EXERCISE

MULTIPLE CHOICE QUESTIONS

1. Choose the correct answers

i. which of the following substances have zero value for their standard enthalpy of formation.

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

ii. Calorie is equivalent to

(a) 4.18J (b)4.18KJ

(c) 0.418J (d) 0.418KJ.

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

(a) the formation of salt and water

(b) the formation of salt

(c) the complete ionization of acids and bases

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

iv. Total heat content of a system is called

(a)Formation (b) Internal energy

(c) heat (d) state function

v. **Heat of __________ of a substance is always negative**

(a)Formation (b) combustion

(c) decomposition (d) solution

vi. **A balloon filled with oxygen is placed in a freezer. Identify system**

(a) balloon (b) oxygen

(c) freezer (d) all of these.

vii. **A bomb calorimeter is used in _________ calorimeter**

(a)constant volume (b) constant pressure

(c) both a and b (d) constant temperature

viii. **Boron Haber Cycle is used to determine lattice energies of**

(a) molecular solids (b) ionic solids

(c) covalent solids (d) metallic solids

ix. **q = ΔH when**

(a) $\Delta V = 0$ (b) P=0

(c) $\Delta E = 0$ (d) none of these.

x. **Enthalpy of combustion for C is -393.5**

C(s) +$O_2(g) \rightarrow CO_2(g)$ $\Delta H_{combustion} = -393.5 KJmole^{-1}$

Enthalpy of formation of CO_2 **would be**

(a) +393.5KJ (b) -393.5KJ

(c)zero (d) cannot be predicted from the given equation

xi. Which of the following is not a state function of a system.

(a) Thermal energy at constant pressure

(b) enthalpy

(c) internal energy

(d) work done

xii. For writing a thermochemical equation for enthalpy of combustion of an element requires,

(a) 1 mole of element as reactant

(b)1 mole of oxide of element as product

(c) Standard states of all the substances

(d) Balanced equation of 1 mole of element

ANSWERS

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

2. Name and define units of thermal energy.

Ans: units of thermal energy:

SI units:

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

Joule (j):

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

Common unit of heat:

Common unit of heat is the calorie.

Calorie:

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

Relationship:

1 calorie = 4.18 joules

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

Ans: system:

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

Surroundings:

The part of the universe except system is called surroundings.

Boundary:

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

State function:

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

Examples:

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

Heat capacity:

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

Internal energy:

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

Enthalpy of a substance (H):

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

$H = E + PV$

4. Classify reactions as exothermic or endothermic.

Ans: (1) exothermic reactions:

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

Examples of exothermic reactions:

(i) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H' =$ -393.5Kj

(ii) $2H_2(g) + O_2(g) \rightarrow H_2O(l)$ $\Delta H' =$-571.6KJ

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

(2) endothermic reactions:

A chemical reaction that proceeds with the absorption of heat is an endothermic reaction. in these reaction heats is transferred from surrounding the system.

Examples of endothermic reactions:

(i) $C(s) + H_2(g) + I_2(g) \rightarrow 2HI(g)$ $\Delta H' =$ +53.8Kj

(ii) $C(s)+H_2O(g)\rightarrow CO(g)+H_2(g)$ ΔH° =+131.4KJ

(iii) $N_2(g)+O_2(g)\rightarrow 2NO(g)$ ΔH° =+180.5KJ

5. Define bond dissociation energy.

Ans: bond dissociation energy:

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

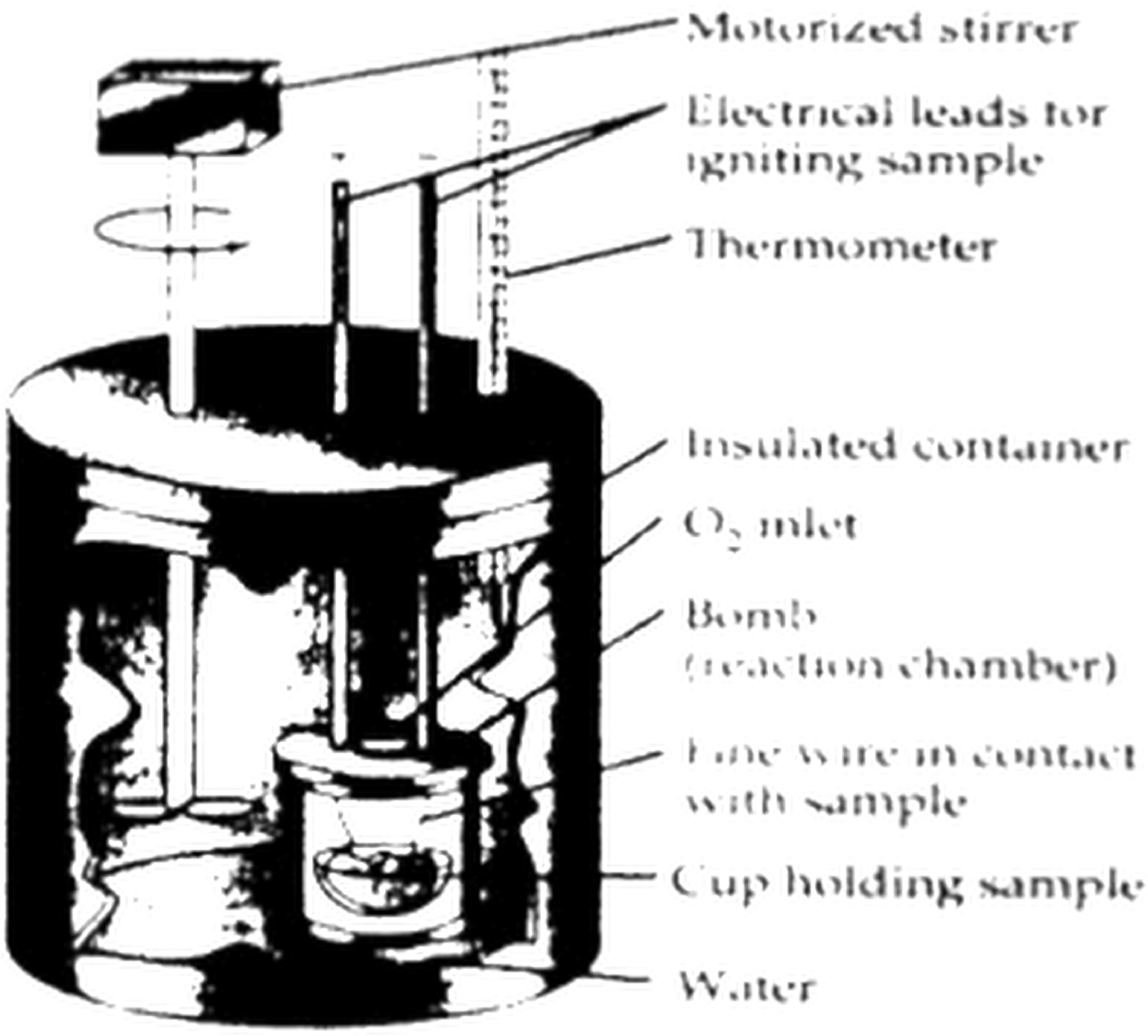
6. Describe how heat of combustion can be used to estimate the energy available from foods.

