \Delta H^\circ_{at.} + \Delta H^\circ_{I.E} + \Delta H^\circ_{at.} + \Delta H^\circ_{E.A}.$$

$$= 108 + 496 + 121 + (-349)$$

$$\Delta H^\circ_x = 376 \text{ Kj/mol.}$$

Acc. To Hess's law;

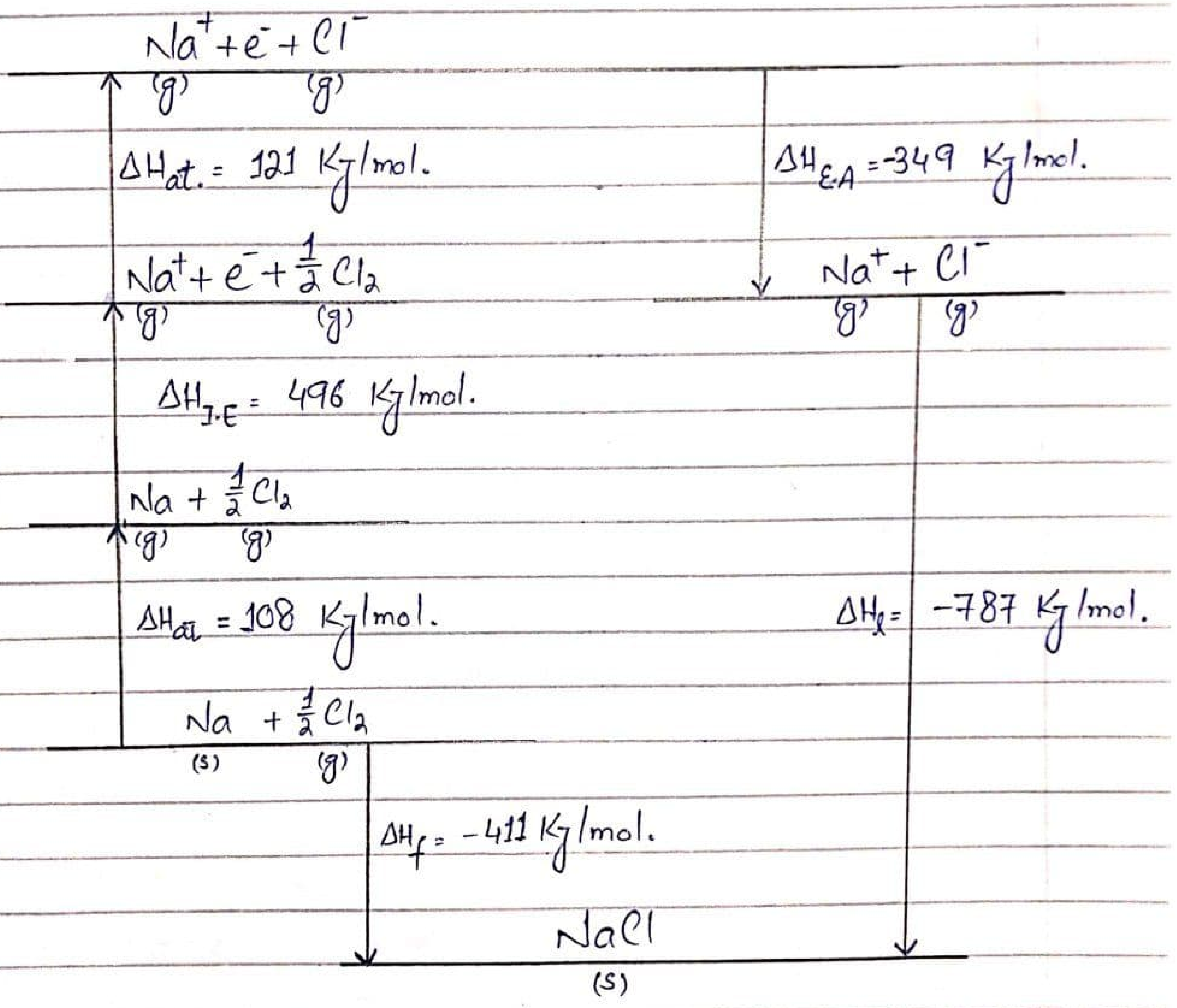
$$\Delta H_f = \Delta H_x + \Delta H_l$$

$$\Delta H_l = \Delta H_f - \Delta H_x$$

$$= -411 - 376$$

$$\Delta H_l = -787 \text{ Kj/mol.}$$

ENERGY CYCLE OF NaCl:-



CHP # 11 THERMOCHEMISTRY

★ SOLVED EXERCISE ★

Q1:- Choose the correct Answers:-

(i)	(d)	(vii)	(a)
(ii)	(a)	(viii)	(b)
(iii)	(c)	(ix)	(d)
(iv)	(a)	(x)	(b)
(v)	(b)	(xi)	(d)
(vi)	(b)	(xii)	(a,c,d) => 3

Q - Name & define units of thermal energy. extra

Unit of heat or thermal energy used in SI system is 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.

