CHEMISTRY

11

CH#7

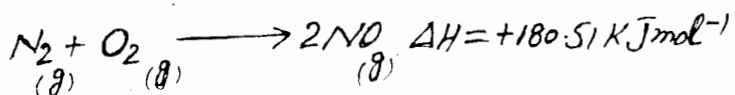Thermochemistry

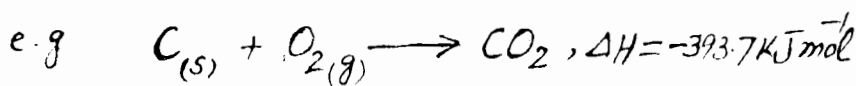These Notes Have been Prepared and Developed By
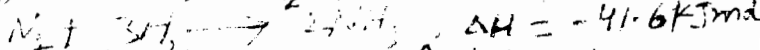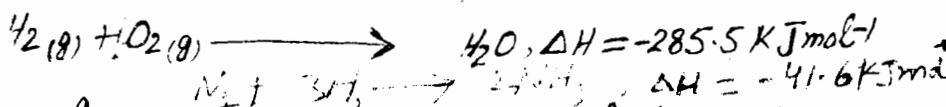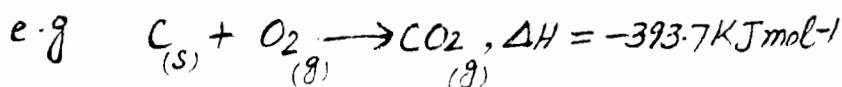
ADNAN SHAFIQUE

Chapter 7
THERMOCHEMISTRY

The branch of Chemistry which deals with heat changes of chemical reactions is called thermochemistry. OR The study of heat changes accompanying a chemical reaction is called thermochemistry

Heat of reaction:- The amount of heat evolved or absorbed in chemical reaction is called heat of reaction. It is denoted by ΔH. The ΔH has negative sign if heat is evolved لجاتی ہے. The ΔH has positive sign if heat is absorbed

e.g

$$C_{(s)} + O_{2(g)} \longrightarrow CO_2 , \Delta H = -393.7 \, KJ\,mol^{-1}$$

$$N_2 + O_{2(g)} \longrightarrow 2NO_{(g)} \quad \Delta H = +180.51 \, KJ\,mol^{-1}$$

Exothermic Reaction:- The reaction in which heat is evolved خارج ہوتی ہے is called exothermic ارمائی تپش reaction. The ΔH is negative for exothermic reaction

e.g

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} , \Delta H = -393.7 \, KJ\,mol^{-1}$$

$$H_{2(g)} + O_{2(g)} \longrightarrow H_2O , \Delta H = -285.5 \, KJ\,mol^{-1}$$

$$N_2 + \ldots \longrightarrow \ldots , \Delta H = -41.6 \, KJ\,mol$$

In an exothermic reaction, heat is given out. So the temperature of the system rises above the room temperature. Finally آخرکار

the temperature of the system again falls to the room temperature because heat produced is lost to the surrounding. We should know that enthalpy of the products (H_2) is less than that of reactants H_1.
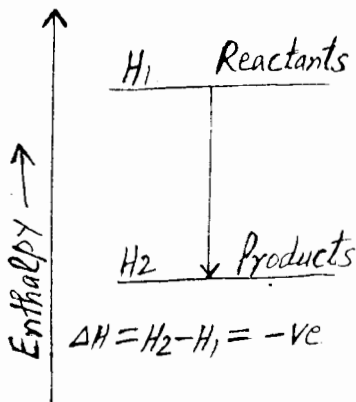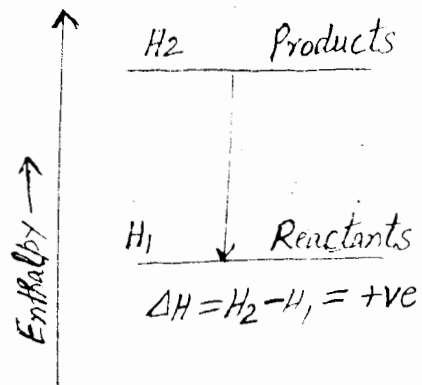
<u>Endothermic Reaction</u> :- The reaction in which heat is absorbed جذب لیا is called endothermic reaction. The ΔH is positive for an endothermic reaction. For example,

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)} , \Delta H = +180.5 \, Kj \, mol^{-1}$$

$$H_2, O \longrightarrow H_2^+ O , \Delta H = 285.5 \, KJm^{-1}$$

$$H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)} , \Delta H = +52.96 \, Kj \, mol^{-1}$$
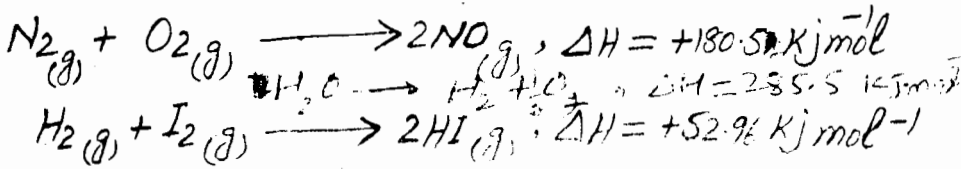
In an endothermic reaction, heat is required. This heat is taken from reactants. So temperature of system falls below the room temperature. Finally, the temperature of system again rises to room temperature because heat is absorbed from surrounding. We may say that enthalpy (heat content) of products H_2 is greater than that of reactants H_1 for an endothermic reaction. It is shown in figure
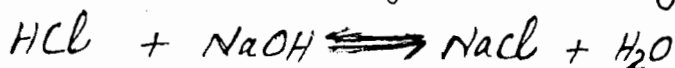
H_1 ___ Reactants

Enthalpy →

H_2 ↓ Products

$\Delta H = H_2 - H_1 = -ve$

(Exothermic reaction)

H_2 ___ Products

Enthalpy →

H_1 ↓ Reactants

$\Delta H = H_2 - H_1 = +ve$

(Endothermic Reaction)

Spontaneous Reaction:- A Process which takes place on its own without any outside assistance and moves ~~from non-equilibrium~~ towards an equilibrium state is called Spontaneous Process or natural Process. OR a reaction which needs energy to start, but once it is started then it takes place on its own is called spontaneous reaction. e.g (i) Burning of coal or sui-gas

(ii) Flow of water from high level to low level.

(iii) Flow of heat from hot body to cold body

(iv) Reaction between strong acid and strong base

$$HCl + NaOH \rightleftharpoons NaCl + H_2O$$

(v) Reaction between Zn and $CuSO_4$ solution.

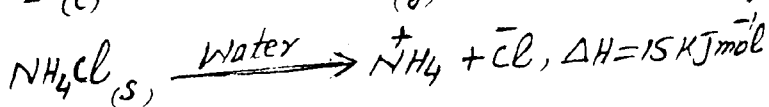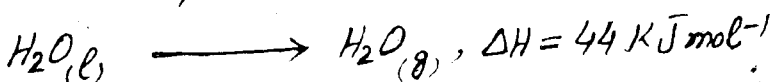$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

The spontaneous reaction (Process) is natural, uni-directional, real and irreversible.

Non-Spontaneous Reaction:- A reaction which is the reverse of spontaneous reaction and does not take place on its own is called non-spontaneous reaction.

e.g (i) Pumping of water uphill.

(ii) Freezing of water in refrigerator.

(iii) $N_2 + O_2 \xrightleftharpoons{\text{Lightning}} 2NO$

Generally a spontaneous reaction takes place by decrease in energy. Therefore an

exothermic reaction should be a spontaneous reaction. This is not always true. There are many endothermic reactions which are spontaneous. For example,

$$H_2O_{(l)} \longrightarrow H_2O_{(g)}, \Delta H = 44 \, KJ \, mol^{-1}$$

$$NH_4Cl_{(s)} \xrightarrow{Water} \overset{+}{N}H_4 + \overset{-}{C}l, \Delta H = 15 \, KJ \, mol$$

System and Surrounding:- Anything under test in the laboratory is called system. OR Anything under consideration in the classroom is called system. We can say that any portion of the universe which is under study is called system. The remaining Portion of the universe except system is called surrounding. A real or imaginary surface which separates the system from surrounding is called **boundary**.
For example (i) A cup of water is a system. The air, table and all things are surroundings
(ii) One mole of oxygen in a cylinder is a system. The cylinder, piston and all objects outside the cylinder are surroundings.
(iii) Consider the reaction between Zn and CuSO₄ solution in a flask. It is a system. The air, flask and all other things are surroundings.

<u>Energy</u> :- The ability (capacity) of a body to do work is called energy. e.g A moving car has kinetic energy. The sui-gas or Petrol has chemical energy in it.

The kinetic energy, Potential energy, chemical energy, electric energy, magnetic energy, heat energy, Solar energy, radiant energy wind energy and nuclear energy are different kinds of energy.

<u>Units of energy</u> :-

There are two units of energy

(i) Calorie   (ii) Joule

<u>Calorie</u> :- The amount of energy required to raise the temperature of one gram of water from $14.5°C$ to $15.5°C$ is called Calorie.

$$1000 \ Cal = 1 \ K.Cal$$

<u>Joule</u> :- When a force of one Newton moves a body of 1Kg mass through 1m distance in its direction, then energy expended is called Joule.

$$1 J = Kg \ m^2 \ s^{-2}$$

$$1 KJ = 1000 \ J$$

$$1 \ Calorie = 4.18 \ Joules$$

Heat :- Heat is a form of energy which Flows From hot to cold body.

Heat is the total K·E of all molecules in a system. Its unit is Calorie, Joule, K·J

Temperature :- Degree of hotness or coldness of a body is called temperature.

oR The average K·E of all molecules in a body is called temperature. Its unit is Centigrade or Fahrenheit. The SI unit is Kelvin

Relation between heat and temperature :-

When a body absorbs heat, then its temperature increases. Let a body absorbs heat q. This heat q is directly proportional to the mass of body and Change of temperature

$$q \propto m \, \Delta T$$

or $q = m \times S \times \Delta T$ where m is mass of body, S = specific heat of body and ΔT = change in temperature

Specific heat (حرارتِ نوعی) :-

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

e·g Sp·heat of water is $4.2 \, J \, g^{-1} K^{-1}$

Sp·heat of ethyl alcohol is $2.5 \, J \, g^{-1} K^{-1}$

State and State function :-

The Condition (حالت) of a system is called state of system. e.g The properties such as temperature, pressure, volume describe the state of a system. There are two types of state. (i) Initial state (ii) final state

Initial State :- The state of a system before it undergoes any change is called initial state

Final State :- The state of a system after it undergoes any change is called final state

Change in state = Final state — Initial state

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

Change in Volume $\Delta V = V_2 - V_1$

Change in Pressure $\Delta P = P_2 - P_1$

State Function :- A macroscopic property which depends upon initial and final states of system and is independent of th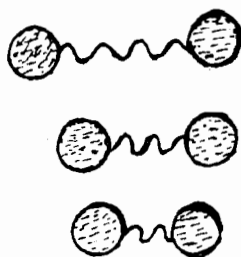e path followed by the system is called state function. e.g Temperature, Pressure, volume, enthalpy and internal energy are state functions.