Ans: constant volume calorimetry:

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

(ii) A bomb calorimeter is used for this purpose. Chemical reaction in a bomb calorimeter takes place under constant volume conditions. A bomb calorimeter is shown in fig

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



Bomb calorimeter

Estimation of energy available from food:

Human beings require three major classes of food

(i) Carbohydrates
(ii) Fats
(iii) 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 combustion. The bomb calorimeter shown n figure is used for measuring the energy available from food, which is just the enthalpy of combustion.

Activity

Weigh 1.8g of glucose and place in the holder cup of bomb calorimeter and seal it. Adjust the pressure of oxygen in the calorimeter to about 25 atm. Immerse calorimeter in an insulated water bath fitted with a motorized stirrer and a thermometer. Record the temperature of water. Suppose it is 25°C. ignite glucose electrically when it will burn energy will flow from the chemicals to the calorimeter and water. Record the temperature of water again. Thermometer will show 31.52°C. if calorimeter has a total heat capacity of 4.321kjk^{-1}. we can calculate energy available from glucose as follows:

Increase in temperature = Δt =31.52°c -25°C= 6.52°C

Heat evolved = Δt x total heat capacity of calorimeter

= 6.52 x 4.321 KJK^{-1}= 28.1729KJ

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

Since 28.1729 KJ of heat was evolved for 0.01 moles of glucose the heat of combustion of glucose per mole = $\frac{28.1729g}{0.01mole^{-1}}$ = 2817.29KJ$mole^{-1}$

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

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

Ans: Hess's law to construct simple energy cycles:

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

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

This reaction can be carried out in two steps.

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

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

NET reaction

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

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

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

For energy cycle see fig.11.4

Example:

Combustion of C to CO_2 evolves 393.5 KJ of energy.

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

This reaction may takes place in two steps.

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

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

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

Energy cycles:

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

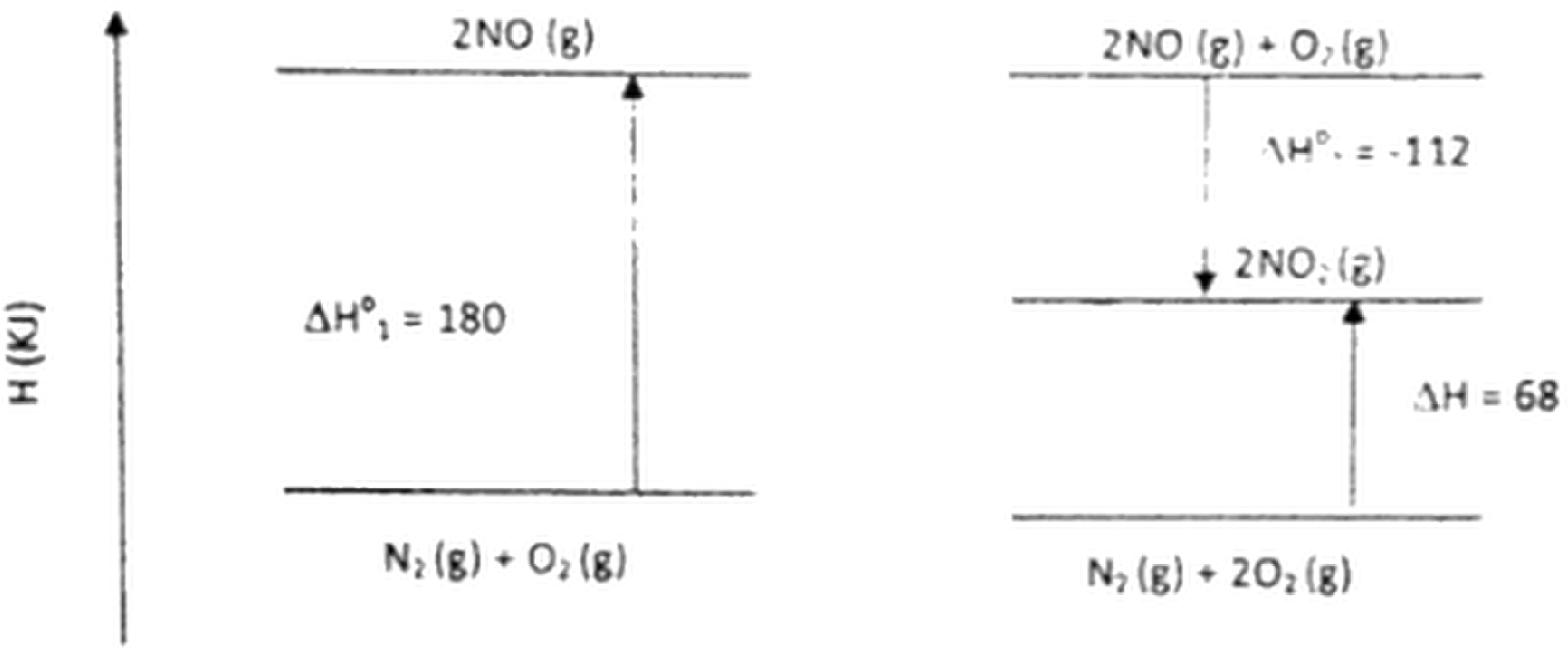


Fig: energy cycle for the reaction between N_2 (g) and O_2 (g) produce NO_2 (g)

