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Where Minds Pollinate

Class 11
Chemistry

Chapter 6
Thermochemistry
Handwritten Notes

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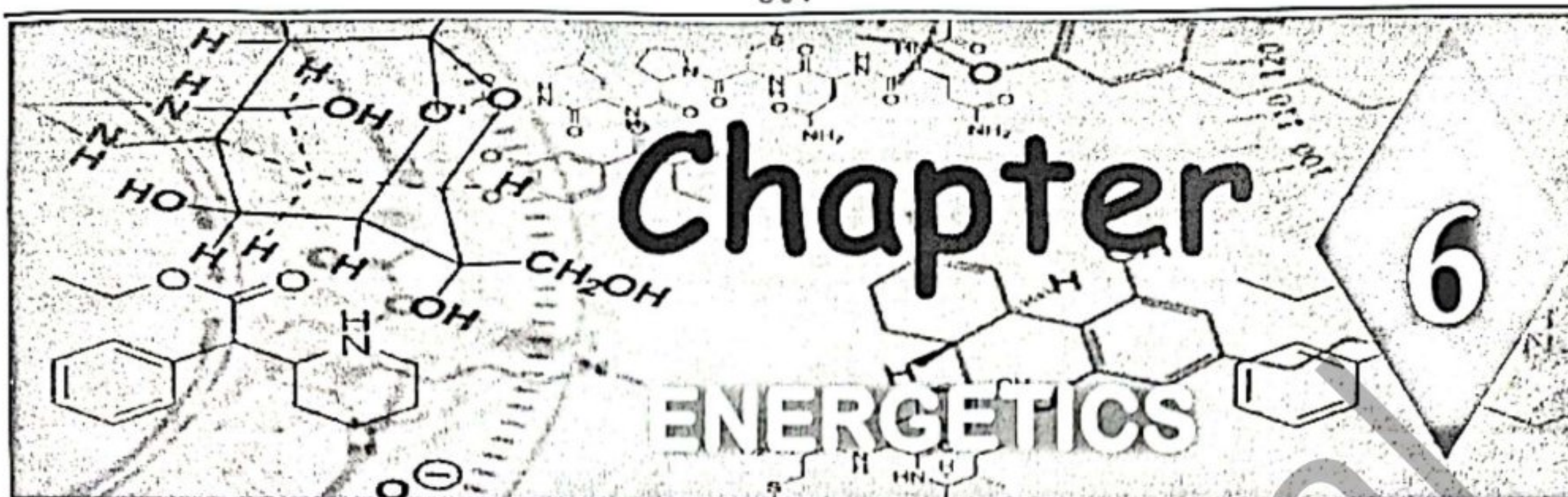
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INTRODUCTION:

Energetics

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

Thermo chemistry:

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

It deals with the:

- Principles and laws of energy changes
- The role of energy in chemical reactions
- Measurement of heat of chemical reaction.

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ENERGY IN CHEMICAL REACTIONS:

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

Units of Thermal energy

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

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

Another common unit of heat is calorie. 1 Calorie = 4.184 Joules

It is defined as heat required to raise the temperature of one gram of water by 1 °C

Definitions of Terms used in Thermodynamics

1. System:

The part of the universe which is under observation is called a system.

2. Surroundings:

The part of the universe except system is called surroundings.

Boundary:

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

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It may be real or imaginary.

e.g. ice melts in a beaker.

In this case, ice is a system and beaker and other things are surrounding.

THERMOCHEMICAL REACTIONS:

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

TYPES OF CHEMICAL REACTIONS

(i) Exothermic Reactions:

(ii) Endothermic Reactions:

Exothermic Reactions	Endothermic Reaction
1. The chemical reaction that proceeds with evolution of heat is called exothermic reaction.	1. A chemical reaction that proceeds with the absorption of heat is called an endothermic reaction.
2. In this reaction, heat transfers from system to surrounding.	2. In this reaction heat is transferred from surrounding to the system.
3. The container becomes hot in which reaction is taking place.	3. The container becomes cool in which reaction is taking place.
4. In these reactions enthalpy of products is less than that of reactants.	4. In these reactions enthalpy of products is more than that of reactants.
5. Dissolving of calcium oxide in water is an example of exothermic reaction. $\text{CaO} + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + \text{Heat}$ $\text{C(s)} + \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)} \quad \Delta H_r^\circ = -393.5\text{KJ}$ $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \longrightarrow 2\text{H}_2\text{O(l)} \quad \Delta H_r^\circ = -571.6\text{KJ}$	5. For examples $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \longrightarrow 2\text{HI(g)} \quad \Delta H_r^\circ = +53.8\text{KJ}$ $\text{C(s)} + \text{H}_2\text{O(g)} \longrightarrow \text{CO(g)} + \text{H}_2\text{(g)} \quad \Delta H_r^\circ = +131.4\text{KJ}$ $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \longrightarrow 2\text{NO(g)} \quad \Delta H_r^\circ = +180.5\text{KJ}$

Concept Assessment Exercise 6.1

Classify the following processes as exothermic or endo thermic.

a) Freezing of water

Freezing occurs with the loss of heat to the surrounding; therefore, it is an exothermic process.

b) Combustion of methane

During combustion process, heat is released to the surrounding, therefore, it is a exothermic process.

c) Sublimation of dry ice:

The conversion of solid into vapours is called sublimation. To convert solid into vapours energy is require, therefore, it is an endothermic process.

d) $\text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O(l)}$

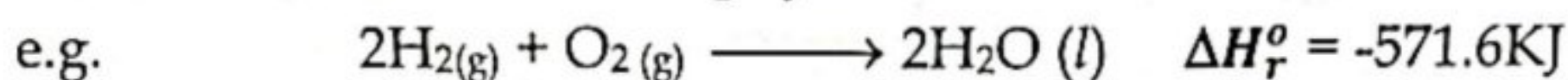
When gaseous water is cooled, it is converted into liquid water. Thus, energy is released to the surrounding, therefore, it is an exothermic process.

e) Decomposition of limestone:

To decompose a substance, energy is required, therefore, it is an endothermic process.

Heat of Reaction (ΔH_r°)

Amount of heat, released or absorbed, when no. of moles of reactant react with each other and form product, under standard conditions is called standard enthalpy of reaction. All the reactions and product must be in their standard physical state.



Relationship between Enthalpy Change and Heat of Reaction or Heat of Combustion of a Reaction.

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

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

The enthalpy changes of a reaction can be positive or negative depending upon the process, for an exothermic process, in which heat is released by the system of the surrounding ΔH is negative for an endothermic process, in which heat is absorbed by the system from the surroundings ΔH is positive. Since, combustion is an exothermic process in which heat is released by the system to its surroundings, ΔH is negative.

Standard states and standard enthalpy changes

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

Conditions for the standard states are as follows:

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

Define the following terms.