Internal Energy :- The sum of all the possible kinds of energies of a system is called internal energy. OR The sum of K.E and P.E of all the particles in a system is called internal energy.
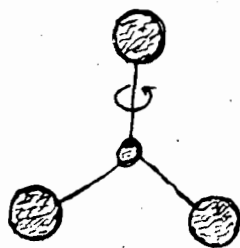
The internal energy is a state function.
The absolute value of internal energy
can not be measured. However the change
in internal energy (ΔE) can be measured.
The internal energy is sum of K.E and P.E
The K.E is due to translational, rotational
and vibrational motions of molecules.
The P.E is due to forces of attraction
between the molecules. The three types of
motions are shown below.
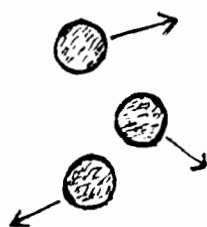
| translational motion | Vibrational motion | rotational motion |

Heat :- The quantity of energy which
flows between system and surroundings due
to their temperature difference is called
heat. It is denoted by q. It is not
a property of system. Therefore it
is not a state function. The transfer
of energy between system and surrounding
takes place in the form of heat or work.

The sign of q is positive when heat is absorbed by the system. The sign of q is negative when heat is evolved by the system. The SI unit of heat is Joule.

Pressure - Volume Work :-

The product of force and distance is called work.   Work = force × distance

$$W = F \times S$$

There are many kinds of work but in chemistry we deal with Pressure - Volume work. For example when a gas evolves during chemical reaction, then piston moves up. So Pressure - Volume work is done by the system (gas). It is shown below.

External Pressure

$$\Delta V = V_2 - V_1$$

Marble chips and dilute HCl
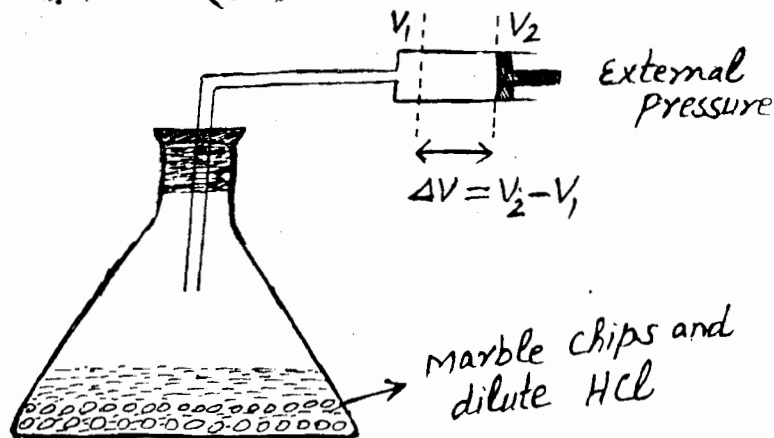
The work done by the system is given as

$$W = -P\Delta V$$ where P is external pressure and ΔV is change in volume

The sign of W is negative when work

is done by the system. The sign of W is positive when work is done on the system." The unit of work is Joule. The work is not a state function.

First law of thermodynamics

The first law of thermodynamics is also called law of conservation of energy. This law states that energy can neither be created nor destroyed but can be changed from one form to another. OR The total energy of system and surrounding remains constant. Consider a gas in a cylinder having a piston. The internal energy of gas is E_1. The heat q is given to the gas. Now internal energy of system becomes E_2. The change in internal energy (ΔE) is given as
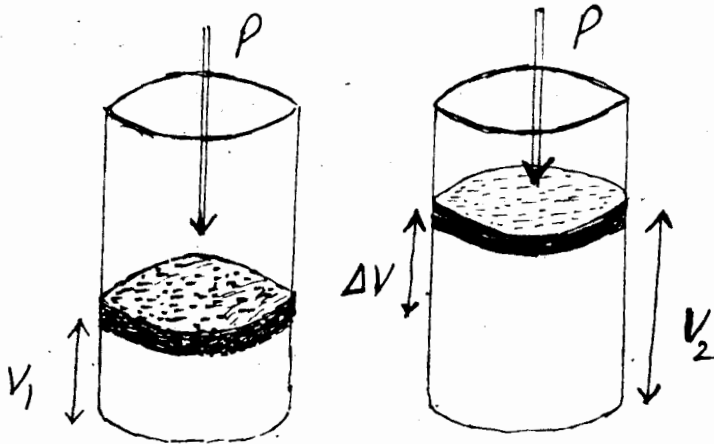
$$\Delta E = E_2 - E_1$$

We have to do work (W) on the piston to keep it in its original position. Thus energy change is equal to sum of heat and work
So
$$\Delta E = q + W$$
$$\Delta E = q + P\Delta V$$

It is mathematical form of first law of thermodynamics. It is used to describe a process at constant volume and constant P.

Expansion of a gas

$$\Delta V = V_2 - V_1$$

Process at Constant Volume:-

When volume of gas remains constant, then Piston of the Cylinder remains at its original Position. According to Ist law of thermodynamics

$$\Delta E = q + \omega$$

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

Because volume is constant, so $\Delta V = 0$

Thus

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

$$\Delta E = q_v$$

It means that at constant volume, the change in internal energy is equal to the heat absorbed by the system. We use Bomb Calorimeter to describe a process at constant volume.

The internal energy of a System,
12 Plus work done by the gas
is called

Enthalpy (Process at Constant Pressure) Enthalpy

Total heat content (حرارت) of a system is called enthalpy. It is denoted by H

It is a state function. Its unit is Joule.

Mathematically enthalpy is equal to sum of internal energy and Pressure – Volume work.

$$H = E + PV \quad —①$$

It is not possible to measure enthalpy of a system. However change in enthalpy (ΔH) can be easily measured.

$$\Delta H = \Delta E + \Delta(PV)$$

$$\text{or} \quad \Delta H = \Delta E + V\Delta P + P\Delta V$$

Because Pressure is Constant, so $\Delta P = 0$

$$\text{Hence} \quad \Delta H = \Delta E + P\Delta V \quad —②$$

For solids and liquids the volume change, $\Delta V = 0$, so eq ② becomes

$$\Delta H = \Delta E$$

According to Ist law of thermodynamics

$$\Delta E = q + w \quad —③$$

If w is work done by the system, then

$$w = -P\Delta V$$

$$\text{So} \quad \Delta E = q - P\Delta V \quad —④$$

We put this value of ΔE in eq (2) and get

$$\Delta H = q - P\Delta V + P\Delta V$$

$$\text{or} \quad \Delta H = q$$

Because Pressure is constant, therefore

$$\Delta H = q_p \quad \text{——} \quad ⑤$$

It means that at constant Pressure, the enthalpy change is equal to heat of reaction. Since most of the reactions take place in open vessels at constant Pressure. So Chemists take more interest in q_p instead of q_v

EXAMPLE:-1 When 2.00 moles of H_2 and 1.00 mole of O_2 at 100^0C and 1 torr pressure react to produce 2.00 moles of gaseous water, 484.5 kJ of energy are evolved. What are (a) ΔH and (b) ΔE for the production of one mole of H_2O (g)

Solution:— (a) Reaction occurs at constant Pressure

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$$
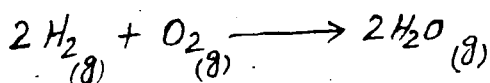
$$\Delta H = q_p = \frac{-484.5}{2} = -242.2 \, KJ \, mol^{-1}$$

(b) $T = 100^0C + 273 = 373K$, $R = 8.314 \, J \, mol^{-1} K^{-1}$

$\Delta n = $ No. of moles of Products — moles of reactants

$\Delta n = 2 - 3 = -1$

$PV = nRT$ or $P\Delta V = \Delta n RT$

$P\Delta V = (-1)(8.314)(373) = -3100$ Joules

$P\Delta V = -3.10 \, KJ$ It is for 2 moles of H_2O
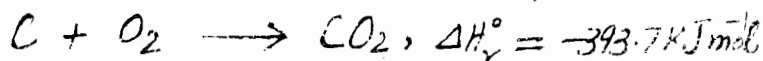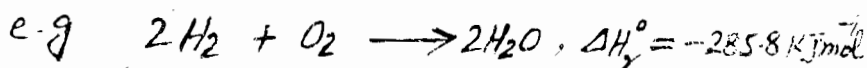
$P\Delta V = \frac{-3.10}{2} = -1.55 \, KJ \, mol^{-1}$

We Know that $\Delta H = \Delta E + P\Delta V$

or $\Delta E = \Delta H - P\Delta V = -242.2 - (-1.55)$

$\Delta E = -242.2 + 1.55$ or $\boxed{\Delta E = -240.65 \, KJ \, mol^{-1}}$

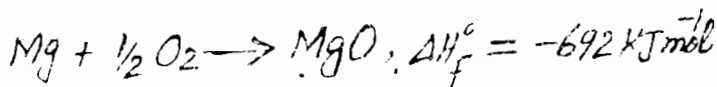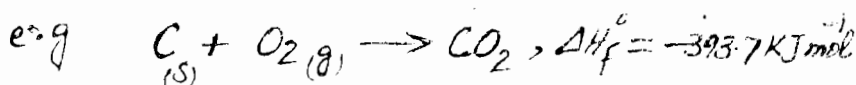## Standard enthalpy of reaction :-

The enthalpy change of a reaction when all reactants and products completely react, to give their products standard (25°C and 1 atm) is called standard enthalpy of reaction. It is denoted by ΔH_r°. Its unit is $KJ\,mol^{-1}$. Its value is negative for an exothermic reaction and positive for an endothermic reaction.

e.g

$$2H_2 + O_2 \longrightarrow 2H_2O \;,\; \Delta H_r^\circ = -285.8\,KJ\,mol^{-1}$$

$$C + O_2 \longrightarrow CO_2 \;,\; \Delta H_r^\circ = -393.7\,KJ\,mol^{-1}$$

Standard enthalpy of formation :-

The enthalpy change when one mole of a compound is formed from its elements under standard conditions is called standard enthalpy of formation. It is denoted by ΔH_f°. Its unit is $KJ\,mol^{-1}$.
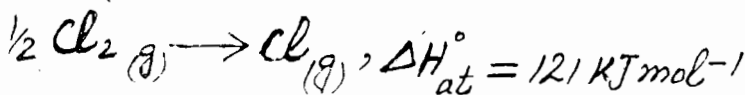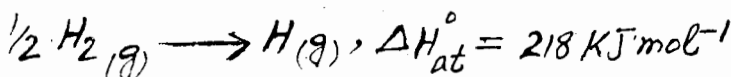
e.g

$$C_{(S)} + O_{2(g)} \longrightarrow CO_2 \;,\; \Delta H_f^\circ = -393.7\,KJ\,mol^{-1}$$

$$Mg + \tfrac{1}{2} O_2 \longrightarrow MgO \;,\; \Delta H_f^\circ = -692\,KJ\,mol^{-1}$$

Some solids have more than one crystalline forms. Each form has its own ΔH_f°.