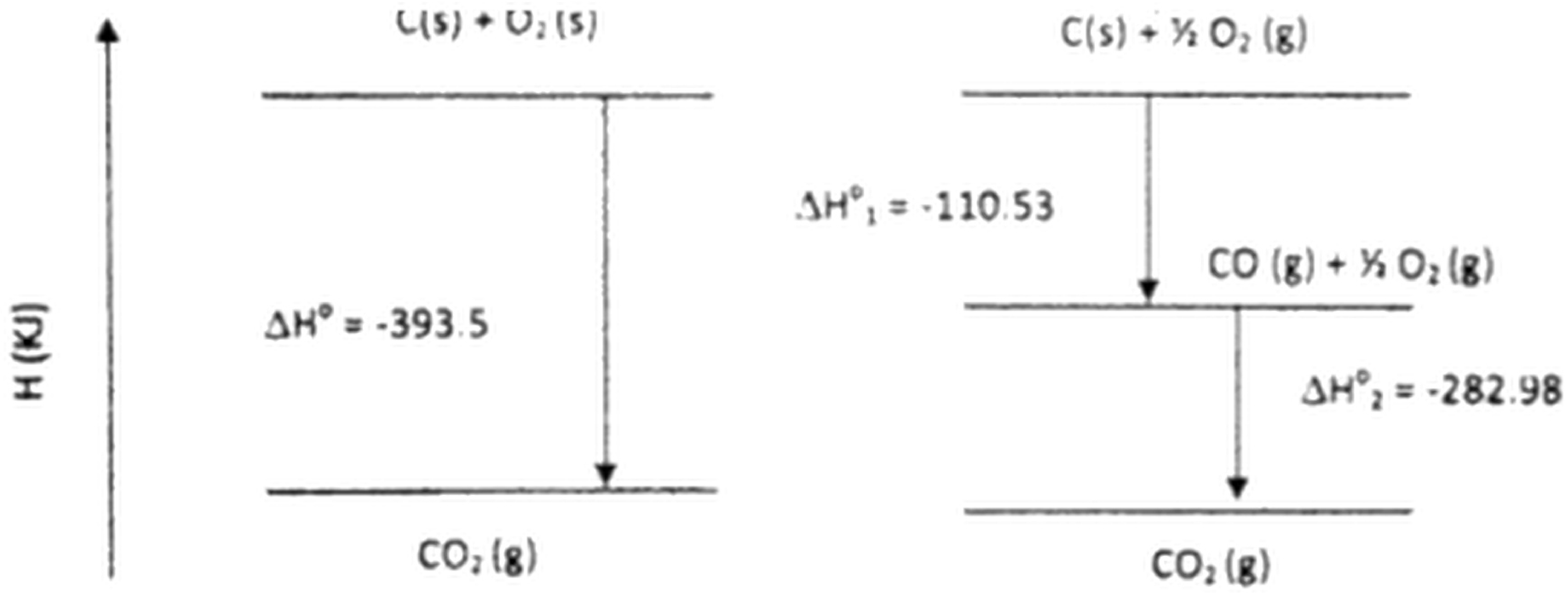


Fig: energy cycle for the reaction between C(g) and O_2 (g) produce CO_2 (g)

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

Ans: relationship between internal energy of a system and thermal energy at constant temperature and pressure:

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

According to the first law of thermodynamics

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

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

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

Rearranging this equation,

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

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

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

Enthalpy:

Enthalpy of a substance is defined as the system's internal energy plus the product of its pressure and volume (H=E +PV).

Absolute value of enthalpy of a system cannot be measured. However, change in enthalpy of a system (ΔH) can be measured.

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

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

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

Thus ΔH - ΔE

Standard enthalpy change:

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

Equation (1) can be written as

$q_p .= \Delta H^{\circ} = \Delta E^{\circ} + \mathrm{P}\Delta V$

Conclusion:

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

9. When ethanol burns in oxygen, carbon dioxide and water are formed

(a) Write the equation which describes this reaction.

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

ΔH_f **for ethanol(l) = -277.0 KJ** $mole^{-1}$

$\Delta H_f CO_2(g) = -393.5 KJmole^{-1}, \Delta H_f water(l) = -285.8 KJmole^{-1}$

Solution:

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

(b) Required equation:

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

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

Given equations:

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

$2C_{(s)} + 3H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow C_2H_5OH_{(l)}$ ΔH_f° = -277.0 kJ $mole^{-1}$.......... (i)

ΔH°_{f} of gaseous CO 20

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ ΔH°_{f} = -393.5 kJ $mole^{-1}$............(ii)

ΔH°_{f} of liquid H2O

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$ ΔH°_{f} = -285.8 kJ $mole^{-1}$ ....(iii)

To get the require equation following steps should be adopted

Step 1: Multiply equation (ii) by 2,

Step 2: Multiply equation (iii) by 3,

Step 3: Reverse equation (i).