1. Standard Enthalpy of Reaction (ΔH_r°)

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

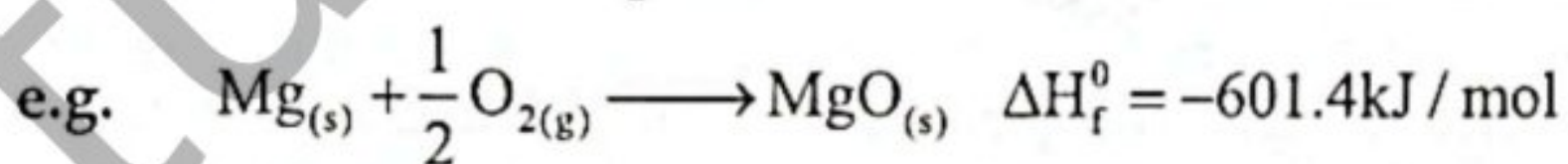
All the reactions and product must be in their standard physical state.



2. Standard Enthalpy of Formation: (ΔH_f°)

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

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



Example 6.1

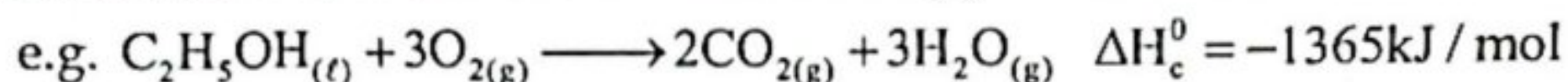
Write thermochemical equation for the formation of H_2O , SO_3 and H_2O_2 .

Solution:

- | | |
|--|--|
| (i) $\text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \longrightarrow \text{H}_2\text{O}(l)$ | $\Delta H_f = -285.8 \text{ kJ mole}^{-1}$ |
| (ii) $\text{S}_{(s)} + \frac{3}{2}\text{O}_{2(g)} \longrightarrow \text{SO}_{3(g)}$ | $\Delta H_f = -395.2 \text{ kJ mole}^{-1}$ |
| (iii) $\text{H}_{2(g)} + \text{O}_{2(g)} \longrightarrow \text{H}_2\text{O}_{2(l)}$ | $\Delta H_f = -191.2 \text{ kJ mole}^{-1}$ |

3. Standard Enthalpy of Combustion (ΔH_c°)

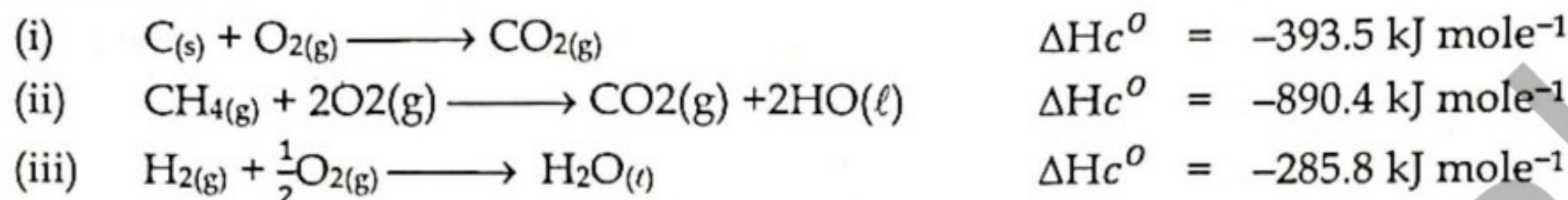
Amount of heat released, when one mole compound is burn in free supply of air (O_2), under standard conditions, is called standard enthalpy of combustion.



Example 6.2

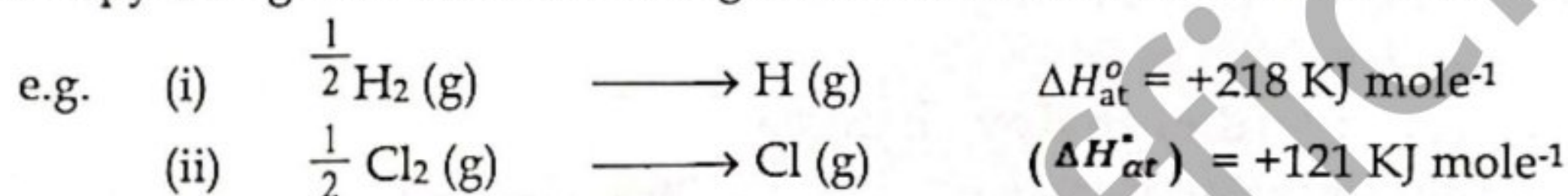
Write thermochemical equation for the combustion of, C, CH_4 and H_2 .

Solution:



4. Standard Enthalpy of Atomization (ΔH_{at}°)

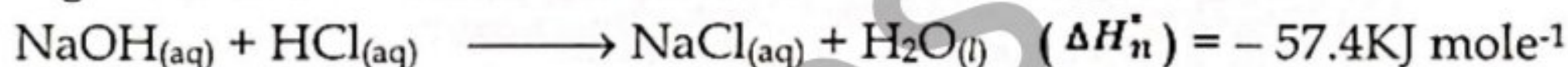
The enthalpy change when one mole of gaseous atoms are formed from its element under standard



5. Standard Enthalpy of Neutralization (ΔH_n°)

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

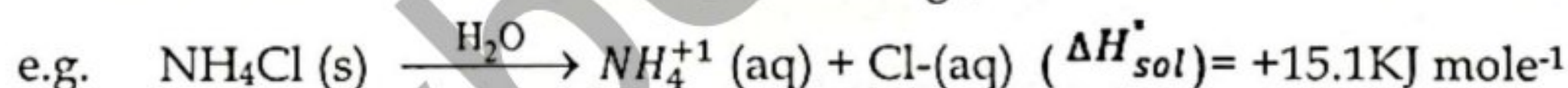
e.g.



It is same for strong acid and base because net chemical change is formation of one mole of water

6. Standard Enthalpy of Solution (ΔH_{sol}°)

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



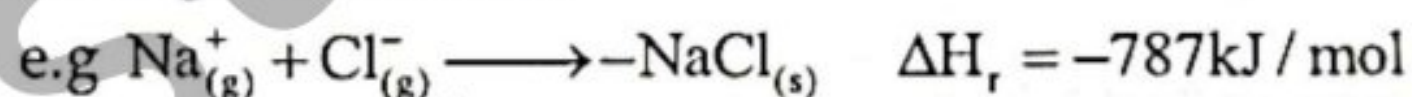
7. Standard Enthalpy of first Electron Affinity ($\Delta H_{E.A.}^\circ$)

Amount of heat released when one mole of gaseous atom gain an electron to form one mole of gaseous ion Under standard conditions



8. Lattice energy (ΔH_{latt}°)

Amount of energy released when one mole ionic compound is formed from its opposite charged ions in gaseous state.