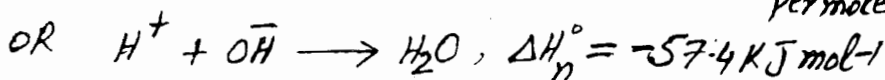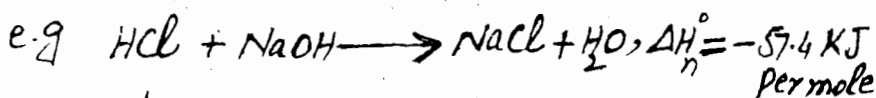## Standard enthalpy of atomization :-

The enthalpy change when one mole of gaseous atoms are formed from the element under standard conditions (25°C and 1 atm)

is called standard enthalpy of atomization.
It is denoted by ΔH°_{at}. Its unit is
$KJ\ mol^{-1}$. For example,

$$\tfrac{1}{2} H_{2\ (g)} \longrightarrow H_{(g)}, \Delta H^\circ_{at} = 218\ KJ\ mol^{-1}$$

$$\tfrac{1}{2} Cl_{2\ (g)} \longrightarrow Cl_{(g)}, \Delta H^\circ_{at} = 121\ KJ\ mol^{-1}$$

Standard enthalpy of neutralization:-

The enthalpy change when one mole of H^+ ions
from an acid react with one mole of OH^- ions
from a base to form one mole of water under
standard conditions is called standard
enthalpy of neutralization. OR The enthalpy
change when one mole of liquid water is
formed from its component ions under
standard conditions is called standard enthalpy
of neutralization. It is denoted by ΔH°_n.
Its unit is $KJ\ mol^{-1}$

e.g $HCl + NaOH \longrightarrow NaCl + H_2O, \Delta H^\circ_n = -57.4\ KJ\ per\ mole$

OR $H^+ + OH^- \longrightarrow H_2O, \Delta H^\circ_n = -57.4\ KJ\ mol^{-1}$

The heat of neutralization of strong acid with
strong base is approximately $-57.4\ KJ\ mol^{-1}$
The heat of neutralization of weak acid (HCN)
with strong base (NaOH) is $-10.03\ KJ\ mol^{-1}$
$HCN + NaOH \longrightarrow NaCi + H_2O, \Delta H_n = -10.03\ KJ\ mol^{-1}$
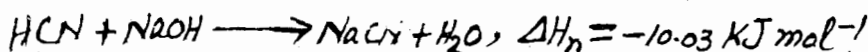
Standard enthalpy of Combustion:-

The enthalpy change when one mole of a substance is completely burnt in an excess of oxygen under standard conditions is called standard enthalpy of Combustion. It is denoted by ΔH_C°. Its unit is $KJ\,mol^{-1}$. For example,

$$C + O_2 \longrightarrow CO_2 \, , \, \Delta H_C^{\circ} = -393.7\,KJ\,mol^{-1}$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O , \, \Delta H_C^{\circ} = -890\,KJ\,mol^{-1}$$

$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O , \, \Delta H_C^{\circ} = -1367\,KJ\,mol^{-1}$$
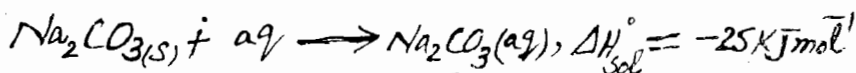
(Ethyl alcohol)
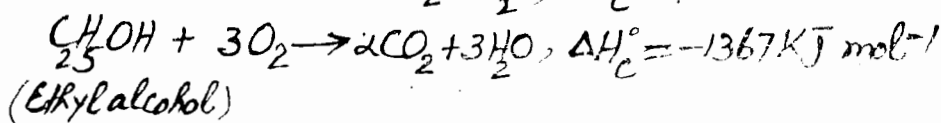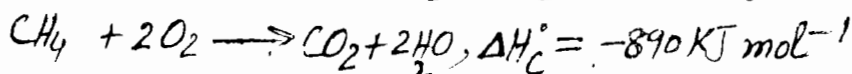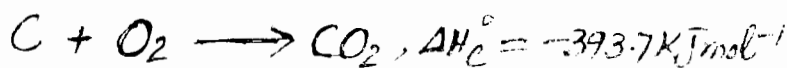
Standard enthalpy of Solution:-

The enthalpy change when one mole of a substance is dissolved in so much Solvent that further dilution produces no enthalpy change under the Standard Conditions is called Standard enthalpy of Solution. It is denoted by ΔH_{sol}°. Its unit is $KJ\,mol^{-1}$.

Examples are given below.

$$NH_4Cl_{(s)} + aq \longrightarrow NH_4Cl\,(aq) , \, \Delta H_{sol}^{\circ} = 16.2\,KJ\,mol^{-1}$$
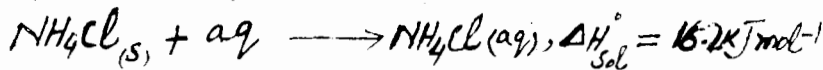
Here ΔH_{sol}° has positive sign, so it is an endothermic process.

$$Na_2CO_{3(s)} + aq \longrightarrow Na_2CO_3(aq) , \, \Delta H_{sol}^{\circ} = -25\,KJ\,mol^{-1}$$

Here enthalpy change has negative sign. So it is an exothermic process.
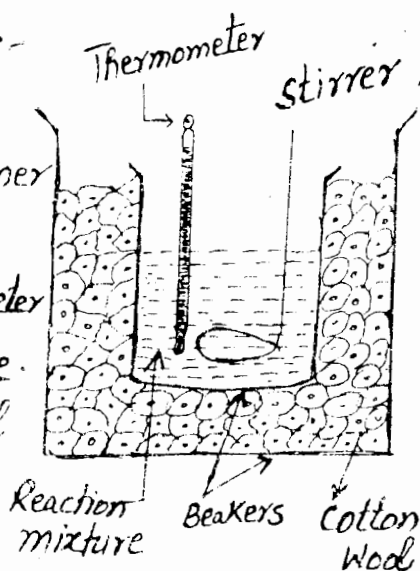
Measurement of enthalpy of reaction

We measure enthalpy of a reaction by a Calorimeter. We use two types of Calorimeters. (i) Glass Calorimeter. (ii) Bomb Calorimeter.

(i) **Glass Calorimeter** :-

It consists of two glass beakers. The inner beaker contains a Stirrer (SL_e), thermometer and reaction mixture. There is cotton wool in between inner and outer beaker.

The cotton wool acts as a heat insulator When reactants are put into inner beaker, then reaction starts. The temperature of the system either rises or falls. The temperature of system is noted before and after the reaction. Then with help of temperature change, mass of reaction mixture and specific heat of reaction mixture we find out heat (q) evolved or absorbed.

Heat, $q = m \times S \times \Delta T$ where m = mass of reactants, S = specific heat of reaction

mixture and ΔT is change in temperature.

EXAMPLE:-2 Neutralization of 100 cm^3 of 0.5 M NaOH at 25 ^{0}C with 100 cm^3 of 0.5 M HCl at 25 ^{0}C raised the temperature of the reaction mixture to 28.5^{0}C. Find the enthalpy of neutralization. Specific heat of water=4.2Jg^{-1} K^{-1}

Solution:- Specific heat of water, $S = 4.2 J g^{-1} K^{-1}$

Volume of NaOH Solution $= 100 \, cm^3$

Volume of HCl Solution $= 100 \, cm^3$

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

Density of Solution (H_2O) $= 1 \, g \, cm^{-3}$

Mass of Solution $=$ density $\times$ volume

$= 1 \times 200 = 200 \, g$

Initial Temperature $T_1 = 25^\circ C + 273 = 298 K$

Final temperature $T_2 = 28.5^\circ C + 273 = 301.5 K$

ΔT, Change in Temperature $= 301.5 - 298 = 3.5 K$

Volume of HCl or NaOH $= 100 cm^3 = \frac{100}{1000} = 0.1 dm^3$

Molarity of HCl or NaOH $= 0.5 M$

$$Molarity = \frac{No. \ of \ moles}{Vol \ of \ solution \ in \ dm^3}$$

No of moles $=$ Molarity $\times$ Vol of sol in dm^3

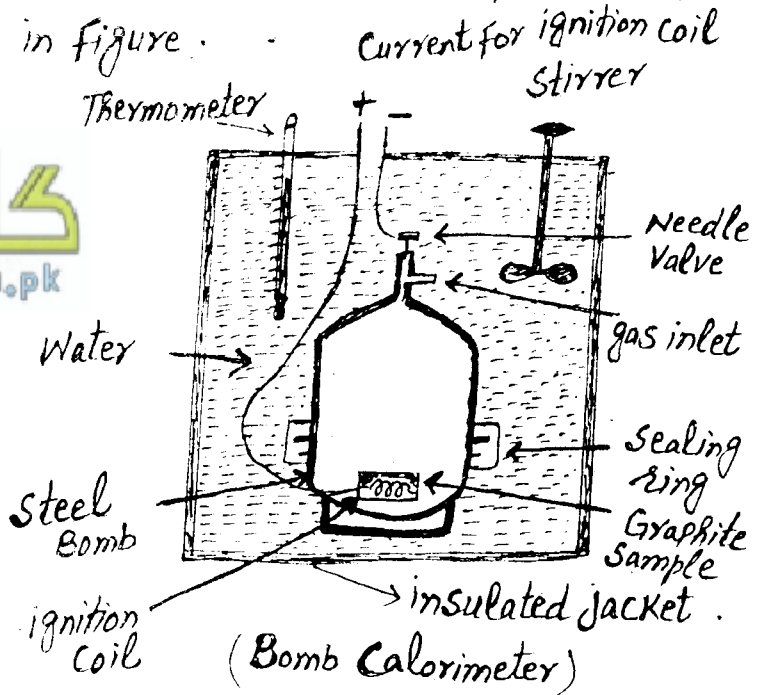No of moles $= 0.5 \times 0.1 = 0.05$ moles

heat evolved, $q = m \times S \times \Delta T$

$= - 200 \times 4.2 \times 3.5$

$= -2940 J = \frac{2940}{1000} = -2.94 KJ$

Enthalpy of neutralization, $\Delta H_n^\circ = \frac{-2.94}{0.05}$

$\Delta H_n^\circ = -58.8 \, KJ \, mol^{-1}$

Bomb Calorimeter:-

A bomb calorimeter is used to determine enthalpy of combustion of food, fuel and other compounds. It is shown in figure.