Step 4: Then add all the resulting equations, we get the required the enthalpy of combustion for ethanol C_2H_5OH

$2C_{(s)} + 2O_{2(g)} \rightarrow 2CO_{2(g)}$ ΔH = -7870 kJ $mole^{-1}$

$3H_{2(g)} + \frac{3}{2}O_{2(g)} \rightarrow 3H_2O_{(l)}$ ΔH = -857.4 kJ $mole^{-1}$

$C_2H_5OH_{(l)} \rightarrow 2C_{(s)} + 3H_{2(g)} + \frac{1}{2}O_{2(g)}$ ΔH = +277.0 kJ $mole^{-1}$

$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ ΔH°_{c} = -1367.4 kJ $mole^{-1}$

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

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

(b) $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_2O(g) \rightarrow NH_{3(g)} + \frac{3}{4}O_{2(g)}$ **(Ans: 321.55 KJ)**

Solution:

(a) $C_6H_{6(l)} \rightarrow 6C_{(s)} + 3H_{2(g)}$

Required equation:

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

$$C_6H_{6(l)} \rightarrow 6C_{(s)} + 3H_{2(g)} \qquad \Delta H^\circ = ?$$

Give equations:

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

$$C_6H_{6(l)} + \frac{15}{2}O_{2(g)} \rightarrow 6CO_2 + 3H_2O_{(l)} \ \Delta H^\circ = \text{-3268 kJ } mole^{-1} \text{ ....(i)}$$

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

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

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

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

To get the require equation following steps should be adopted.

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

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

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

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

$$6CO_{2(g)} \rightarrow 6C_{(s)} + 6O_{2(g)} \qquad \Delta H^\circ = \text{+2361.0 kJ } mole^{-1}$$

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

$$C_6H_{6(l)} + \frac{15}{2}O_{2(g)} \rightarrow 6CO_2 + 3H_2O_{(l)} \ \Delta H^\circ = \text{-3268 KJ } mole^{-1}$$

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

(b) $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_2O(g) \rightarrow NH_{3(g)} + \frac{3}{4}O_{2(g)}$

Required equation:

$\frac{1}{2}N_{2(g)} + \frac{3}{2}H_2O(g) \rightarrow NH_{3(g)} + \frac{3}{4}O_{2(g)} \qquad \Delta H' = ?$

Given equations:

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

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

Heat of formation of gaseous H20cm

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

To get the require equation following steps should be adopted

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

Step 1: Take equation (i) as such.

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

$\frac{1}{2}N_{2(g)} + \frac{3}{4}H_{2(g)} \rightarrow NH_{3(g)} \qquad \Delta H' = -46.1kJ$

$\frac{1}{2}H_2O(g) \rightarrow \frac{3}{2}H_{2(g)} + \frac{3}{4}O_{2(g)} \qquad \Delta H' = +387.65$ kJ

$\frac{1}{2}N_{2(g)} + \frac{3}{2}H_2O(g) \rightarrow NH_{3(g)} + \frac{3}{4}O_{2(g)} \quad \Delta H' = +321.55$ kJ

11. The heat of combustion of liquid benzene, C_6H_6 to form H_2O and CO_2 at 1 atm and 25°C is -3268 KJmole of benzene. What is the heat of formation of liquid benzene under these conditions. (ans:+49.5 KJ/mole)

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

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

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

$C_6H_{6(l)} + \frac{15}{2}O_{2(g)} \rightarrow 6CO_2 + 3H_2O_{(l)}$ $\Delta H'$ = -3268kJ $mole^{-1}$ (i)

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

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

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

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

To get the require equation following steps should be adopted.

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

Step 3: Reverse equation (i).

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

$6C_{(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)}$ $\Delta H'$ = -2361.0 kJ mole

$3H_{2(g)} + \frac{3}{2}O_{2(g)} \rightarrow 3H_2O_{(l)}$ $\Delta H'$ = -857,4 kJ mole

$6CO_2 + 3H_2O_{(l)} \rightarrow C_6H_{6(l)} + \frac{15}{2}O_{2(g)}$ $\Delta H'$ = +3268 0 kJ mole

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$6C_{(s)} + 3H_{2(g)} \rightarrow C_6H_{6(l)}$ $\Delta H'$ = +49.6 kJ mole"

12. Specify conditions for the standard heats of reactions.

Ans: Condition for Standard Heat of Reaction:

AH varies with conditions. we use standardized ΔH values. These values are calculated when all the substances are in their standard state

Conditions for the standard states are as follows:

1. Standard state for a gas is 1 atm.
2. Standard state for an element or a compound is the most stable physical

state at 1 atm and 25°C (298 K).

3. Standard state for a substance in aqueous solution is 1M concentration

Now we will define important enthalpies.

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

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

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

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

$N_{2(g)} + 2O_{2(g)} \rightarrow 2N_2O(g)\ \Delta H' = 68KJ$

This reaction can be carried out in two steps.

$N_{2(g)} + 2O_{2(g)} \rightarrow 2NO(g)\ \ \Delta H_1' = 180KJ$

$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_2(g)\ \ \Delta H_2' = -112KJ$

Net reaction: $N_{2(g)} + 2O_{2(g)} \rightarrow 2N_2O(g)\ \Delta H_1' + \Delta H_2' = 68KJ$

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

$\Delta H' = \Delta H_1' + \Delta H_2' = 68KJ$

For energy cycle see fig. 11.4.

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

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}\quad \Delta H' = -393.5KJ$

This reaction may takes place in two steps.

$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}\ \ \Delta H_1' = -110.52KJ$

$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}\ \Delta H_2' = -282.98KJ$

Net reaction $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}\ \Delta H_1' + \Delta H_2' = -393.51KJ$

Energy cycles:

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

Fig. shows energy cycle for this reaction.