Another common unit of heat is the 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.

1 Calorie = 4.18 Joules

Q :- Define the terms system, surrounding, boundary, state function, heat capacity, internal energy, enthalpy of substance. extra

- **System**
  The part of universe, which is under observation is called system.
- **Surrounding**
  Part of universe, which is not part of system is called surrounding.
- **Boundary**
  A real or imaginary part which separates

system from surrounding is called boundary.

- **State Function**

Macroscopic properties, which are used to describe behaviour of gaseous system, are called state function. e.g. Pressure (P), Volume (V).

- **Heat Capacity**

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

- **Internal Energy**

Sum of all types of energies of the particles of a system is called internal energy.

i.e. E = K.E + P.E

- **Enthalpy of Substance**

Sum of internal energy and products of Pressure, volume is known as enthalpy.

Q4- Classify reactions as exothermic & endothermic.

- **Exothermic Reaction**

A thermochemical reaction, that proceeds with the evolution of heat is called an exothermic reaction.

In this reaction, heat transfers from system to surrounding.

e.g. $C + O_2 \longrightarrow CO_2$ $\Delta H = -393.5$ KJ mol^{-1}

- **Endothermic Reaction**

A chemical reaction that proceeds with the absorption of heat, is called endothermic reaction.

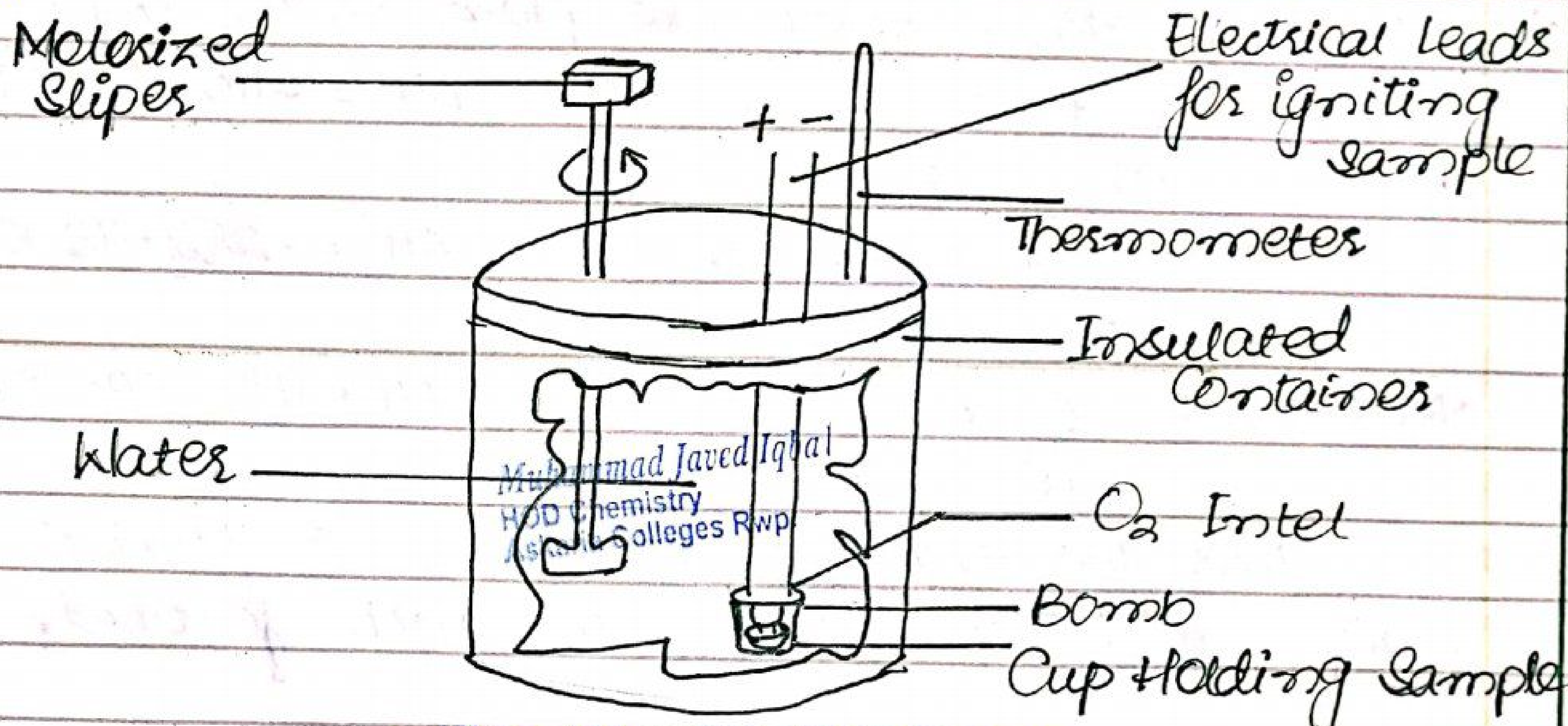
In this reaction heat transfers from surrounding to system

e.g. $N_2 + O_2 \longrightarrow 2NO$ $\Delta H = 180.5$ KJ mol^{-1}

Q :- Define bond dissociation energy. extra

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

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



▲ **BOMB CALORIMETER**

Human beings require three major classes of food
- Carbohydrates
- Fats
- 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 is used for measuring the energy available from food, which is just the enthalpy of combustion we can understand. **(See Activity 1.2 on pg 300)**

Q :- Apply Hess's law to construct simple energy cycles. extra

Combustion of C to CO_2 evolves 393.5 KJ of energy.