(Bomb Calorimeter)

It consists of a ~~strong~~ cylindrical steel vessel, called bomb. It is lined with enamel to prevent (روکنا) corrosion (زنگ لگنا) There is an ignition coil and a platinum crucible (cup) inside the bomb. The bomb is immersed (surrounded) by water kept in an insulated jacket. A known mass (about one gram) of test substance is placed in platinum crucible. The lid is screwed on tightly and oxygen gas is provided (entered) at a pressure of 20—25 atm. The initial temperature is

noted by thermometer. The test substance is ignited (اگ بھڑنا) by passing electric current through the ignition coil. The heat evolves due to ignition of substance. The water is stirred continuously. The rise in temperature is noted after every 30 sec. In this way we note the maximum temperature. Then we determine heat of combustion by following formula.

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

where q is heat of combustion, C is heat Capacity of Calorimeter and ΔT is increase of temperature.

EXAMPLE 3: 10.16g of graphite is burnt in a bomb calorimeter and the temperature rise recorded is 3.87K. Calculate the enthalpy of combustion of graphite, if the heat capacity of the calorimeter (bomb, water, etc.) is 86.02 k J K⁻¹

Solution:- Mass of graphite = 10.16 g

No of moles of graphite = $\frac{10.16}{12}$ = 0.843 moles

Heat Capacity of bomb Calorimeter, $C = 86.02 KJ K^{-1}$

rise in temperature, $\Delta T = 3.87 K$

Heat of Combustion of graphite, $q = ?$

$$q = C \times \Delta T$$
$$= 86.02 \times 3.87 = 332.89 KJ$$
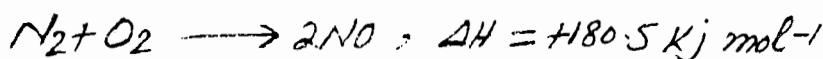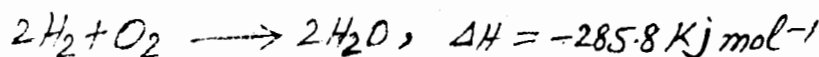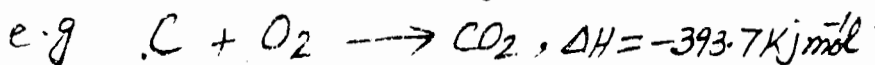
Heat of Combustion Per mole = $\frac{332.89}{0.843} = 395 KJ \, mol^{-1}$

Since heat is evolved during Combustion, so its sign, is negative. Hence Heat of Combustion $= -395 KJ \, mol^{-1}$

Thermochemical Equation

An equation which indicates the heat evolved or absorbed during the chemical reaction is called thermochemical equation. The reaction in which heat is evolved is called an exothermic reaction. Its enthalpy sign is negative. A reaction in which heat is absorbed لیا جاتا ہے is called an endothermic reaction. Its enthalpy sign is positive.

e.g $C + O_2 \longrightarrow CO_2$, $\Delta H = -393.7 Kj\,mol^{-1}$

$2H_2 + O_2 \longrightarrow 2H_2O$, $\Delta H = -285.8\,Kj\,mol^{-1}$

$N_2 + O_2 \longrightarrow 2NO$; $\Delta H = +180.5\,Kj\,mol^{-1}$

Laws of thermochemistry

There are two laws of thermochemistry.

(i) First Law of thermochemistry

(ii) Second law of thermochemistry. The second law of thermochemistry is also called Hess's law.

First law of thermochemistry: This law states that heat of decomposition of a compound is always equal and opposite to heat of formation of that compound. For example

$C + O_2 \longrightarrow CO_2$, $\Delta H = -393.7 Kj\,mol^{-1}$

$CO_2 \longrightarrow C + O_2$, $\Delta H = +393.7\,Kj\,mol^{-1}$
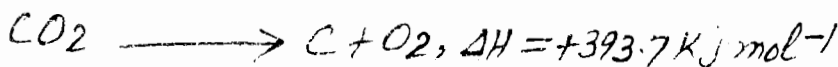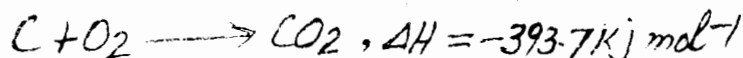
Hess's Law of Constant Heat Summation

This law was put forward by G.H. Hess in 1840.
This law states that overall enthalpy change
is same if a chemical reaction takes
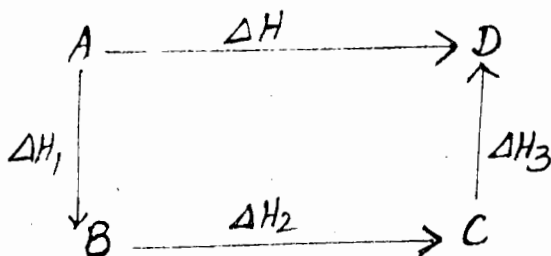place in one step or in several (many) steps.
OR The overall enthalpy change depends upon
initial and final states of a reaction and ~~not~~ is
independent ~~upon~~ of path followed by the reaction

Mathematically,

$$\sum \Delta H (cycle) = 0$$

It means that sum of all enthalpy changes
in a cyclic process is equal to zero.
Hess's law is an application of the law of
conservation of energy. Consider a general
reaction in which Substance A is converted
into D. The reaction takes place in one
step or in three steps

$$
\begin{array}{ccc}
A & \xrightarrow{\;\;\Delta H\;\;} & D \\
\Delta H_1 \downarrow & & \uparrow \Delta H_3 \\
B & \xrightarrow{\;\;\Delta H_2\;\;} & C
\end{array}
$$

According to Hess's law
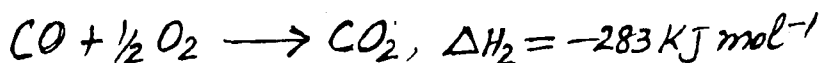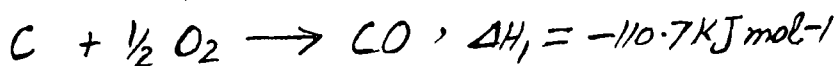
$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Now we give examples of Hess's law.

Example(i):- The formation of Carbon dioxide takes place by two ways.

First Way is single step Process

$$C + O_2 \longrightarrow CO_2 , \Delta H = -393.7 KJ\, mol^{-1}$$

Second way is two step Process

$$C + \tfrac{1}{2} O_2 \longrightarrow CO , \Delta H_1 = -110.7 KJ\, mol^{-1}$$

$$CO + \tfrac{1}{2} O_2 \longrightarrow CO_2 , \Delta H_2 = -283 KJ\, mol^{-1}$$

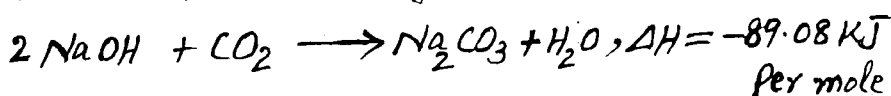The enthalpy change is Same in both Cases

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

$$-393.7 = -110.7 + (-283)$$

$$-393.7 KJ = -393.7 KJ$$

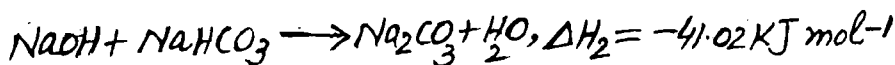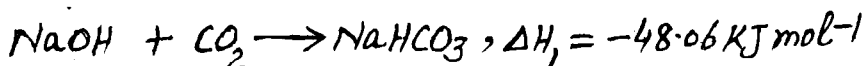Thus Hess's Law is Proved.

Example (ii):- The formation of Sodium Carbonate takes place by two ways.

First way is a single step process

$$2 NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O , \Delta H = -89.08 KJ \text{ per mole}$$

Second way is a two step process.

$$NaOH + CO_2 \longrightarrow NaHCO_3 , \Delta H_1 = -48.06 KJ\, mol^{-1}$$

$$NaOH + NaHCO_3 \longrightarrow Na_2CO_3 + H_2O , \Delta H_2 = -41.02 KJ\, mol^{-1}$$

The enthalpy Change in both Cases is Same

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

$$-89.08 = -48.06 + (-41.02)$$

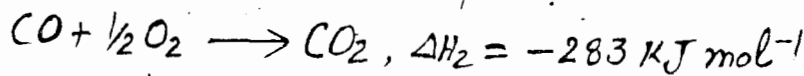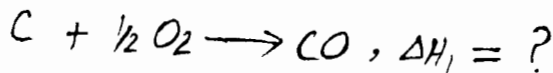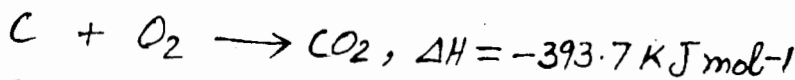$$-89.08 = -89.08 KJ \quad \text{Hence Hess's Law Proved.}$$

Applications of Hess's Law

There are many reactions which are very slow or they do not give single product. So their ΔH cannot be measured directly. Therefore their ΔH is measured indirectly by Hess's law.

(1) Carbon tetrachloride (CCl_4) can not be directly prepared by reaction of Carbon (graphite) and chlorine. Moreover decomposition of CCl_4 is not easy. Thus heat of formation of CCl_4 is measured indirectly by using Hess's law.