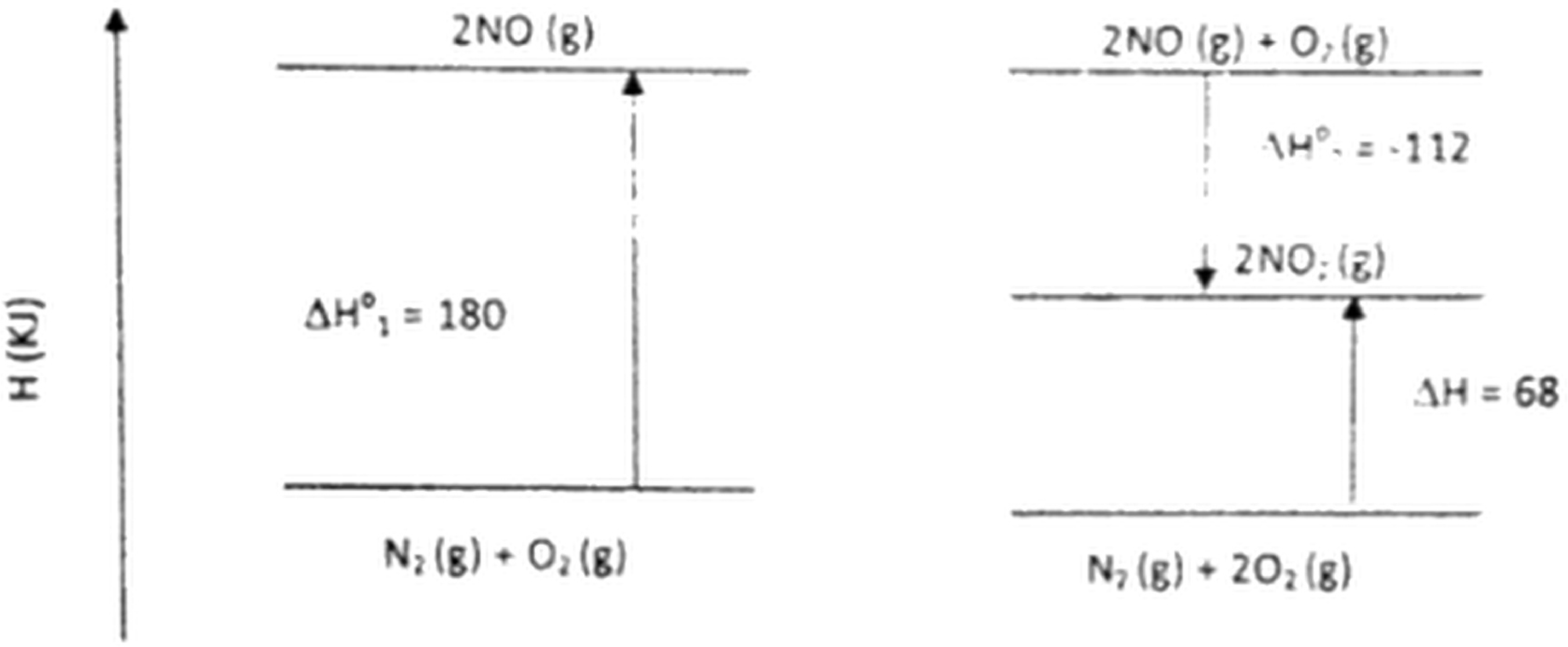


Fig: energy cycle for the reaction between N_2 (g) and O_2 (g) produce NO_2 (g)

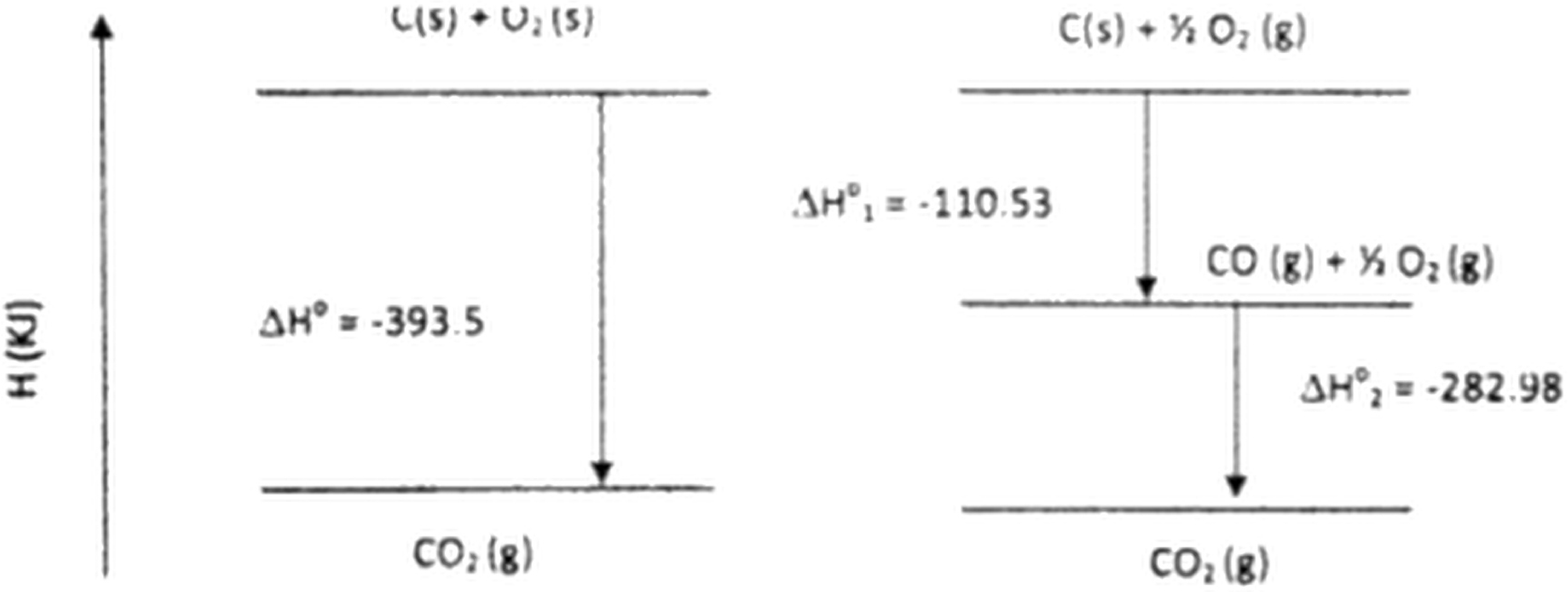


Fig: energy cycle for the reaction between C(g) and O_2 (g) produce CO_2 (g)

14. State and explain First law of Thermodynamics.

Ans: First Law of Thermodynamics:

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

OR

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

OR

Total energy of the universe always remain conserve.