Bond Energy

Bond Dissociation Energy:

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

Bond Energy:

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

When a chemical reaction occurs, old bonds are broken and new bonds are formed. Breaking bonds always requires energy, and forming a bond always releases energy. The difference between bond dissociation energy and bond energy determines whether the reaction absorbs or releases energy overall. For any chemical reaction, the enthalpy change is the sum of the bond dissociation energies of the reactants minus the sum of the bond energies of the products.

Example 6.3

We can theoretically calculate bond energy of a bond from the known bond energy data. Example, we can calculate bond energy on H—Cl as follows;

Bond dissociation energy of $H_2 = 436 \text{ kJ/mol}$.

Bond dissociation energy of $Cl_2 = 243 \text{ kJ/mol}$.

Bond energy of HCl = ?

Total energy absorbed in bond breaking = Total energy released in bond formation

$$\begin{array}{rcll} \text{Bond dissociation energy of H-H} & + & \text{Bond dissociation energy of Cl-Cl} & = 2 (\text{Bond energy of H-Cl}) \\ 436 & + & 242 & = 2 (\text{Bond energy of H-Cl}) \\ & & & 679 = 2 (\text{Bond energy of H-Cl}) \end{array}$$

Bond energy of H—Cl = 339 kJ/mol .

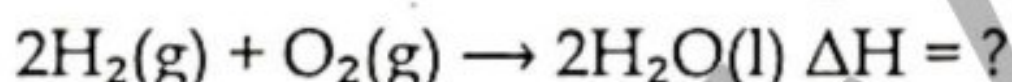
Thus theoretically calculated bond energy of HCl = 339 kJ/mol .

Experimentally determined bond energy of HCl = 431.5 kJ/mol .

This is theoretical values are average. These do not take into many factors like electronegativity differences of atoms. For any chemical reaction, the enthalpy change is the sum of bond dissociation energies of the reactants minus the sum of bond energies of products.

$$\Delta H = \sum H (\text{bonds broken}) - \sum H (\text{bonds formed})$$

For the reaction between H_2 and O_2 to produce H_2O .



$$\Delta H^0 = 2(\text{B.D.E of } H_2(g)) + \text{B.D.E of } O_2(g) - 4(\text{B.E of O-H bonds})$$

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

$$= 872 \text{ kJ} + 493.6 \text{ kJ} - 1840 \text{ kJ}$$

$$= -474.4 \text{ kJ}$$

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

Variability in Bond Energies

Some bond energies are precise, others are approximate.

1. Diatomic molecules (H_2 , O_2 , N_2 , Cl_2) have relatively accurate bond energies.
2. Complex molecules have more approximate bond energies due to factors like neighboring atoms and molecular geometry.
3. Bond strengths vary in different compounds (e.g., O-H in methanol vs. water).

HEAT CAPACITY

Define (a) Heat capacity (b) Specific heat capacity (c) Molar heat capacity

It is define as;

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

The different forms of energy can be converted into one another. Any other form of energy can be completely transformed into heat energy. But at constant temperature heat cannot be completely converted into another form of energy. Temperature is not the same as heat.

Temperature difference determines the direction in which heat flows spontaneously. But quantity of heat within a substance at a given temperature is directly proportional to its mass. Therefore, amount of heat absorbed by a substance is proportional to the temperature change.

$$q \propto \Delta T$$

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

Specific heat capacity:

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

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

Molar heat capacity:

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

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

Calorimetry:

It is the science of measuring heat of a chemical reaction by measuring the temperature change is called Calorimetry. Calorimeters measure the heat released from a system either at constant pressure ($q_p = \Delta H$) or at constant volume ($q_v = \Delta E$).

Thus there are two types of calorimetry.