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

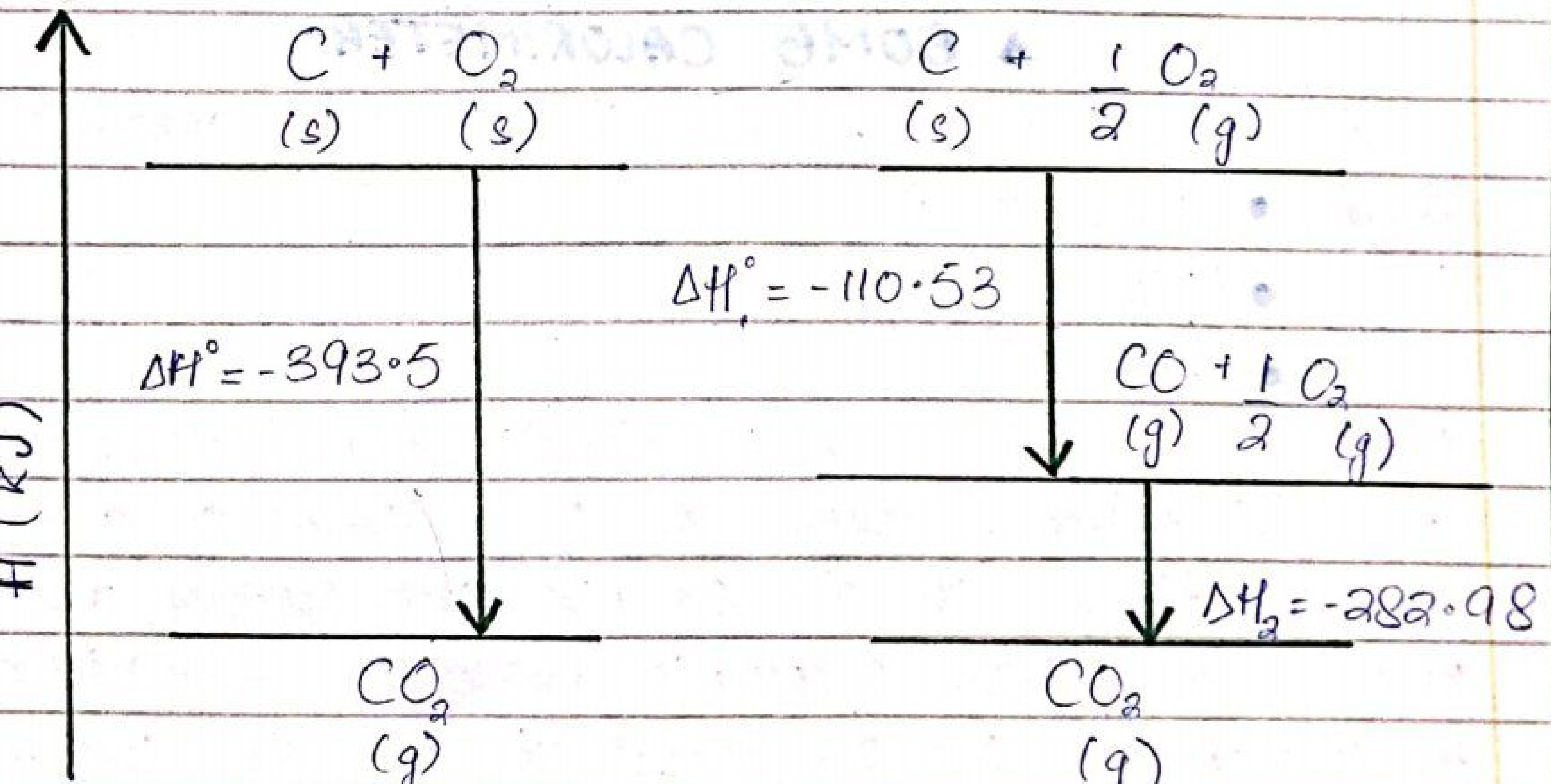
This reaction may take place in two steps.

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{(g)} \quad \Delta H^\circ = -110.52 \text{ KJ}$$

$$CO_{(g)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H_2^\circ = -282.98 \text{ KJ}$$

Net Reaction: $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H^\circ + H_2^\circ = -393.51 \text{ KJ}$

Thus the enthalpy change in a chemical reaction is independent of the path followed.