Mathematically:

A system can exchange energy with its surroundings in two distinct ways.

Energy can be transferred as heat or work.

Heat and work can be transferred into or out of the system. Because energy must be conserved, the energy change of the system is linked to the flow of heat and work.

$\Delta E = q + w$

This equation is the mathematical form of first law of thermodynamics. Where ΔE represents the change in the system's internal energy, q represents heat and w represents work.

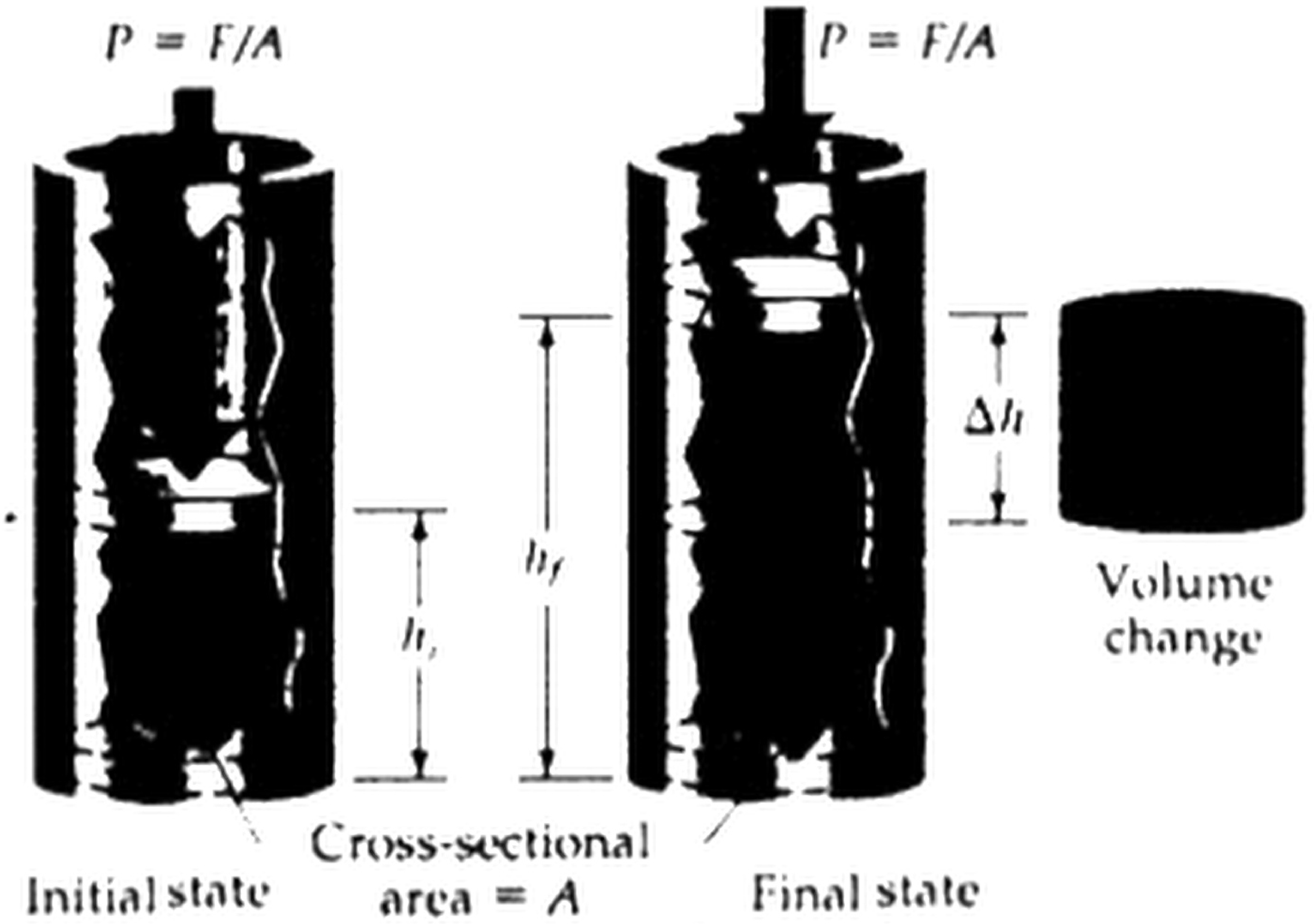
Conversion of signs:

W has positive sign when work is done on the system and negative when work is done by the system.

q is positive when system absorbs heat and negative when loses heat.

Explanation:

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



Pressure – volume work

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

ΔE = q + w

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

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

F = PXA ------------ (1)

Work done on the piston is:

Work = force x area

W = F x Δh --- -(2)

From equations 1 and 2, we get

W = PxAx Δh --------- (3)

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

ΔV = A. Δh

Therefore equation 3 becomes

W = P x ΔV

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

W= -P ΔV

Pressure - volume work:

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

ΔE = q - P ΔV

15. 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.

(Ans: 180 atm. dm^3)

Solution: Here P = 10 atm

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

As w = P ΔV

So w = 10 x 18

= 180 atm. dm^3

16. Camphor ($C_{10}H_{16}O$) has heat of combustion of 5903.6 kJ/mole. A sample of camphor having mass of 0.12049 is burned in a bomb calorimeter. The temperature Increases by 2.28°C. Calculate heat capacity of the calorimeter.