(2) During combustion (burning) of Aluminium and Boron a protective layer is formed on their surfaces so Al and B do not burn completely. Hence enthalpy of formation of Al_2O_3 and B_2O_3 are, measured indirectly by using Hess's Law.

$$2Al + \tfrac{3}{2} O_2 \longrightarrow Al_2O_3, \Delta H = -1675\, KJ\, mol^{-1}$$
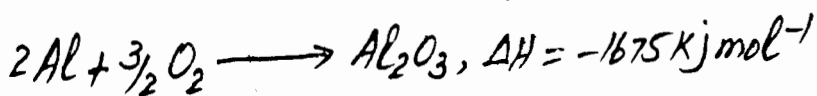
③ The heat of formation of CO cannot be measured directly due to formation of CO_2 with it. Therefore it is indirectly measured by Hess's law.

$$C + O_2 \longrightarrow CO_2, \Delta H = -393.7\, KJ\, mol^{-1}$$
$$C + \tfrac{1}{2} O_2 \longrightarrow CO, \Delta H_1 = ?$$
$$CO + \tfrac{1}{2} O_2 \longrightarrow CO_2, \Delta H_2 = -283\, KJ\, mol^{-1}$$

By adding the last two equations, we get the First equation. Therefore

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

$$-393.7 \, KJ = \Delta H_1 + (-283 \, KJ)$$
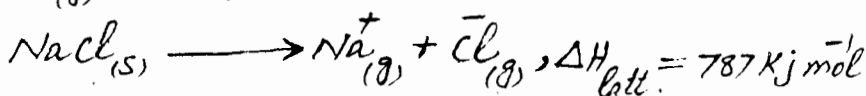
$$\Delta H_1 = -393.7 + 283$$

$$\Delta H_1 = -110.7 \, KJ \, mol^{-1}$$

It is the heat of formation of Carbon monoxide.

Lattice Energy

The enthalpy change when one mole of an ionic crystal is formed from its gaseous ions is called lattice energy. OR the enthalpy change when one mole of ionic crystal is broken into its isolated ions is called lattice energy. It is denoted by ΔH_{Latt}. Its unit is $Kj \, mol^{-1}$.

For example

$$Na^+_{(g)} + \bar{Cl}_{(g)} \longrightarrow NaCl_{(s)} , \quad \Delta H_{latt} = -787 \, Kj \, mol^{-1}$$

$$NaCl_{(s)} \longrightarrow Na^+_{(g)} + \bar{Cl}_{(g)} , \quad \Delta H_{latt} = 787 \, Kj \, mol^{-1}$$
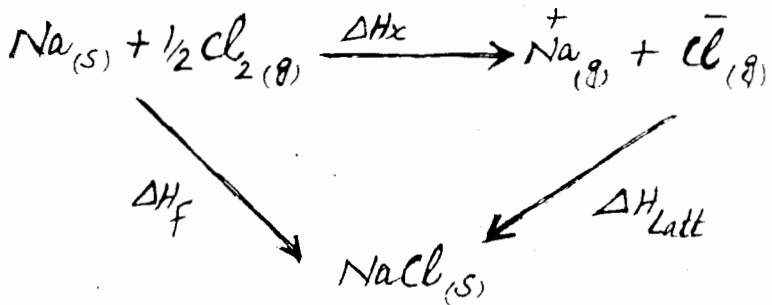
Born-Haber Cycle

Born and Haber were two chemists. They gave a method to determine the lattice energy of an ionic compound. The Born-Haber cycle is a special application of Hess's law. The Born-Haber cycle states that sum of all enthalpy changes in a
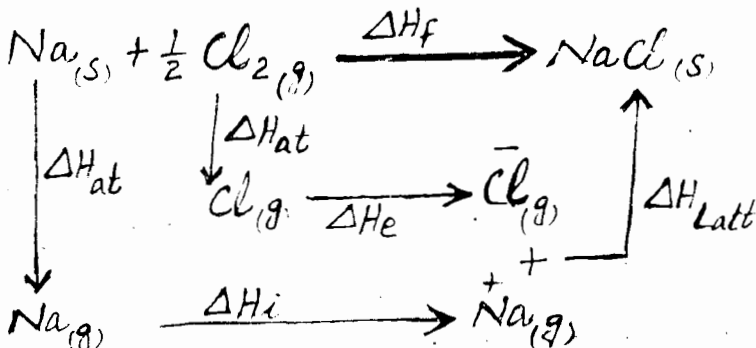
cyclic process is equal to zero.

$$\Sigma \Delta H = 0$$

The energy triangle of sodium chloride is shown in figure.

$$Na_{(S)} + \frac{1}{2} Cl_{2(g)} \xrightarrow{\Delta H_x} Na^+_{(g)} + \bar{Cl}_{(g)}$$

ΔH_f

ΔH_{Latt}

$$NaCl_{(S)}$$

Here ΔH_f is enthalpy of formation. ΔH_{Latt} is lattice energy and ΔH_x is total energy involved in changing sodium and chlorine into gaseous ions. When we extend energy triangle, then we get complete energy cycle. It is called Born - Haber cycle. It is shown below. The Born — Haber cycle is used to determine lattice energy.

$$Na_{(S)} + \frac{1}{2} Cl_{2(g)} \xrightarrow{\Delta H_f} NaCl_{(S)}$$

ΔH_{at}

ΔH_{at}

$Cl_{(g)} \xrightarrow{\Delta H_e} \bar{Cl}_{(g)}$

ΔH_{Latt}

$Na_{(g)} \xrightarrow{\Delta H_i} Na^+_{(g)}$

The formation of NaCl takes place by two routes
(i) Direct route   (ii) Indirect route

Direct Route :- Na and Cl_2 react directly and form NaCl. It is an exothermic process. The enthalpy is called enthalpy of formation.

$$Na_{(S)} + \frac{1}{2} Cl_{2(g)} \longrightarrow NaCl , \Delta H_f = -411 kJ \, mol^{-1}$$
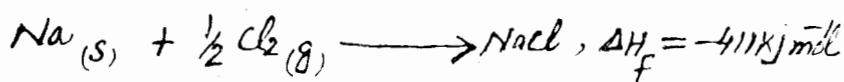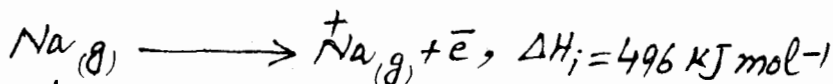
Indirect Route :- Indirect route consists of five steps.

(i) Atomization of Na :- Solid Na changes into gaseous Na. It is an endothermic process. The enthalpy is called enthalpy of atomization

$$Na_{(S)} \longrightarrow Na_{(g)} , \Delta H_{at} = 108 \, KJ \, mol^{-1}$$
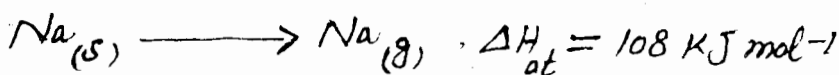
(ii) Ionization of Na :- Na atom loses an electron to form Na^+ ion. It is an endothermic. Process. The enthalpy is called enthalpy of ionization.

$$Na_{(g)} \longrightarrow Na^+_{(g)} + \bar{e} , \Delta H_i = 496 \, KJ \, mol^{-1}$$

(iii) Atomization of Cl_2 :- Cl_2 molecule changes into Cl – atoms. It is an endothermic process. The enthalpy is called enthalpy of atomization or dissociation

$$\frac{1}{2} Cl_{2(g)} \longrightarrow Cl_{(g)} , \Delta H_{at} = 121 \, KJ \, mol^{-1}.$$
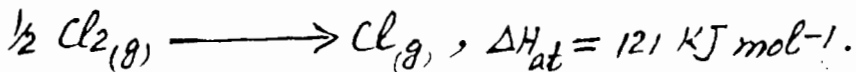
(iv) Formation of Chloride ion :- The chlorine atom gains an electron to form Chloride ($\bar{Cl}$) ion. The heat is evolved in this process. So it is

an exothermic process. The enthalpy is called electron affinity.

$$Cl_{(g)} + \bar{e} \longrightarrow \bar{Cl}_{(g)} \;,\; \Delta H_e = -349 \, KJ \, mol^{-1}$$

(V) <u>Formation of NaCl</u> :- Here Na^+ and $\bar{Cl}$ ions combine and form solid NaCl. The process is called lattice formation and enthalpy is called lattice energy (ΔH_{Latt})

$$Na^+_{(g)} + \bar{Cl}_{(g)} \longrightarrow NaCl_{(s)} \;,\; \Delta H_{Latt} = ?$$
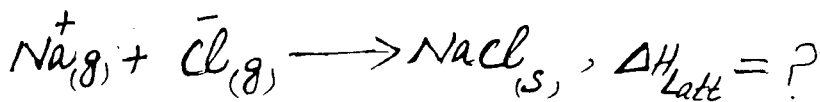
According to Hess's Law enthalpy change involved in direct route or indirect route is same.

$$\Delta H_f = \Delta H_{at} + \Delta H_i + \Delta H_{at} + \Delta H_e + \Delta H_{Latt}$$

$$-411 = 108 + 496 + 121 - 349 + \Delta H_{Latt}$$

$$-411 \, KJ = 725 - 349 + \Delta H_{Latt}$$

$$-411 \, KJ = 376 \, KJ + \Delta H_{Latt}$$

$$\Delta H_{Latt} = -411 \, KJ - 376 \, KJ$$

$$\Delta H_{Latt} = -787 \, KJ \, mol^{-1}$$

Similarly lattice energy of any compound can be determined. Lattice energy is very helpful to discuss structure, bonding and properties of an ionic compound.

EXERCISE

Q.1 Select the suitable answer from the given choices.

(i) If an endothermic reaction is allowed to take place very rapidly in the air, the temperature of the surrounding air
   (a) remains constant   (b) increases
   (c) decreases   (d) remain unchanged

(ii) In endothermic reactions, the heat content of the
   (a) products is more than that of reactants
   (b) reactants is more than that of products
   (c) both (a) and (b)
   (d) reactants and products are equal

(iii) Calorie is equivalent to
   (a) 0.4184J   (b) 41.84J   (c) 4.184J   (d) 418.4J

(iv) The change in heat energy of a chemical reaction at constant temperature and pressure is called
   (a) enthalpy change   (c) heat of sublimation
   (b) bond energy   (d) internal energy change

(v) Which of the following statements is contrary to the first law of thermodynamics?
   (a) Energy can neither be created nor destroyed.
   (b) One form of energy can be transferred into an equivalent amount of other kinds of energy.
   (c) In an adiabatic process, the work done is independent of its path.
   (d) Continuous production of mechanical work without supplying an equivalent amount of heat is possible.

(vi) For a given process, the heat changes at constant pressure (q_p) and at constant volume (q_v) are related to each other as:
   (a) $q_p = q_v$ (b) $q_p < q_v$ (c) $q_p > q_v$ (d) $q_p = q_v/2$

(vii) For the reaction: $NaOH + HCl \rightarrow NaCl + H_2O$ the change in enthalpy is called
   (a) heat of reaction   (b) heat of formation
   (c) heat of neutralization   (d) heat of combustion

(viii) The net heat change in a chemical reaction is same. whether it is brought about in two or more different ways in one or several steps It is known as
   (a) Henry's law   (c) Joule's principle
   (b) Hess's law   (d) Law of conservation of energy

(ix) Enthalpy of neutralization of all the strong acids and strong bases has the same value because.
   (a) neutralization leads to the formation of salt and water.
   (b) strong acids and bases are ionic substances.
   (c) acids always give rise to H^{+1} ions and bases always furnish OH^{-1} ions.
   (d) the net chemical change involve the combination of H^+ and OH ions to form water.