- i. Constant pressure Calorimetry
- ii. Constant Volume Calorimetry

1. Constant Pressure Calorimetry:

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

Coffee cup calorimeter

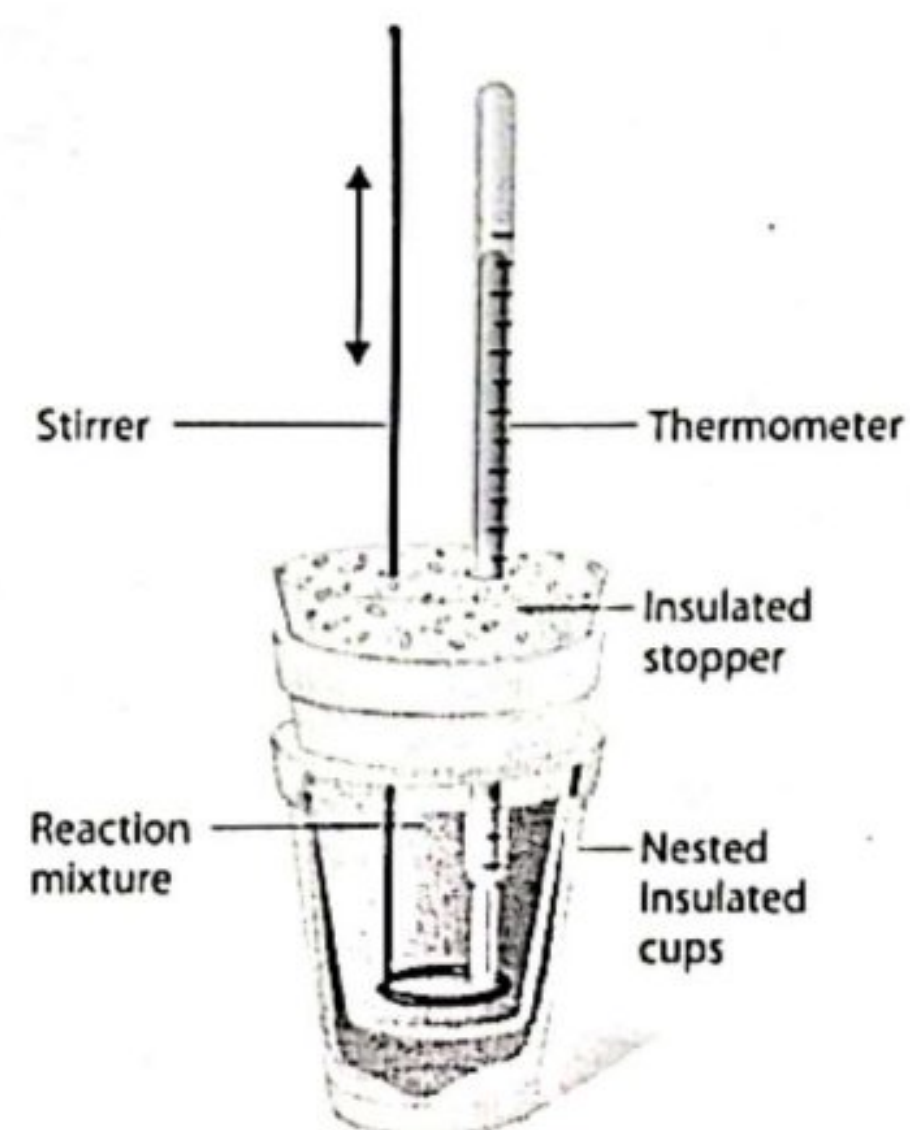
$$q = m \times c \times \Delta T$$

Where

m = mass of reactants

c = specific heat of reaction mixture

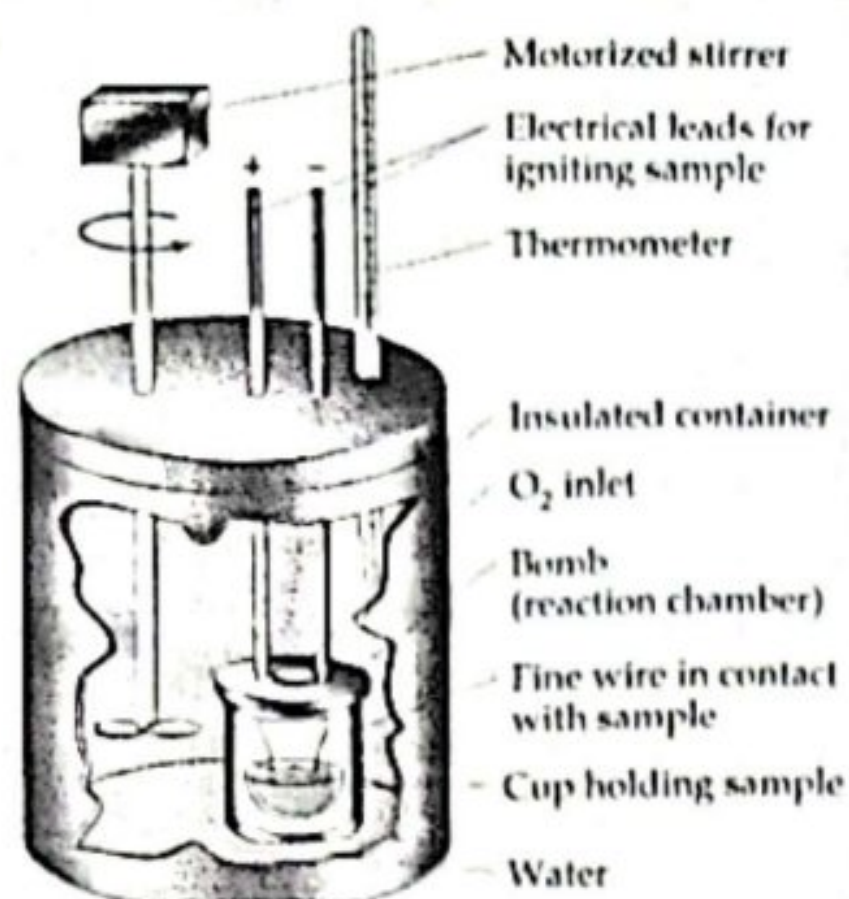
ΔT = change in temperature.



2. Constant Volume Calorimetry

The technique in which heat energy is calculated in a calorimeter at constant volume is Constant volume calorimetry. This technique is used for accurate determination of the enthalpy of

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



Hess's Law of constant Heat Summation:

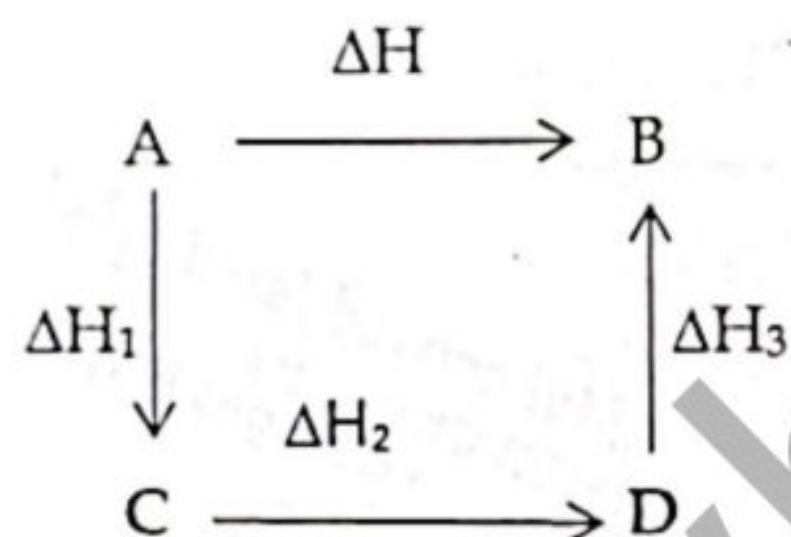
Q. Demonstrate Hess's law with the help of two suitable examples.

Ans. G.H. Hess stated this law in 1840.

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

Mathematically:

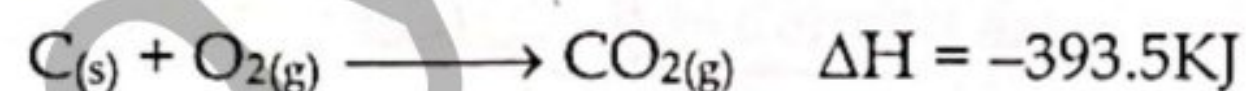
$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$



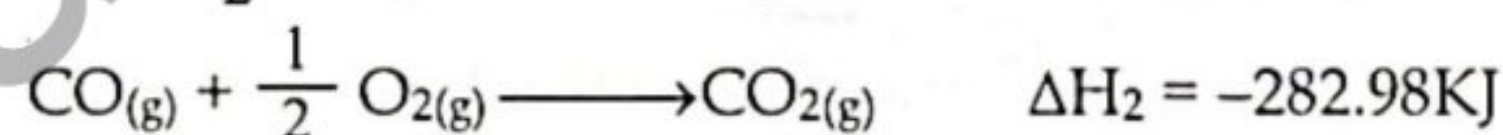
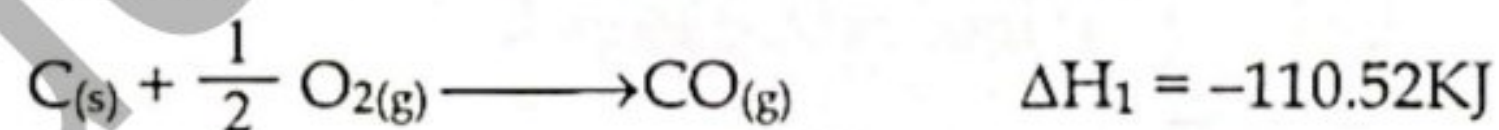
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Explanation: Carbon dioxide can be prepared by two methods;

One-Step Method:



Two-Step Method:



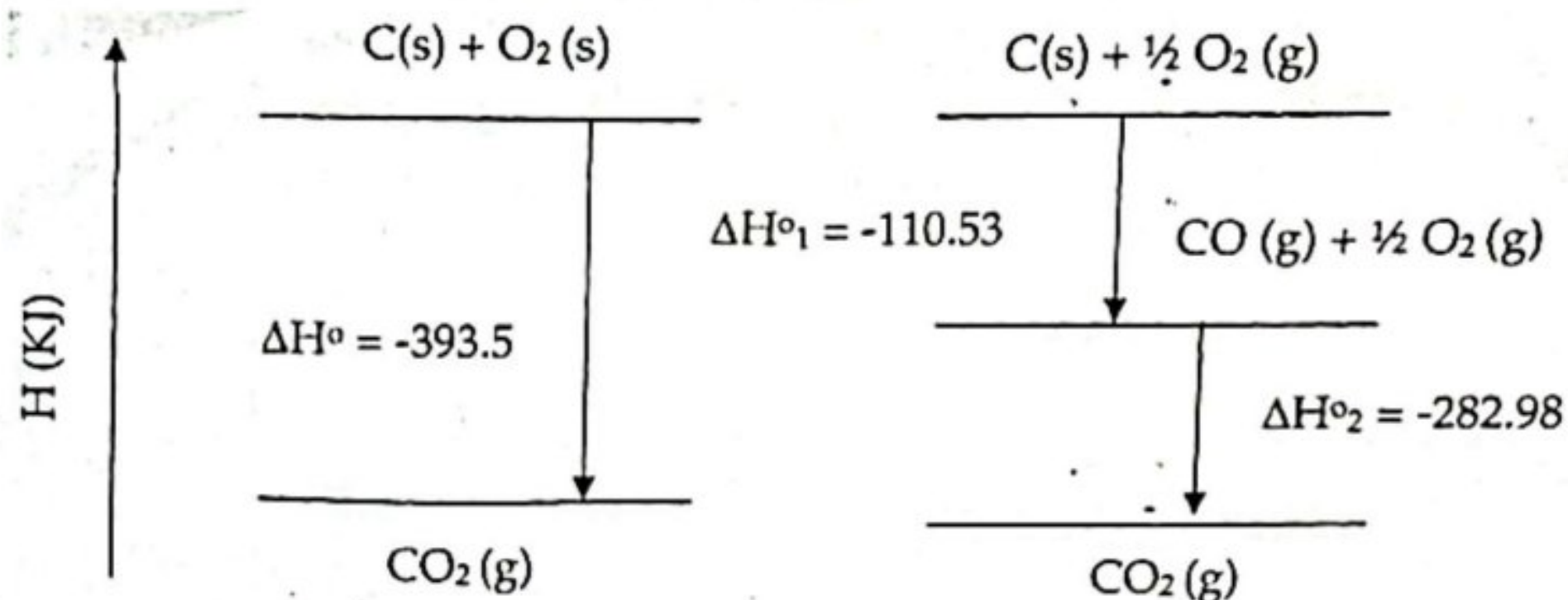
According to Hess's Law;

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

$$\Delta H = -110.52 - 282.98$$

$$\Delta H = -393.51 \text{ kJ/mol}$$

Energy cycle are



Importance of Hess's Law:

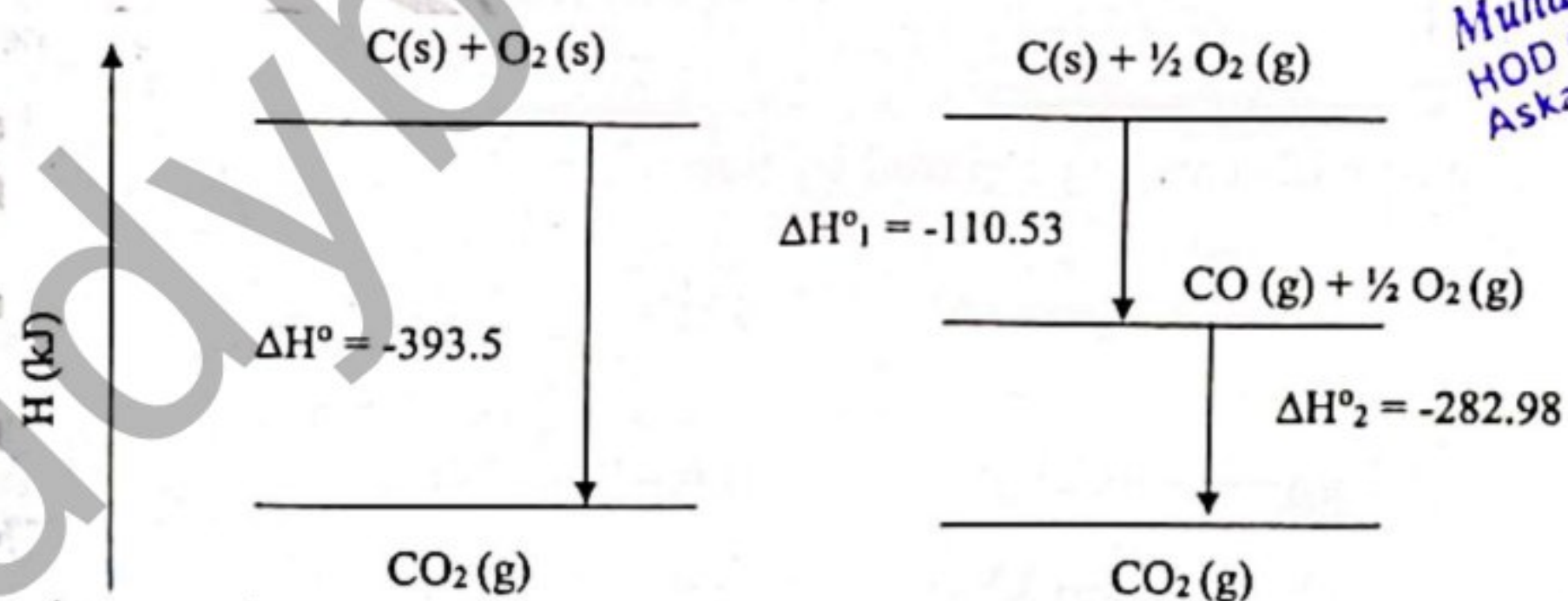
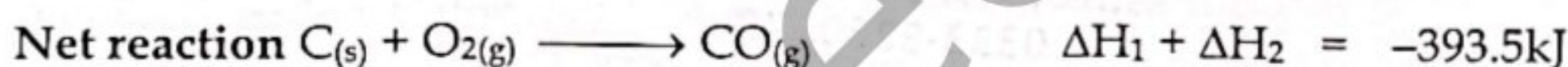
- These are many compounds which cannot be prepared directly from their elements. Some of these compounds cannot be decomposed into their constituent elements e.g. CCl_4 . So, its enthalpy of formation cannot be determined directly by calorimetry.
- Some elements do not burn completely due to the formation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

Example 6.6

Combustion of C to CO_2 evolves 393.5 KJ of energy.