(Ans:3.2798KJ/K/mole)

Solution: Mass of camphor = m = 0.1204 g

Increase in temperature = ΔT = 2.28°C or 2.28 K

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

Molar mass of camphor ($C_{10}H_{16}O$) = 12 x10 + 1x16+16

= 152 g $mole^{1}$

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

1 mole of camphor produce heat = 5903.6 kJ

7.92 x 10^{-4} moles of camphor produce heat = 5903.6 x 7.92 x 10^{-4}

= 4.675 kJ

In a constant volume calorimeter

Heat evolved = ΔT x Total heat capacity of calorimeter

4.675 kJ = 2.28 x Total heat capacity of calorimeter

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

or Total heat capacity of calorimeter = $\frac{4.675}{2.28}$ = 205 kJ K^{-1}

17. In a coffee-cup calorimeter 100 cm^3 of 0.1M HCl and 100 cm^3 of 1.0M NaOH are mixed at 24.6°C raised temperature by 6.9°C. Calculate the enthalpy of neutralization of HCl by NaOH from the given data. Heat capacity of water is 4.18 J/g°C.

(Ans: -57.684 KJ/mole).

Solution:

Volume of HCl = 100 cm^3

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

Volume of NaOH = 100 cm^3

Density of water= 1 g cm^3

Total mass of reaction mixture (m) = 200 cm^3 x 1g. cm^3 = 200g

Rise in temperature = ΔT = 6.9°C

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

q= mxCxΔT

q= 200g x 42 J $g^{-1} C^{-1}$ x 6.9°C

q= 5.796 x 10^3 J

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

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

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

Consider chemical equation.

$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H2O_{(l)}$

1 mole 1 mole 1 mole

0 1 mole 0.1 mole 0.1 mole

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

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

= 57.96 kJ $mole^{-1}$

Thus heat evolved at constant pressure will be

$q_p = \Delta H^{\circ}_n$ = - 57.96 kJ $mole^{-1}$

18. Calculate ΔH° for the reaction

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

from the following data

$S(s) + \frac{3}{2} O_2(g) \rightarrow SO_3(g) \quad \Delta H^{\circ}$ **= -395.2 KJ**

$2SO_2(g)O_2(g) \rightarrow 2SO_3(g) \quad \Delta H^{\circ}$ **= -198.2 KJ (Ans: -296.11 KJ)**

Solution:

Required equation:

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

$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \qquad \Delta H^{\circ} = ?$

Given equations:

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

$S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g)\ \Delta H^{\circ}$ = -395.2 KJ .... (1)

$2SO_{2(s)} + O_{2(g)} \rightarrow 2SO_{3(g)}\ \Delta H^{\circ}$ = -198.2 kJ ....(ii)

To get the require equation following steps should be adopted.

Step 1: Divide equation (ii) by 2,

Step 2: Take equation (i) without any change

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

$S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g)\ \Delta H^{\circ}$ = -395.2 kJ ...(i)

$2SO_{2(s)} + O_{2(g)} \rightarrow 2SO_{3(g)}\ \Delta H^{\circ}$ = +99.1 kJ ....(ii)

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

19. An aluminium frying pan weighs 745g is heated on a stove from 25°C to 205°C. What is q for the frying pan? C_p for Al Is 24.35 J $mole^{-1}K^{-1}$ (Ans: 120.94 kJ)

Solution:

Mass of Al frying pan = 745 g

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

Initial temperature= T_1 = 25°C

Final temperature= T_2 = 205°C

Change in temperature = ΔT = 205°C -25°C

= 180 °C

or = 180K

Heat capacity of Al = C_p = 24.35 J $mole^{-1}K^{-1}$

q = nx C_p x ΔT

= 27.596 mole x 24.35 J $mole^{-1}K^{-1}$ x 180K

= 120953 J

= 120.953 kJ

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

(a) C_4H_9OH **(Butanol)**

(b) Rust, Fe_3O_4

(c) Acetic acid CH_3CO_2H

(d) Urea $(NH_2)_2CO$

Solution:

(a) C_4H_9OH (Butanol):

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

(b) Rust, Fe_3O_4:

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

(c) Acetic acid CH_3CO_2H:

$$2C(s)+2H_2(g)+O_2(g)\rightarrow CH_3CO_2H(l)$$

(d) Urea $(NH_2)_2CO$:

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

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

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

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

(Ans: -2817KJ $mole^{-1}$)

(c) Heats of combustions of C and H2 are -393.5KJ $mole^{-1}$ and -285.8KJ $mole^{-1}$ respectively. Determine the heat of formation of glucose. (Ans: -1258.8 kJ/mole)

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

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

Heat produced by burning 1g of Glucose = 15.65 KJ

Heat produced. by burning 1 mole (180) of Glucose = 15.65 x 180

= 2817 KJ

ΔH_c° for Glucose = -2817 KJ $mole^{-1}$

(C) Solution:

Required equation:

Heat of combustion of $C_6H_{12}O_{6(g)}$

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

Given equations:

Heat of combustion of glucose

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

Heat of combustion of C

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

Heat of combustion of H_2

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$ ΔH° = -285.8 kJ $mole^{-1}$ ....(iii)

To get the require equation following steps should be adopted.

Step 1: Multiply equation (ii) by 6.

Step 2: Multiply equation (iii) by 6.

Step 3: Reverse equation (i).

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

6C + 6020) - 6CO2(0)

ΔH = -2361 kJ $mole^{-1}$

6H2(g) + 3020) — 6H2O

ΔH = -1714.8 kJ $mole^{-1}$

6CO2g) + BH20m — CoH12O6(a) + 602(a) ΔH = +2817.28 kJ $mole^{-1}$

6C+ 6H2(g) + 302(e) — C,H,200) ΔH = -1258.52 kJ $mole^{-1}$

22. Write the balanced chemical equation associated with each of the following enthalpy changes.

(a) Heat of sublimation of iodine.

(b) Heat of formation of gaseous atomic Iodine.

(c) Heat of formation $C_2H_3Cl(g)$

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

Ans:

(a) Heat of Sublimation of Iodine.

$I_2(s) \rightarrow I_2(g)$ ΔH = positive

(b) Heat of Formation of Gaseous Atomic Iodine.

$\frac{1}{2} I_2(g) \rightarrow I(g)$ ΔH = positive

Heat of Formation of $C_2H_3Cl(g)$.