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

Chemical reactions are generally carried out in open containers. Therefore, these reaction 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 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,

$$\Delta E = q_p - P\Delta V$$
$$q_p = \Delta E + P\Delta V \quad — ①$$

q_p represents the heat absorbed or evolved by the reaction at constant pressure and is known as enthalpy change i.e. ΔH. Therefore equation ① can be written as,

$$\Delta H = \Delta E + P\Delta V \quad — ②$$

Since, there is no appreciable volume change in reactions involving solids or liquids, so $\Delta V = 0$

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

Enthalpy change at pressure of 1 atm and temperature 25°C is called standard enthalpy change and is denoted by ΔH°. So, equation ② becomes,

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

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

Q6:- When ethanol burns in oxygen, carbon dioxide and water are formed.

a) Write the equation which describes this reaction.

$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$

b) Using the following data, calculate the enthalpy of combustion for ethanol (C_2H_5OH).

ΔH_f for ethanol (l) = $-277.0\ KJ\ mol^{-1}$

ΔH_f for CO_2 (g) = $-393.2\ KJ\ mol^{-1}$

ΔH_f for H_2O (l) = $-285.8\ KJ\ mol^{-1}$

eq ① $2C + 3H_2 + \frac{1}{2}O_2 \rightarrow C_2H_5OH \quad \Delta H = -277.0\ kJ\ mol^{-1}$

eq ② $C + O_2 \longrightarrow CO_2 \quad \Delta H = -393.5\ kJ\ mol^{-1}$

eq ③ $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O \quad \Delta H = -285.8\ kJ\ mol^{-1}$

Multiplying eq ② with '2'

eq ④ $2C + 2O_2 \longrightarrow 2CO_2 \quad \Delta H = -787\ kJ\ mol^{-1}$

Multiplying eq ③ with '3'

eq ⑤ $3H_2 + \frac{3}{2}O_2 \longrightarrow 3H_2O \quad \Delta H = -857.4\ kJ\ mol^{-1}$

Adding eq ④ & ⑤

$$2C + 3H_2 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O \quad \Delta H = -1644.4\ kJ\ mol^{-1}$$

eq ① **(Subtracting)** $C_2H_5OH \longrightarrow 2C + 3H_2 + \frac{1}{2}O_2 \quad \Delta H = 277.0\ kJ\ mol^{-1}$

$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O \quad \Delta H = -1367.4\ kJ\ mol^{-1}$$

Q7:- Calculate from the data in table 11.1 & 11.12 the enthalpy changes of the following reactions at standard condition.

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

eq ① $C + O_2 \longrightarrow CO_2 \quad \Delta H = -393.5\ kJ\ mol^{-1}$

eq ② $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O \quad \Delta H = -285.8\ kJ\ mol^{-1}$

eq ③ $C_6H_6 + \frac{15}{2} O_2 \longrightarrow 6CO_2 + 3H_2O \quad \Delta H = -3268\ kJ\ mol^{-1}$

Multiplying eq ① with '6'

eq ④ $6C + 6O_2 \longrightarrow 6CO_2 \quad \Delta H = -2361\ kJ\ mol^{-1}$

Multiplying eq ② with '3'

eq ⑤ $3H_2 + \frac{3}{2} O_2 \longrightarrow 3H_2O \quad \Delta H = -857.4\ kJ/mol^{-1}$

Adding eq ④ & ⑤

$6C + 3H_2 + \frac{15}{2} O_2 \longrightarrow 6CO_2 + 3H_2O \quad \Delta H = -3218\ kJ\ mol^{-1}$

eq ③ subtracting $6CO_2 + 3H_2O \longrightarrow C_6H_6 + \frac{15}{2} O_2 \quad \Delta H = 3268\ kJ\ mol^{-1}$

$6C + 3H_2O \longrightarrow C_6H_6 \quad \Delta H = 49.6\ kJ\ mol^{-1}$

Q8:- The heat of combustion of liquid benzene, C_6H_6 to form H_2O & CO_2 at 1 atm and 25°C is -3268 kJ mol⁻¹ of benzene. What is the heat of formation of liquid benzene under these conditions.

$6C + 3H_2 \longrightarrow C_6H_6 \quad \Delta H = ?$

eq① $C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O \quad \Delta H = -3268\ kJmol^{-1}$

eq② $C + O_2 \longrightarrow CO_2 \quad \Delta H = -393.5\ kJmol^{-1}$

eq③ $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O \quad \Delta H = -285.8\ kJmol^{-1}$

Multiply eq ② with '6'

$6C + 6O_2 \rightarrow 6CO_2 \quad \Delta H = -2361\ kJmol^{-1}$

Multiply eq ③ with '3'

$3H_2 + \frac{3}{2}O_2 \longrightarrow 3H_2O \quad \Delta H = -857.4\ kJmol^{-1}$

Adding eq ④ & ⑤

$6C + \frac{15}{2}O_2 + 3H_2 \longrightarrow 3H_2O + 6CO_2 \quad \Delta H = -3218.4\ kJmol^{-1}$

eq① $6CO_2 + 3H_2O \longrightarrow C_6H_6 + \frac{15}{2}O_2 \quad \Delta H = +3268\ kJmol^{-1}$

Subtracting

$6C + 3H_2 \longrightarrow C_6H_6 \quad \Delta H = 49.6\ kJmol^{-1}$

Q - Specify conditions for the standard heats of reactions. extra

Conditions for the standard states are as follows:-

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

solution is 1M concentration.