This reaction may take place in two steps.

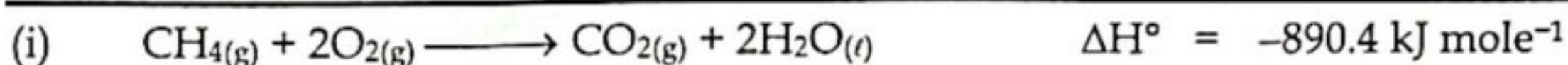


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Figure 6.4 Energy cycle for the reaction between $\text{C}_{(s)}$ and $\text{O}_{2(g)}$ to produce $\text{CO}_2(g)$ which steps in this cycle is/are exothermic?

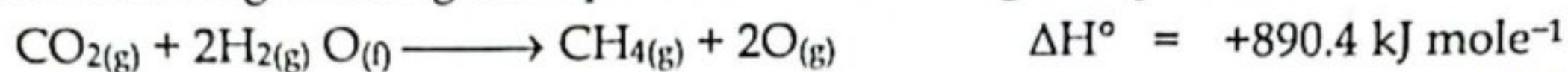
Example 6.7

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





Equation (iii) has $C_{(s)}$ as reactant which is needed in the required equation. Thus equation (iii) will be used as such. Equation (ii) has $H_{2(g)}$ as reactant but the required equation needs $2H_{2(g)}$, thus equation (ii) will be used after multiplying by 2. Equation (i) has $CH_{4(g)}$ as reactant, but this is needed as product in the required equation. Thus equation (i) must be reversed and the sign of ΔH° changed according. Adding the equations and deleting the species that occur on both sides we get.



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Example 6.8

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



Solution:

$$\begin{aligned} \Delta H^\circ_{\text{reaction}} &= \sum \text{coeff}_p \Delta H_f (\text{products}) - \sum \text{coeff}_r \Delta H_f (\text{reactants}) \\ &= [16 \times \Delta H_f \text{ for } CO_{2(g)} + 18 \times \Delta H_f \text{ for } H_2O_{(l)}] \\ &= [2 \times \Delta H_f \text{ for } C_8H_{18(l)} + 25 \times \Delta H_f \text{ for } O_{2(g)}] \\ &= 16(-393.5 \text{ kJ}) + 18(-285.8 \text{ kJ}) - 2(-269 \text{ kJ}) - 25(0) \\ &= -6296 \text{ kJ} - 5144.4 \text{ kJ} + 538 \text{ kJ} + 0 \\ &= -11440.4 \text{ kJ} + 538 \text{ kJ} \\ &= -10902.4 \text{ kJ} \\ &= -1.09 \times 10^4 \text{ kJ} \end{aligned}$$

Born Haber Cycle:

Q.Explain Born-Haber Cycle by using $NaCl$ as example for lattice energy calculation.

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

"Energy Change in a cycle process is always zero."

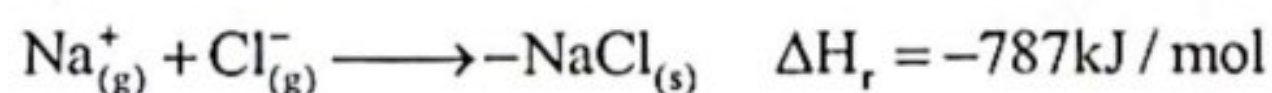
It is used to find the lattice energy of binary ionic compound.

Lattice Energy:

It is define as;

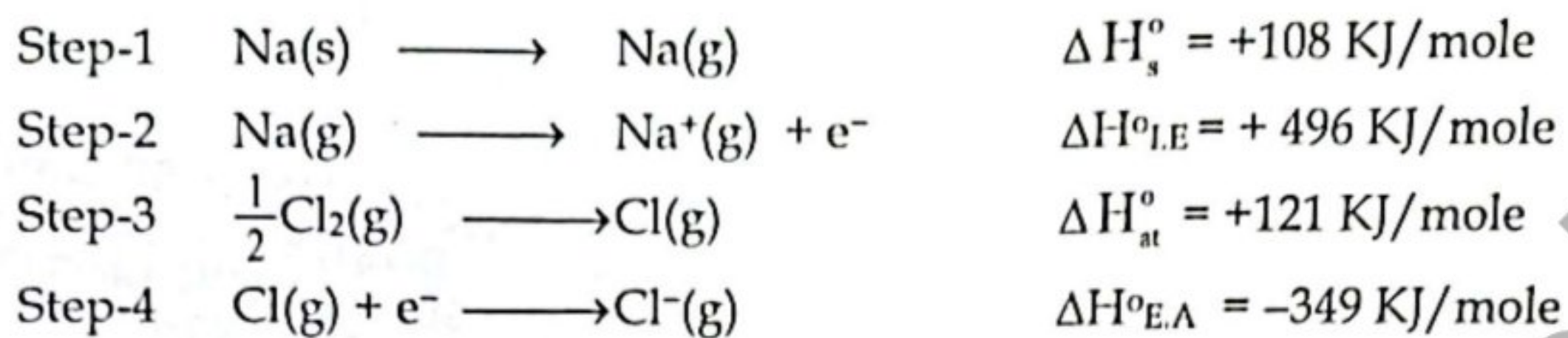
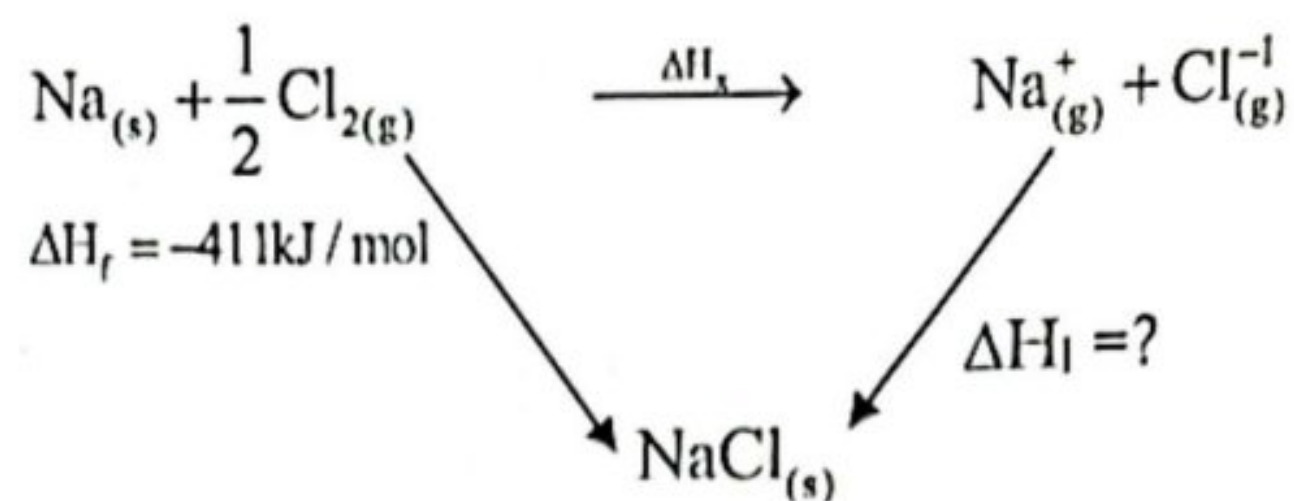
"Amount of energy released when one mole ionic compound is formed from its opposite charged ions in gaseous state."

e.g.