(Answer) (i) c   (ii) a   (iii) c   (iv) a   (v) d
     (vi) c   (vii) c   (viii) b   (ix) d

Q.2 Fill in the blanks with suitable words.

(i) The substance undergoing a physical or a chemical change forms a chemical_____.

(ii) The change in internal energy ____be measured.

(iii) Solids which have more than one crystalline forms possess ____values of heats of formation.

(iv) A process is called _____ if it takes place on its own without any external assistance.

(v) A _____ is a macroscopic property of a system which is ____of the path adopted to bring about that change.

(Answer) (i) system   (ii) can   (iii) different   (vi) spontaneous
     (v) state function, independent.

Q.3 Indicate the true or false as the case may be.

(i) It is necessary that a spontaneous reaction should be exothermic.

(ii) Amount of heat absorbed at constant volume is internal energy change.

(iii) The work done by the system is given the positive sign.

(iv) Enthalpy is a state function but internal energy is not.

(v) Total heat content of a system is called enthalpy of the system.

(Answer) (i) false   (ii) true   (iii) false   (iv) false   (v) true

Q.4 Define the following terms and give three examples of each

(i) System   (ii) Surroundings   (iii) State function   (iv) units of energy

(v) Exothermic reaction   (vi) Endothermic reaction

(vii) Internal energy of the system   (viii) Enthalpy of the system.

Answer: see page No. 1, 4, 5, 7, ____.

Q.5 Differentiate between the following:

(i) Internal energy and enthalpy

(ii) Internal energy change and enthalpy change

(iii) Exothermic and endothermic reactions

(b) Define the following enthalpies and give two examples of each.

(i) Standard enthalpy of reaction

(ii) Standard enthalpy of combustion

(iii) Standard enthalpy of atomization

(iv) Standard enthalpy of solution

Answer: (a) see page No. 1, 7, 12 ____ (b) see page No. 14, 15, 16

Q.6 (a) What are spontaneous and non-spontaneous processes. Give examples.

(b) Explain that burning of a candle is a spontaneous process.

(c) Is it true that a non-spontaneous process never happens in the universe? Explain it.

Answer (a) see page No. __3, 4__

(b) The burning of Candle is a spontaneous process. The reason is that once burning of Candle starts, it takes place on its own without any outside assistance. The burning candle will stop only by wind pressure or by finishing wax.

(C):- No, it is not true that a non-spontaneous process never happens in the universe. For example,

(i) Transfer of heat from cold body to hot surrounding in a refrigerator.

(ii) Liquifaction of a gas by Joule Thomson effect.

Q.7 (a) What is the first law of thermodynamics. How does it explain that:

(i) $q_v = \Delta E$ (ii) $q_p = \Delta H$

(b) How will you differentiate between ΔE and ΔH? it is true that ΔH and ΔE have the same values for the reactions taking place in the solution state.

Answer: (a) see page No. __11, 12__

(b) ΔE is internal energy change. It is amount of heat absorbed or evolved by a system at constant volume. It means that $\Delta E = q_v$

Its formula is $\Delta E = q - P\Delta V$

ΔH is enthalpy change. It is amount of heat absorbed or evolved by a system at constant pressure. It means that $\Delta H = q_p$

Its formula is $\Delta H = \Delta E + P\Delta V$

For solid, liquid and solution state, $\Delta V = 0$.

So $\Delta H = \Delta E$. Thus it is true that ΔH and ΔE have same values for reactions in solution state.

Q.8(a)What is the difference between heat and temperature? Write
Mathematical relationship between these two parameters.
(b)How do you measure the heat of combustion of a substance by
bomb calorimeter.
Ans:- see page No .   6 , 18, 19, 20
Q.9Define heat of neutralization and explain with examples?
Ans:- see page No.   15
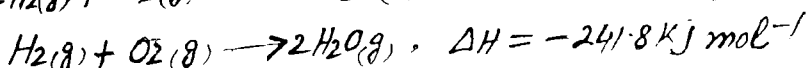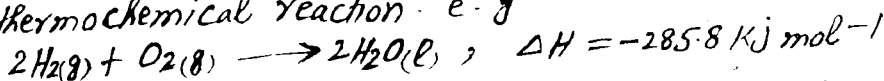Q.10(a) state the laws of thermo chemistry and show how are they based
· On the first law of thermodynamic.
(b) What is a thermo chemical equation . Give three examples. What
information do they convey?
(c)Why is it necessary to mention the physical states of reactants
and products in a thermo chemical reaction?
Ans:- (a) see page No .   21, 22   (b) see page No. 21

(c) The enthalpy of reaction depends upon Physical states
of reactants and Products. By changing Physical state
of Substances, enthalpy of reaction changes. Thus it is
necessary to mention "Physical states of Substances in
thermochemical reaction. e.g

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} \; ; \quad \Delta H = -285.8 \, KJ \, mol^{-1}$$

$$H_{2(g)} + O_2_{(g)} \longrightarrow 2H_2O_{(g)} \; , \quad \Delta H = -241.8 \, KJ \, mol^{-1}$$

Q.11 (a) Define and explain Hess,s law of constant heat summation.
Explain it with examples and give its application.
(b) Hess,s law help us to calculate the heats of those reactions, which
cannot be normally carried out in a laboratory. Explain it.
Ans:- see page No.   22
Q.12 (a) What is lattice energy? How does Born-Haber cycle help to
Calculate the lattice energy of NaC1?
(B) justify that heat of formation of compound is the sum of all the
other enthalpies.
Ans:- see page No.   25, 26

Q13. 50 cm³ of 1.0 M HCl is mixed with 50 cm³ of 1.00 M NaOH in a glass
calorimeter. The temperature of the resultant mixture increases from
21.0°C to 27.5°C. Assume, that calorimeter losses of heat are
negligible. Calculate the enthalpy change mole' for the reactions. The
density of solution to be considered is 1gcm⁻³ and specific heat is
4.18 Jg⁻¹k⁻¹.

Solution:— volume of $HCl = 50 \, cm^3$, Vol of $NaOH = 50 \, cm^3$.
Total volume of Solution $= 50 + 50 = 100 \, cm^3$
Molarity of HCl or NaOH $= 1.00$
Density of solution $= 1g \, cm^{-3}$
Specific heat of Solution $= 4.18 \, JK^{-1}g^{-1}$

$Initial\ temperature = 21°C = 21+273 = 294K$

$Final\ temperature = 27.5°C = 27.5+273 = 300.5K$

$rise\ in\ temperature = 300.5-294 = 6.5K$

$density\ of\ solution = \dfrac{mass\ of\ solution}{Volume\ of\ solution}$

$mass\ of\ solution = density\ of\ solution \times vol\ of\ solution$

$$= 1 \times 100 = 100\,g$$

$Heat\ evolved.\ q = -m \times S \times \Delta T$

$$= -100 \times 4.18 \times 6.5 = -2707J$$

$$= \dfrac{-2707}{1000} = -2.71\,KJ$$

$Volume\ of\ HCl\ or\ NaOH\ solution = 50\,Cm^3 = \dfrac{50}{1000} = 0.05\,dm^3$

$molarity\ of\ HCl\ or\ NaOH\ solution = 1.00$

$Number\ of\ moles\ of\ HCl\ or\ NaOH = molarity \times volume$

$$= 1 \times 0.05 = 0.05$$

$Enthalpy\ of\ neutralization\ Per\ mole = -\dfrac{2.71}{0.05}$

$$\Delta H_n = -54.2\,KJ\,mol^{-1}$$

Q.14 Hydrazine (C_2H_4) is a rocket fuel. It burns in O_2 to give N_2 and H_2O.

$$N_2H_4(l) + O_2(g) \quad \rightarrow \quad N_2(g) + 2H_2O(g)$$
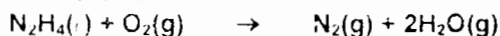
1.00 g of N_2H_4 is burned in a bomb calorimeter. An increase of temperature 3.51°C is recorded. The heat capacity of calorimeter is 5.5 kJK⁻¹. Calculate the quantity of heat evolved. Also, calculate the heat of combustion of 1 mole of N_2H_4

Solution:- $mass\ of\ hydrazine\ burnd = 1\,g$

$increase\ of\ temperature, \Delta T = 3.51°C = 3.51K$

$Heat\ Capacity\ of\ Calorimeter, S = 5.5\,KJ\,K^{-1}$

$Heat\ evolved = -m \times S \times \Delta T$

$$= -1 \times 5.5 \times 3.51$$

$$= -19.3\,KJ\,g^{-1}$$

Molecular mass of hydrazine $(N_2H_4) = 28 + 4 = 32$

Heat evolved per mole of hydrazine $= 32 (-19.3) \, KJ$

$$= -618 \, KJ \, mol^{-1}$$

Q.15 Octane (C_8H_{18}) is a motor fuel. 1.80 g of a sample of octane is burned in a bomb calorimeter having heat capacity 11.66 kJK^{-1}. The temperature of the calorimeter increases from 21.36°C to 28.78°C. Calculate the heat of combustion for 1 g of octane. Also, calculate the heat for 1 mole of octane.