Q :- Sketch reaction pathway diagram in term of enthalpy changes of the reaction.

⇒Energy Triangle of NaCl extra

$$\begin{tikzcd}
Na_{(s)} + \frac{1}{2}Cl_{2(g)} \arrow[rr, "\Delta H_x"] \arrow[dr, "\Delta H_f = -411\ kJmol^{-1}"'] & & Na^{+}_{(g)} + Cl^{-}_{(g)} \arrow[dl, "\Delta H_l = ?"] \\
& NaCl_{(s)} &
\end{tikzcd}$$

$Na_{(s)} \longrightarrow Na_{(g)}$ $\Delta H^\circ_{at} = 108\ kJmol^{-1}$

$Na_{(g)} \longrightarrow Na^{+}_{(g)} + e^{-}$ $\Delta H^\circ_{I.E} = 496\ kJmol^{-1}$

$\frac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)}$ $\Delta H^\circ_{at} = 121\ kJmol^{-1}$

$Cl_{(g)} + e^{-} \longrightarrow Cl^{-}_{(g)}$ $\Delta H^\circ_{E-A} = -349\ kJmol^{-1}$

Muhammad Javed Iqbal
HOD Chemistry
Askaria Colleges Rwp.

$$\Delta H^\circ_x = \Delta H^\circ_{at} + \Delta H^\circ_{I.E} + \Delta H^\circ_{at} + \Delta H^\circ_{EA}$$