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

Energy Triangle of $NaCl$:



$$\begin{aligned}
 \Delta H_x^\circ &= \Delta H_{\text{at}}^\circ + \Delta H_{\text{I.E}}^\circ + \Delta H_{\text{at}}^\circ + \Delta H_{\text{E.A}}^\circ \\
 &= +108 \text{ KJ} + 496 \text{ KJ} + 121 \text{ KJ} + (-349 \text{ KJ})
 \end{aligned}$$

$$\Delta H_x^\circ = 376 \text{ kJ/mol}$$

According To Hess's law;

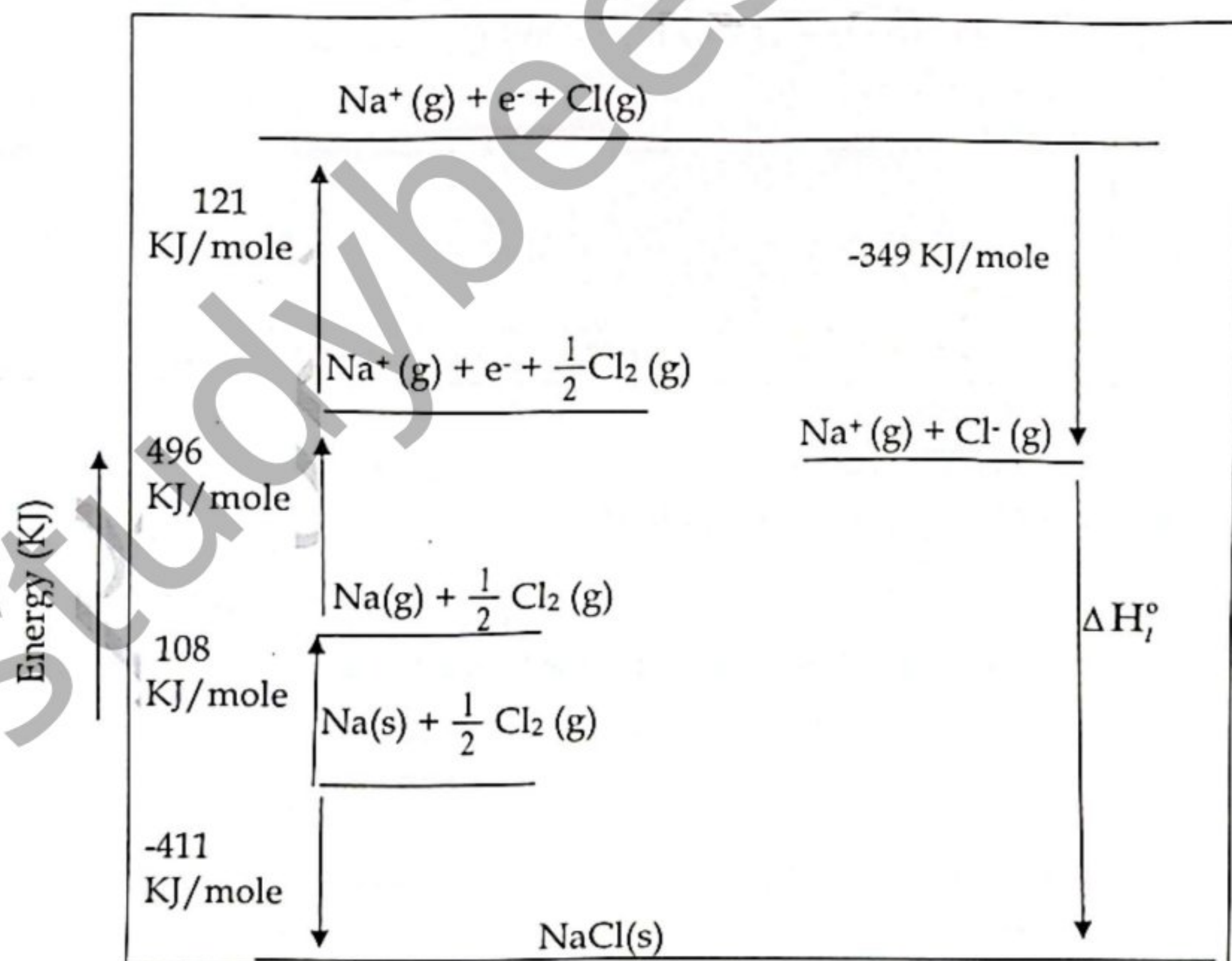
$$\Delta H_f = \Delta H_x + \Delta H_{(l)}$$

$$\Delta H_{(l)} = \Delta H_{f(l)} - \Delta H_x$$

$$= -411 - 376$$

$$\Delta H_{(l)} = -787 \text{ kJ/mol}$$

Energy Cycle of NaCl:



Concept Assessment Exercise 6.5

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

1. Standard enthalpy of formation of $\text{MgO} = -602 \text{ kJ mole}^{-1}$
2. Standard enthalpy of sublimation of $\text{Mg} = 150 \text{ kJ mole}^{-1}$
3. Ionization energy of Mg(g) to form $\text{Mg}^{2+}(\text{g}) = 2180 \text{ kJ mole}^{-1}$
4. Standard enthalpy of atomization of $\text{O}_2 = 247 \text{ kJ mole}^{-1}$
5. Electron affinity of O(g) to form $\text{O}^{1-}(\text{g}) = -141 \text{ kJ mole}^{-1}$
6. Electron affinity of $\text{O}^{1-}(\text{g})$ to form $\text{O}^{2-}(\text{g}) = 878 \text{ kJ mole}^{-1}$

Steps for Lattice Energy of MgO

1. $\text{Mg(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{MgO(s)} \quad \Delta H_f = -602 \text{ kJ mole}^{-1}$
2. $\text{Mg(s)} \rightarrow \text{Mg(g)} \quad \Delta H_s = 150 \text{ kJ mole}^{-1}$
3. $\text{Mg(g)} \rightarrow \text{Mg}^{2+}(\text{g}) + 2\text{e}^- \quad \Delta H_{\text{I.E}} = 2180 \text{ kJ mole}^{-1}$
4. $\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{O(g)} \quad \Delta H_{\text{at}} = 247 \text{ kJ mole}^{-1}$
5. $\text{O(g)} + \text{e}^- \rightarrow \text{O}^-(\text{g}) \quad \Delta H_{\text{E.A1}} = -141 \text{ kJ mole}^{-1}$
6. $\text{O}^-(\text{g}) + \text{e}^- \rightarrow \text{O}^{2-}(\text{g}) \quad \Delta H_{\text{E.A2}} = 878 \text{ kJ mole}^{-1}$
7. $\text{Mg}^{2+}(\text{g}) + \text{O}^{2-}(\text{g}) \rightarrow \text{MgO(s)} \quad \Delta H_l = ?$