Solution: - mass of octane burned $= 1.8 \, g$

Heat Capacity of Calorimeter, $S = 11.66 \, KJ \, K^{-1}$

Initial temperature $= 21.36°C = 21.36 + 273 = 294.36 \, K$

Final temperature $= 28.78°C = 28.78 + 273 = 301.78 \, K$

rise of temperature, $\Delta T = 301.78 - 294.36 = 7.42 \, K$

Heat of Combustion $= \, ?$

Heat evolved in combustion $= -m \times S \times \Delta T$

$$= -1.8 \times 11.66 \times 7.42$$

$$= -155.73 \, KJ$$

Heat of Combustion Per gram of octane $= -\dfrac{155.73}{1.8}$

$$= -86.51 \, KJ \, g^{-1}$$

Molecular mass of octane $(C_8H_{18}) = 96 + 18 = 114$

Heat of Combustion for one mole of octane $= 114 (-86.51)$

$$= -9862.14 \, KJ \, mol^{-1}$$

Q.16 By applying, Hess's law calculate the enthalpy change for the formation of an aqueous solution of NH_4Cl from NH_3 gas and HCl. The results for the various reactios and pressures are as follows.
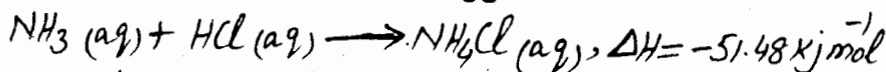
(i) $NH_3 (g) + aq \rightarrow NH_3 (aq)$ $\Delta H = -35.16$ kJ mol^{-1}

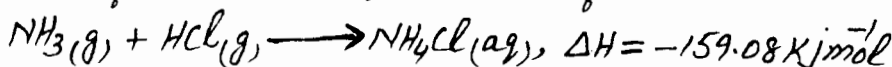(ii) $HCl (g) + aq \rightarrow HCl (aq)$ $\Delta H = -72.41$ kJ mol^{-1}

(iii) $NH_3 (aq) + HCl (aq) \rightarrow NH_4Cl(aq)$ $\Delta H = -51.48$ kJ mol^{-1}

Solution:-

$NH_3 (g) + aq \longrightarrow NH_3(aq), \quad \Delta H = -35.16 \, KJ \, mol^{-1}$

$HCl (g) + aq \longrightarrow HCl(aq), \quad \Delta H = -72.41 \, KJ \, mol^{-1}$
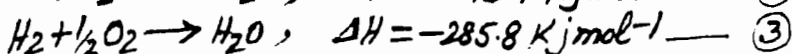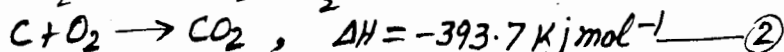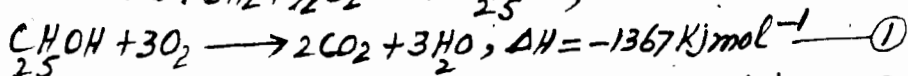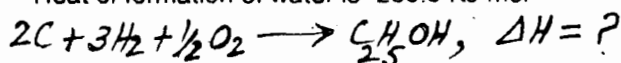
$$NH_3 (aq) + HCl (aq) \longrightarrow NH_4Cl (aq), \Delta H = -51.48 \, Kj\,mol^{-1}$$

By adding above three equations, we get

$$NH_3 (g) + HCl (g) \longrightarrow NH_4Cl (aq), \Delta H = -159.08 \, Kj\,mol^{-1}$$
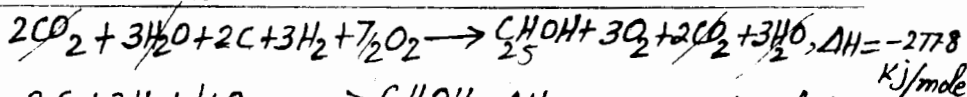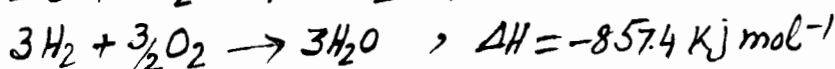
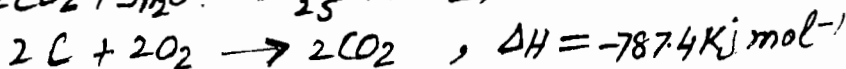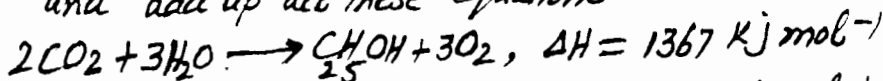**Q.17** Calculate the heat of formation of ethyl alcohol form the following Information.

(i) Heat of combustion of ethyl alcohol is -1367 kj mol⁻¹

(ii) Heat of formation of carbon dioxide is -393.7 kj mol⁻¹

(iii) Heat of formation of water is -285.8 KJ mol⁻¹

Solution:-

$$2C + 3H_2 + \tfrac{1}{2}O_2 \longrightarrow C_2H_5OH, \quad \Delta H = ?$$

$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O, \quad \Delta H = -1367 \, Kj\,mol^{-1} \quad \textcircled{1}$$

$$C + O_2 \longrightarrow CO_2, \quad \Delta H = -393.7 \, Kj\,mol^{-1} \quad \textcircled{2}$$

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O, \quad \Delta H = -285.8 \, Kj\,mol^{-1} \quad \textcircled{3}$$
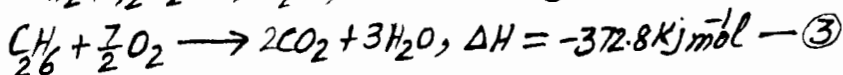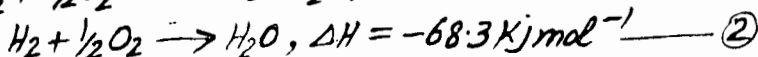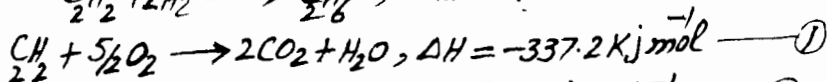
Reverse eq (1), Multiply eq (2) by 2 and eq (3) by 3 and add up all these equations
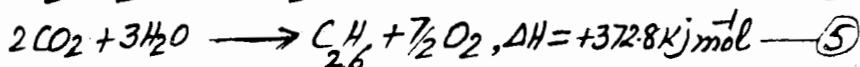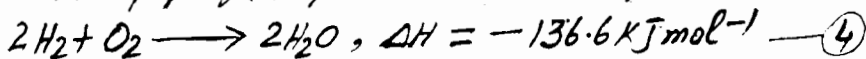
$$2CO_2 + 3H_2O \longrightarrow C_2H_5OH + 3O_2, \quad \Delta H = 1367 \, Kj\,mol^{-1}$$

$$2C + 2O_2 \longrightarrow 2CO_2, \quad \Delta H = -787.4 \, Kj\,mol^{-1}$$

$$3H_2 + \tfrac{3}{2}O_2 \longrightarrow 3H_2O, \quad \Delta H = -857.4 \, Kj\,mol^{-1}$$

$$2CO_2 + 3H_2O + 2C + 3H_2 + \tfrac{7}{2}O_2 \longrightarrow C_2H_5OH + 3O_2 + 2CO_2 + 3H_2O, \Delta H = -277.8 \, Kj/mole$$

$$2C + 3H_2 + \tfrac{1}{2}O_2 \longrightarrow C_2H_5OH, \quad \Delta H = -277.8 \, Kj\,mol^{-1}$$
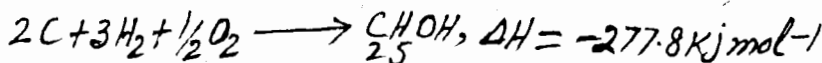
Q.18 If the heats of combustion of C_2H_2, H_2 and C_2H_6 are -337.2, -68.3 and -372.8 k calories respectively, then calculate the he at of the following reaction.
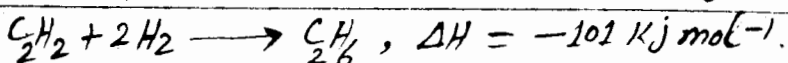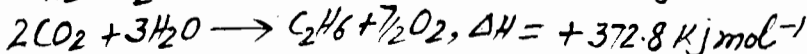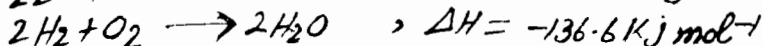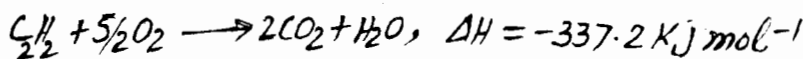
$$C_2H_2(g) + H_2(g) \longrightarrow C_2H_6 (g)$$

Solution:-

$$C_2H_2 + 2H_2 \longrightarrow C_2H_6, \quad \Delta H = ?$$

$$C_2H_2 + \tfrac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O, \Delta H = -337.2 \, Kj\,mol^{-1} \quad \textcircled{1}$$

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O, \quad \Delta H = -68.3 \, Kj\,mol^{-1} \quad \textcircled{2}$$

$$C_2H_6 + \tfrac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O, \quad \Delta H = -372.8 \, Kj\,mol^{-1} \quad \textcircled{3}$$
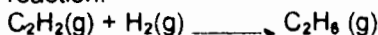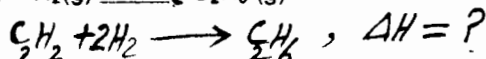
Multiply eq (2) by 2 and Reverse eq (3)

$$2H_2 + O_2 \longrightarrow 2H_2O, \quad \Delta H = -136.6 \, Kj\,mol^{-1} \quad \textcircled{4}$$

$$2CO_2 + 3H_2O \longrightarrow C_2H_6 + \tfrac{7}{2}O_2, \Delta H = +372.8 \, Kj\,mol^{-1} \quad \textcircled{5}$$

Add eq (1), (4) and (5)

$$C_2H_2 + 5/2 O_2 \longrightarrow 2CO_2 + H_2O, \quad \Delta H = -337.2 \, KJ \, mol^{-1}$$
$$2H_2 + O_2 \longrightarrow 2H_2O, \quad \Delta H = -136.6 \, KJ \, mol^{-1}$$
$$2CO_2 + 3H_2O \longrightarrow C_2H_6 + 7/2 O_2, \quad \Delta H = +372.8 \, KJ \, mol^{-1}$$
$$\overline{C_2H_2 + 2H_2 \longrightarrow C_2H_6, \quad \Delta H = -101 \, KJ \, mol^{-1}.}$$

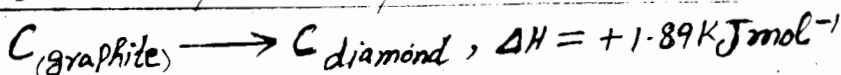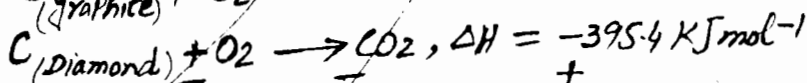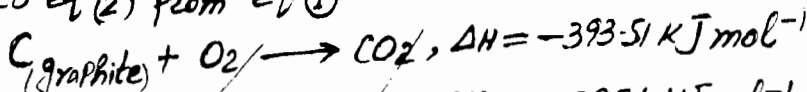**Q.19** Graphite and diamond are two forms of carbon. The of combustion of graphite at 25^0C is -393.51f kJ mol^{-1} and that of diamond is -395.4 KJ mol^{-1}

What is the enthalpy change of the process? Graphite $\longrightarrow$ Diamond at the same temperature?