$2C(s) + \frac{3}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow C_2H_3Cl(g)$ ΔH = positive

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

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

ΔH = positive = 3268 KJ $mole^{-1}$

23. The standard combustion enthalpies of carbon, hydrogen and acetic acid are -393.5 KJ mole, -285.8K $mole^{-1}$ and -875 KJ $mole^{-1}$ respectively. Deduce the value of standard enthalpy of formation of

acetic acid, CH_3COOH

(Ans: -483.6 kJ/mole)

Solution:

Required equation:

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

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

Given equations:

Heat of combustion of glucose

$CH_3COOH_{(l)} + 2O_{2(g)} \rightarrow 2CO_{2(g)} 2C_{(s)} + 2H_2O_{(l)}$ ΔH° = -875 kJ $mole^{-1}$ ....(i)

Heat of combustion of C

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

Heat of combustion of H_2

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

To get the require equation following steps should be adopted

Step 1: Multiply equation (ii) by 2.

Step 2: Multiply equation (iii) by 2.

Step 3: Reverse equation (i)

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

$2C_{(s)} + 2O_{2(g)} \rightarrow 2CO_{2(g)}$ ΔH° = -3935 kJ $mole^{-1}$

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ ΔH° =-285.8 kJ $mole^{-1}$

$2C_{(s)} + 2HO_{2(g)} \rightarrow CH_3COOH_{(l)} 2C_{(s)} + 2O_{2(g)}$ ΔH° = -393 5 kJ $mole^{-1}$

$2C_{(s)} + 2H_{2(g)} + O_{2(g)} \rightarrow CH_3COOH_{(l)}$ ΔH° = -393 5 kJ $mole^{-1}$

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

$FeO(s) + Fe_2O_3(g) \rightarrow Fe_3O_4(s)$ ΔH° **= -1118 KJ**

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

Solution: Required equation:

The required conversion is

$2Fe_3O_4(s) + O_2 \rightarrow 2Fe_2O_3(s)$ ΔH° = ?

Given equations:

$3Fe(s) + 2O_2(g) \rightarrow Fe_3O_4(s)$ ΔH° = .1118 kJ……..(i)

$2Fe(s) + \frac{3}{2}O_2(g) \rightarrow Fe_2O_3(s)$ ΔH° = -824.2 kJ…….(ii)

As we know that

$\Delta H^{\circ}_{reaction} = \sum coeff_p \Delta H_f^{\circ}(products) - \sum coeff_p \Delta H_f^{\circ}(reacants)$

= [3 x (-824.2)] – [2 X (-1118) + (0)]

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

Thus the required conversion is exothermic.

25. Which of the following processes would you expect to be endothermic?

(a) $H_2O_{(g)} \rightarrow H_2O_{(l)}$

(b) $NH_{3(g)} + HCl(g) \rightarrow NH_4Cl_{(s)}$

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

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

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

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

Ans:

Note:

Lighter → Denser

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

ΔH = Negative

Denser_Lighter

Energy is taken in and the reaction will be endothermic.

ΔH = Positive

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

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

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

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

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

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

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

$C_2H_5OH(l) \rightarrow C_2H_5OH(g)$ ΔH **= 42.2 KJ** $mole^{-1}$

Ans:

i. As we know that evaporation is a cooling process and when we put few drops of ethanol on our palm these drops absorb heat from the body and the surrounding due to which they evaporate and the temperature of the palm decreases and a cooling effect can be experienced.

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

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

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

$CO(g)+2H_2(g)\xrightarrow{catalyst}CH_3OH(l)$

Standard enthalpies of formation of CH_3OH and CO are -238.7 KJ $mole^{-1}$ and -110.5KJ $mole^{-1}$ respectively. Will the reverse reaction exothermic or endothermic? Explain.

(Ans: exothermic)

Solution:

Required equation:

The reverse of the given equation ie.

Given equations:

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

Heat of formation of CH_3OH

$C_{(s)} + 2H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow CH_3OH_{(l)}\ \Delta H^\circ =$ -238.7 kJ $mole^{-1}$ .... (i)

Heat of formation of combustion of H_2

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

To get the require equation following steps should be adopted.

Step 1: Reverse equation (i)

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

$$CH_3OH_{(l)} \rightarrow C_{(s)} + 2H_{2(g)} + \frac{1}{2}O_{2(g)} \ \Delta H^o = +238.7 \text{ kJ } mole^{-1}$$

$$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)} \qquad \Delta H^o = -110.5 \text{ kJ } mole^{-1}$$

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

Conclusion

Hence, the reverse of the given reaction is endothermic.

28. Methane is the major substance in natural gas. How much heat is released when 20 g of methane burns in excess of air under standard conditions. The standard enthalpies of CO_2, H_2O and CH_4 are -393.5 KJ/mole, -285.8 kJ/mole and -74.6 kJ/mole respectively. (Ans: 1100.625 kJ)

Solution:

Required equation:

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

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

Given equations:

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

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

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

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

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

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

To get the require equation following steps should be adopted

Step 1: Multiply equation (iii) by 2.

Step 2: Reverse equation (i).

Step 3: Then add all the equations, we get

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ ΔH° = -393.5 kJ $mole^{-1}$

$2H_{2(s)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ ΔH° = -571.5 kJ $mole^{-1}$

$CH_4 \rightarrow C_{(s)} + 2H_{2(g)}$ ΔH° = +74.6 kJ $mole^{-1}$

$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$ ΔH° = -890.5 kJ $mole^{-1}$

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

Given mass of CH_4 = 20 g

Molar mass of CH_4 = 12 + 1x4 = 16 g $mole^{-1}$

Number of moles of CH_4 = 3 = 1.25 moles

So,

1 mole of CH_4 produce heat = -890.5 kJ

1.25 mole of CH_4 produce heat = -890.5 x 1.25 = -1113.125 kJ

29. Evaluate the importance of Hess's Law.

Ans: i. Determination of heat of formation:

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

ii. Determination of heat of transition:

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

iii. Determination of heat of hydration:

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

iv. Determination of heats of various reactions:

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