$$= (108) + (496) + (121) + (-349)$$

$$\Delta H^\circ_x = 376\ kJ/mol^{-1}$$

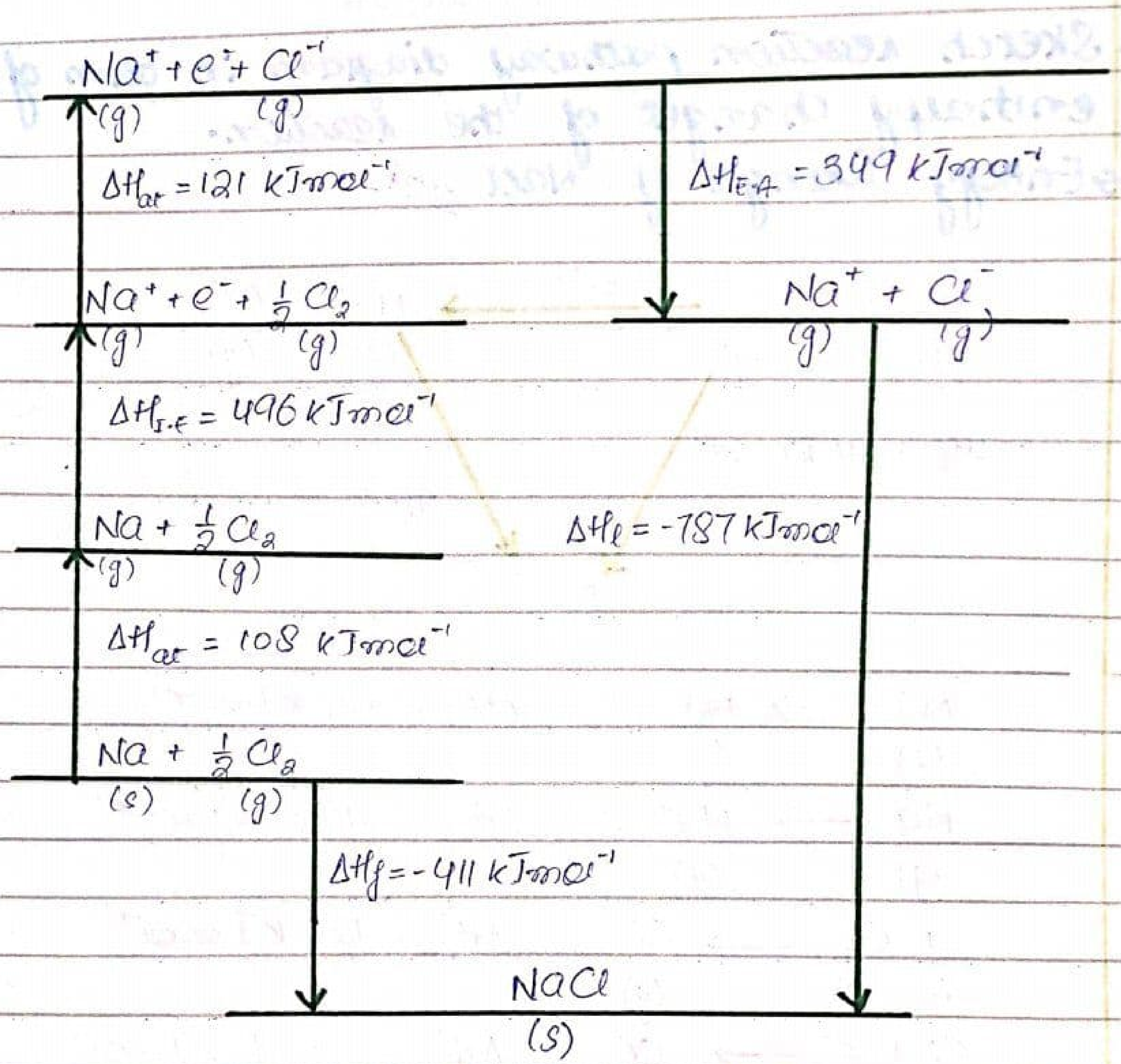
According to Hess's Law,

$$\Delta H_f = \Delta H_x + \Delta H_l$$

$$\Delta H_l = \Delta H_f - \Delta H_x$$

$$= -411 - 376$$

$$\Delta H_l = -787\ kJmol^{-1}$$



Q :- State and Explain First law of Thermodynamics.

extra

This law is also called law of conservation of energy. According to this law,

> "Energy can neither be created, nor destroyed, but can be converted from to another."

A system can exchange energy with its surroundings in two distinct ways. Energy can be transferred as heat or work.

Explanation

Consider a cylinder having moveable piston. Given amount of gas is enclosed in it. When heat is given to the system (cylinder) and work is done on it, internal energy of the gas increases from E_1 to E_2.

$$\Delta E = E_2 - E_1$$

$$\boxed{\Delta E = q + W}$$

Signs

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

(ii) When internal energy of the system decreases, ΔE is -ve.

(iii) When heat is given to the system, q is +ve.

(iv) When heat is given by the system, q is -ve.

(v) When work is done on the system, W is +ve.

(vi) When work is done by the system, W is -ve.

Q :- Calculate the work associated with the expansion of a gas from 50 dm^3 to 68 dm^3 at a constant external pressure of 10 atm. extra

Data:-

Work done, W = ?

Volume, V_1 = 50 dm^3

" V_2 = 68 dm^3

Pressure, P = 10 atm.

Solution:-

Firstly, $\Delta V = V_2 - V_1$

$= 68 - 50$

$\Delta V = 18\ dm^3$

Now, as we know, $W = P.\Delta V$

$= 10(18)$

$W = 180\ J$

Q :- Camphor ($C_{10}H_{16}O$) has a heat of combustion of 5903.6 kJ mol^{-1}. A sample of Camphor having mass of 0.1204 g is burned in a bomb calorimeter. The temperature increases by 2.28°C. Calculate heat capacity of the extra calorimeter?

Data :-

Heat of combustion of camphor $= -5903.6\ kJ\,mol^{-1}$

Mass of camphor $= 0.1204\,g$

Change in temperature, $\Delta T = 2.28\ K$

Heat Capacity, $C = ?$

Solution :-

as we know, no. of moles $= \frac{\text{mass in grams}}{\text{molar mass}}$

so, no. of moles of camphor $= \frac{0.1204}{152}$

$= 7.92 \times 10^{-4}$ moles

1 mole of camphor has heat of combustion $= -5903.6\ kJ\,mol^{-1}$

7.92×10^{-4} " " " " " $= -5903.6 \times 7.92 \times 10^{-4}$

$= -4.676\ kJ/mol$

we also know, $q = C \times \Delta T$

$$C = \frac{q}{\Delta T}$$

$$= \frac{-4.676}{2.28}$$

$$C = -2.05\ kJ\,mol^{-1}K^{-1}$$

Q :- In a coffee-cup calorimeter $100\ cm^3$ of $1.0\ M$ of HCl and $100\ cm^3$ of $1.0\ M$ of NaOH are mixed at $24.6^\circ C$ raised temperature by $6.9^\circ C$. Calculate the enthalpy of neutralization of HCl by NaOH by the given data. Heat capacity of water is $4.18\ Jg^{-1}\,{}^\circ C$. extra

Data:-

Volume of HCl, $V_{HCl} = 100\ cm^3 = 0.1\ dm^3$

Molarity of HCl, $M_{HCl} = 1.0\ M$

Volume of NaOH, $V_{NaOH} = 100\ cm^3 = 0.1\ dm^3$

Molarity of NaOH, $M_{NaOH} = 1.0\ M$

Change in temperature, $\Delta T = 6.9\ K$

Specific heat capacity, $C = 4.18\ J g^{-1}\ °C$

Enthalpy of neutralization, $q = ?$

Solution:-

Total Volume, $V_T = 100 + 100 = 200\ cm^3$

$= 0.2\ dm^3$

as $\text{density} = \frac{\text{mass}}{\text{volume}}$

so, $m = \rho \times V$

$= 1 \times 200\ cm^3\ (\because \rho \text{ of } H_2O = 1)$

$= 200\ g.$

Now, $q = mC.\Delta T$

$= 200^{g} \times 4.18^{J g^{-1}} \times 6.9^{K}$

$= 5768.4\ J/mol$

~~$= 57.684\ kJ\ mol^{-1}$~~

we know, $\text{Molarity} = \frac{\text{No. of moles}}{\text{Vol of sol in } dm^3}$