Solution:-

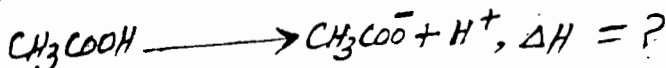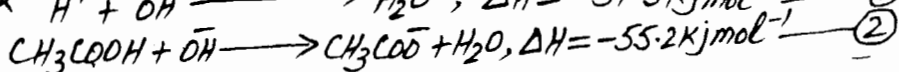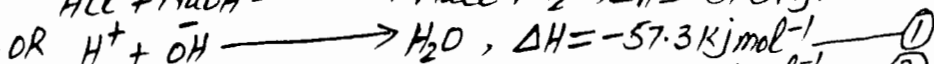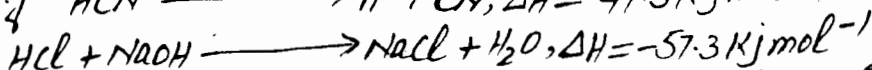$$C_{(graphite)} \xrightarrow{\quad\quad} C_{(diamond)}, \quad \Delta H = ?$$

$$C_{(graphite)} + O_2 \longrightarrow CO_2, \quad \Delta H = -393.51 \, KJ \, mol^{-1}$$
$$C_{diamond} + O_2 \longrightarrow CO_2, \quad \Delta H = -395.4 \, KJ \, mol^{-1}$$

Subtract eq (2) from eq ①

$$C_{(graphite)} + O_2 \longrightarrow CO_2, \quad \Delta H = -393.51 \, KJ \, mol^{-1}$$
$$C_{(Diamond)} + O_2 \longrightarrow CO_2, \quad \Delta H = -395.4 \, KJ \, mol^{-1}$$
$$+$$
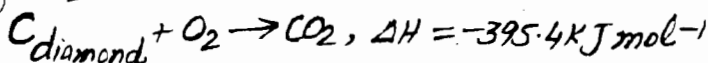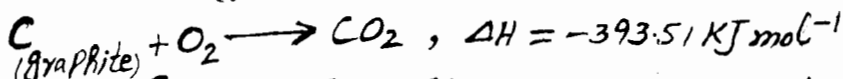
$$\overline{C_{(graphite)} \longrightarrow C_{diamond}, \quad \Delta H = +1.89 \, KJ \, mol^{-1}}$$

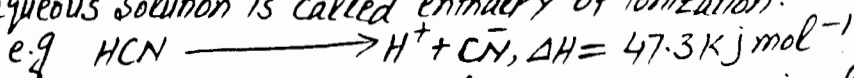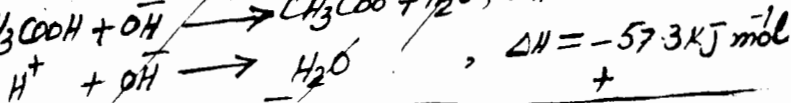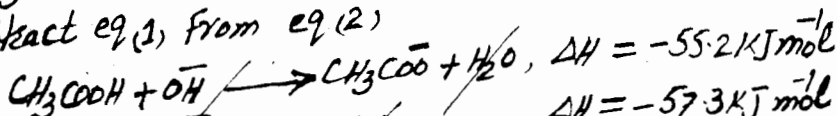**Q.20** What is the meaning of the term enthalpy of ionization? If the heat of neutralization of HCl and NaOH is -57.3 kJ mol^{-1} and heat of neutralization of CH_3OOH with NaOH is -55.2 kJ mol^{-1}. Calculate the enthalpy of ionization of CH_3COOH.

Solution:- **Enthalpy of ionization:-** The amount of enthalpy (heat) required to ionize one mole of a weak electrolyte in aqueous solution is called enthalpy of ionization.

e.g $HCN \longrightarrow H^+ + C\bar{N}, \quad \Delta H = 47.3 \, KJ \, mol^{-1}$

$HCl + NaOH \longrightarrow NaCl + H_2O, \quad \Delta H = -57.3 \, KJ \, mol^{-1}$

OR $H^+ + \bar{OH} \longrightarrow H_2O, \quad \Delta H = -57.3 \, KJ \, mol^{-1}$ ①

$CH_3COOH + \bar{OH} \longrightarrow CH_3CO\bar{O} + H_2O, \quad \Delta H = -55.2 \, KJ \, mol^{-1}$ ②

$CH_3COOH \longrightarrow CH_3CO\bar{O} + H^+, \quad \Delta H = ?$

Subtract eq (1) from eq (2)

$$CH_3COOH + \bar{OH} \longrightarrow CH_3CO\bar{O} + H_2O, \quad \Delta H = -55.2 \, KJ \, mol^{-1}$$
$$H^+ + \bar{OH} \longrightarrow H_2O, \quad \Delta H = -57.3 \, KJ \, mol^{-1}$$
$$+$$

$CH_3COOH - H^+ \longrightarrow CH_3COO^-, \Delta H = +2.1\, Kj\,mol^{-1}$

or $\quad CH_3COOH \longrightarrow CH_3COO^- + H^+, \Delta H = +2.1\, Kj\,mol^{-1}$
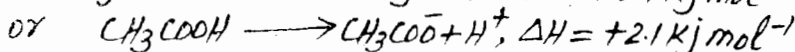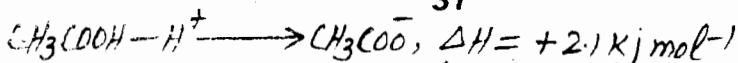
Q.21 (a) Explain what is meant by the following terms.
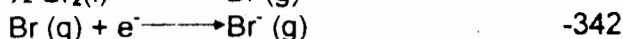 (i) Atomization energy
 (ii) Lattice energy
 (b) Draw a complete fully labeled Born Haber cycle for the formation of potassium bromide.
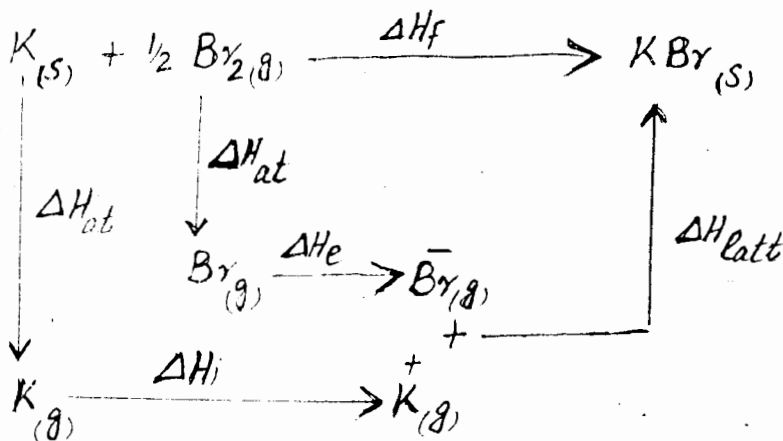 **(c)** Using the information give in the table below, calculate the Lattice energy of potassium bromide.

Reactions:- $\qquad\qquad\qquad\qquad\qquad\qquad \Delta H\ /KJ\ mol^{-1}$

Reaction	ΔH
$K(s) + 1/2\, Br_2\,(l) \longrightarrow K^+Br^-\,(s)$	- 392
$K(s) \longrightarrow K(g)$	+90
$K(g) \longrightarrow K^+(g) + e^-$	+420
$½\, Br_2(l) \longrightarrow Br(g)$	+112
$Br(g) + e^- \longrightarrow Br^-(g)$	-342

(a):- See page NO. 14, 15, 25

(b):- Born Haber Cycle for KBr is shown below.

(C) $\Delta H_f = -392\, kj\,mol^{-1}$, ΔH_{at} of $K = 90\, kj\,mol^{-1}$

ΔH_i of $K = 420\, kj\,mol^{-1}$, ΔH_{at} of $Br = 112\, kj\,mol^{-1}$

ΔH_e of $Br = -342\, kj\,mol^{-1}$, $\Delta H_{latt} = ?$

According to Hess's Law

$\Delta H_f = \Delta H_{at} + \Delta H_i + \Delta H_{at} + \Delta H_e + \Delta H_{latt}$

$-392 = 90 + 420 + 112 - 342 + \Delta H_{latt}$

$\Delta H_{latt} = -392 - 280 = -672\, kj\,mol^{-1}$

Hence lattice energy of KBr is $-672\, kj\,mol^{-1}$

السلام علیکم ورحمتہ اللہ وبرکاتہ

مختصر تعارف

کافی عرصہ سے خواہش تھی کہ ایک ایسی ویب سائٹ بناؤں جس پر طالب العلموں کیلئے کچھ تعلیمی مواد جمع کر سکوں۔ اللہ تعالیٰ نے توفیق دی اور میں نے ایک سال کی محنت کے بعد ایک سائٹ "گلدستہ ڈاٹ پی کے" کے نام سے بنائی جو کہ قرآن و حدیث، اصلاحی، دلچسپ، تاریخی قصے واقعات، اُردو انگلش تحریریں، شاعری و اقوال زریں، F.Sc اور B.Sc کے مضامین کے آن لائن نوٹس، اسلامک، تفریحی، معلوماتی وال پیپرز، حمد و نعت، فرقہ واریت سے پاک اسلامی بیانات، پنجابی نظمیں و ترانے اور کمپیوٹر و انٹرنیٹ کی دنیا کے بارے میں ٹپس، آن لائن کمائی کرنے کے مستند طریقہ کار۔ کے ساتھ ساتھ اور بھی بہت سی چیزوں پر مشتمل ہے۔ اور انشاء اللہ میں مزید وقت کے ساتھ ساتھ اضافہ کرتا جاؤں گا۔ آپ کی قیمتی رائے کی ضرورت ہے۔ عرنان شفیق

اہم نوٹ

ذیل میں جو نوٹس مہیا کیے گئے ہیں وہ کئی گھنٹوں کی لگاتار محنت کے مرتب ہوئے ہیں۔ اور آپ کو بالکل مفت مہیا کر رہے کیے جا رہے ہیں۔ آپ سے ان کی قیمت صرف اتنی سی متوقع ہے کہ ایک بار درودّ ابراھیمی اپنی زبان سے ادا کر دیں۔

بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ

اللَّهُمَّ صَلِّ عَلَى مُحَمَّدٍ
وَعَلَى آلِ مُحَمَّدٍ كَمَا صَلَّيْتَ
عَلَى إِبْرَاهِيمَ وَعَلَى آلِ إِبْرَاهِيمَ
إِنَّكَ حَمِيدٌ مَجِيدٌ
اللَّهُمَّ بَارِكْ عَلَى مُحَمَّدٍ وَعَلَى
آلِ مُحَمَّدٍ كَمَا بَارَكْتَ عَلَى
إِبْرَاهِيمَ وَعَلَى آلِ إِبْرَاهِيمَ
إِنَّكَ حَمِيدٌ مَجِيدٌ