or No. of Moles = Molarity × Vol of solution

$= 1 \times 0.1$

$= 0.1$ moles

Heat evolved by 0.1 moles $= 5.768\ kJ\ mol^{-1}$

" " by 1 mole $= \frac{5.768}{0.1}$

$= 57.68\ kJ\ mol^{-1}$

Q1:- Calculate $\Delta H°$ for the reaction

$S + O_2 \longrightarrow SO_2$

from the following data

eq① $\underset{(s)}{S} + \underset{(g)}{\frac{3}{2}O_2} \longrightarrow \underset{(g)}{SO_3}$ $\Delta H^\circ = -395.2\ kJ/mol$

eq② $\underset{(g)}{2SO_2} + \underset{(g)}{O_2} \longrightarrow \underset{(g)}{2SO_3}$ $\Delta H^\circ = -198.2\ kJ\,mol^{-1}$

Dividing equation (ii) with '2'

eq③ $SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$ $\Delta H^\circ = -99.1\ kJ\,mol^{-1}$

Subtracting equation ③ & ①

$$SO_3 \longrightarrow SO_2 + \frac{1}{2}O_2 \quad \Delta H = 99.1\ kJ\,mol^{-1}$$

$$S + \frac{3}{2}O_2 \longrightarrow SO_3 \quad \Delta H = -395.2\ kJ\,mol^{-1}$$

$$S + O_2 \longrightarrow SO_2 \quad \Delta H = -296.1\ kJ\,mol^{-1}$$

Q :- An aluminium frying pan weighs 745 g 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 J mole⁻¹ K⁻¹!

extra

Data :-

mass in gram of Al = 745 g

Temperature, $T_1 = 25°C$

" $T_2 = 205°C$

$q = ?$

C_p for Al = 24.35 J mol⁻¹ K⁻¹

Solution:-

Firstly, No. of moles of Al = $\frac{\text{mass in grams}}{\text{molar mass}}$

$= \frac{745}{25}$

$= 27.592$ moles

now, $\Delta T = T_2 - T_1$

$= 205 - 25$

$\Delta T = 180°C$ or $180\ K$

we know, $q = n \cdot C_p \cdot \Delta T$

$= 27.592 \times 24.35 \times 180$

$= 120936.97\ J$

Q.15:- **Write the balanced equation for the formation reaction of each of the following substances**

(a) C_4H_9OH (Butanol)

$$4C + 5H_2 + \frac{1}{2}O_2 \longrightarrow C_4H_9OH$$

(b) Rust, Fe_3O_4

$$3Fe + 2O_2 \longrightarrow Fe_3O_4$$

(c) Acetic Acid, CH_3CO_2H

$$2C + 2H_2 + O_2 \longrightarrow CH_3CO_2H$$

(d) Urea, $(NH_2)_2CO$

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

Q.:- **The human body burns glucose for energy. Burning 1.0 g of glucose produces 15.65 kJ of heat.**

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

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

(b) Determine the molar heat of combustion of glucose.

Given mass of glucose = 1.0 g

Molar mass of glucose ($C_6H_{12}O_6$) = 180 g

No. of moles of glucose = $\frac{1}{180}$

= 5.56×10^{-3} moles

Given heat produced by glucose = 15.65 kJ.

Solution:-

5.56×10^{-3} moles of glucose produce heat = 15.65 kJ

1 mole of glucose produce heat = $\frac{15.65}{5.56 \times 10^{-3}}$

= 2817.28 kJ

(C) Heats of combustions of C and H_2 are $-393.5\ kJmol^{-1}$ and $-285.8\ kJmol^{-1}$ respectively. Determine the heat of formation of glucose.

eq ① $C + O_2 \longrightarrow CO_2 \qquad \Delta H = -393.5\ kJmol^{-1}$

eq ② $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O \qquad \Delta H = -285.8\ kJmol^{-1}$

eq ③ $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O \quad \Delta H = -2802\ kJmol^{-1}$

Multiplying eq ① with '6'

eq ④ $6C + 6O_2 \longrightarrow 6CO_2 \qquad \Delta H = -2361\ kJmol^{-1}$

Multiplying eq ② with '6'

eq ⑤ $6H_2 + 3O_2 \longrightarrow 6H_2O \qquad \Delta H = -1714.8\ kJmol^{-1}$

Adding eq ④ & ⑤

$6C + 6H_2 + 9O_2 \longrightarrow 6CO_2 + 6H_2O \quad \Delta H = -4075.8\ kJmol^{-1}$

eq ③ → Subtracting $6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2 \quad \Delta H = -2802\ kJmol^{-1}$

$6C + 6H_2 + 3O_2 \longrightarrow C_6H_{12}O_6 \quad \Delta H = -1273.8\ kJmol^{-1}$

Q :- Sketch the balanced chemical equation associated with each of the following enthalpy changes.

extra

(a) Heat of sublimation of iodine

$I_{2(s)} \longrightarrow I_{2(g)}$

(b) Heat of formation of gaseous atomic iodine.

$\frac{1}{2} I_{2(s)} \longrightarrow I_{(g)}$

(c) Heat of formation of $C_2H_3Cl_{(g)}$.

$2C + \frac{3}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow C_2H_3Cl$

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

$C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O$

Q27:- The standard combustion enthalpies of carbon, hydrogen and acetic acid are -393.5 kJ mol⁻¹, -285.8 kJ mol⁻¹ and -875 kJ mol⁻¹ respectively. Deduce the value of standard enthalpy of formation of acetic acid, CH_3COOH.

$2C + 2H_2 + O_2 \longrightarrow CH_3COOH \quad \Delta H = ?$

eq ① $CH_3COOH + 2O_2 \longrightarrow 2CO_2 + 2H_2O \quad \Delta H = -875\ kJ\,mol^{-1}$

eq ② $C + O_2 \longrightarrow CO_2 \quad \Delta H = -393.5\ kJ\,mol^{-1}$

eq ③ $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O \quad \Delta H = -258.8\ kJ\,mol^{-1}$

Multiplying eq ② with '2'

eq ④ $2C + 2O_2 \longrightarrow 2CO_2 \quad \Delta H = -787\ kJ\,mol^{-1}$

Multiplying eq ③ with '2'

eq ⑤ $2H_2 + O_2 \longrightarrow 2H_2O \quad \Delta H = -517.6\ kJ\,mol^{-1}$

Adding eq ④ & ⑤

$$2C + 2H_2 + 3O_2 \longrightarrow 2CO_2 + 2H_2O \quad \Delta H = -1304.6\ kJmol^{-1}$$

eq① $$2CO_2 + 2H_2O \longrightarrow CH_3COOH + 2O_2 \quad \Delta H = 875\ kJmol^{-1}$$

subtracting

$$2C + 2H_2 + O_2 \longrightarrow CH_3COOH \quad \Delta H =$$

Q.12:- Is the conversion of magnetite, Fe_3O_4 to hematite, Fe_2O_3 by oxygen is endothermic or exothermic? Justify your answer.

eq① $$\underset{(s)}{3Fe} + \underset{(g)}{2O_2} \longrightarrow Fe_3O_4 \quad \Delta H = -1118\ kJmol^{-1}$$

eq② $$2Fe + \frac{3}{2}O_2 \longrightarrow Fe_2O_3 \quad \Delta H = -824.2\ kJmol^{-1}$$

$$2Fe_3O_4 + \frac{1}{2}O_2 \longrightarrow 3Fe_2O_3 \quad \Delta H = ?$$

$$\Delta H^\circ_{reaction} = \left[\sum coefficient \cdot \Delta H_{product}\right] - \left[\sum coefficient \cdot \Delta H_{reactant}\right]$$

$$= \left[3 \times (-824.2)\right] - \left[2 \times (-1118) + \frac{1}{2}(0)\right]$$

$$= -236\ kJmol^{-1}$$

Q:- Which of the following processes would you expect to be endothermic? extra

a) exothermic
b) exothermic
c) endothermic
d) endothermic
e) endothermic
f) exothermic

Q:- Cooling effect is experienced when few drops of ethanol are put on your palm. Justify this statement. extra

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

Ethanol is a liquid of very low density. Its evaporation rate is very fast i.e. its particles have high kinetic energy, so, when we put it on our palm, it starts to evaporate quickly and ultimately it lowers the temperature of our palm and cooling effect is experienced.

Q19:- In some countries liquid methanol is being used as an alternative fuel in cars and trucks. Industrially ethanol is produced by the following reaction.

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

Standard enthalpies of formation of CH_3OH and CO are $-238.7\ kJmol^{-1}$ and $-110.5\ kJmol^{-1}$ respectively. Will the reverse reaction be exothermic or endothermic. Justify your stand.

eq①→ $$C + 2H_2 + \frac{1}{2}O_2 \longrightarrow CH_3OH \quad \Delta H^\circ = -238.7\ kJmol$$

eq②→ $$C_2 + \frac{1}{2}O_2 \longrightarrow CO \quad \Delta H^\circ = -110.5\ kJmol^{-1}$$

$$CH_3OH \longrightarrow CO + 2H_2 \quad \Delta H = ?$$

$$CH_3OH \longrightarrow C + 2H_2 + \frac{1}{2}O_2 \quad \Delta H = 238.7\ kJmol^{-1}$$

$$C + \frac{1}{2}O_2 \longrightarrow CO \quad \Delta H = +110.5\ kJ$$

$$CH_3OH \longrightarrow CO + 2H_2 \quad \Delta H = 128.2\ kJ$$

• Thus the reverse of the reaction is endothermic. However, the original given reaction is exothermic.