Calculation

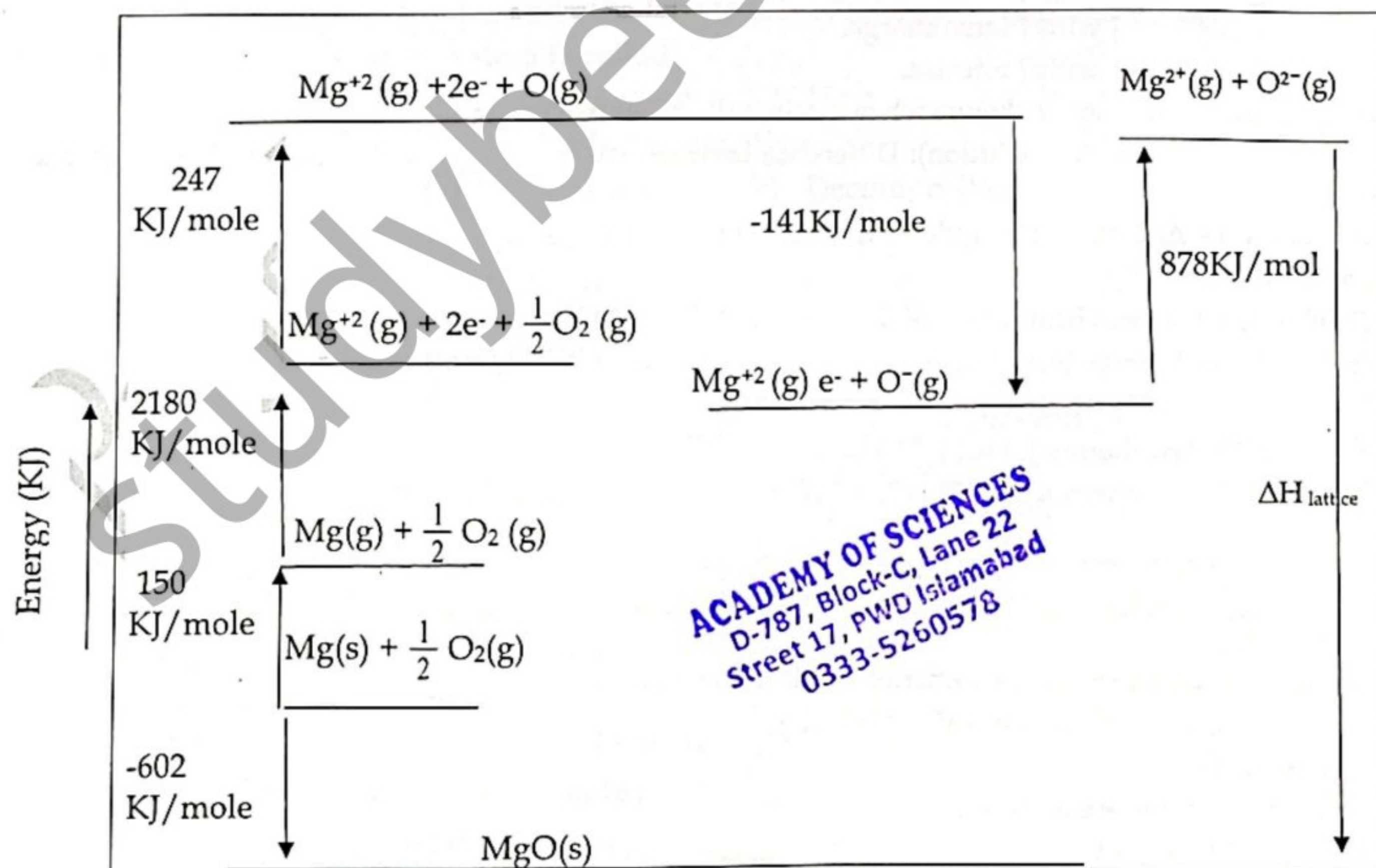
$$\Delta H_f = \Delta H_s + \Delta H_{\text{I.E}} + \Delta H_{\text{at}} + \Delta H_{\text{E.A1}} + \Delta H_{\text{E.A2}} + \Delta H_{\text{lattice}}$$

$$-602 \text{ kJ mole}^{-1} = 150 \text{ kJ mole}^{-1} + 2180 \text{ kJ mole}^{-1} + 247 \text{ kJ mole}^{-1} + (-141 \text{ kJ mole}^{-1}) + 878 \text{ kJ mole}^{-1} + \Delta H_{\text{lattice}}$$

$$\Delta H_{\text{lattice}} = -602 - 3314$$

$$\Delta H_{\text{lattice}} = -3916 \text{ kJ mole}^{-1}$$

Born Haber cycle of MgO



Factors Affecting Lattice energy

Lattice energy depend upon charge density higher will be charge density higher will be lattice energy ionic and vice versa

Charge density = Ionic charge/ionic radius

Two main factors influence lattice energy:

1. **Ionic Charge:** Higher charges = stronger electrostatic attraction = higher lattice energy.
2. **Ionic Radius:** Smaller radius = stronger electrostatic attraction = higher lattice energy.

Concept Assessment Exercise 6.6

Which of following has higher lattice energy and why

- a. LiF vs NaF: LiF has higher lattice energy

Reason. smaller Li^+ ion

- b. NaCl vs MgCl_2 : MgCl_2 has higher lattice energy

Reason Mg^{2+} has higher charge than Na^+

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Role of Hydration in the Dissolving Process

Heat of Solution: Heat released/absorbed when a solute dissolves in a solvent.

Heat of Hydration: Heat released/absorbed when a solute dissolves in water.

Main Points about Heat of Hydration

1. What happens when a solute dissolves in water:

Forces between solute particles need to be broken.

Solute particles bond with water molecules.

2. Energy changes:

Lattice energy: Energy to break solute particles apart.

Heat of hydration: Energy released when solute particles bond with water.

3. Trends:

Heat of hydration $\uparrow$ with $\uparrow$ ionic charge.

Heat of hydration $\downarrow$ with $\uparrow$ ion size.

4. **Heat of solvation:** Energy change when a solute dissolves in a solvent.

5. **Enthalpy of solution ($\Delta H_{\text{solution}}$):** Difference between lattice energy ($\Delta H_{\text{lattice}}$) and hydration energy (ΔH_{hyd}).

$$\Delta H_{\text{solution}} = \Delta H_{\text{lattice}} - \Delta H_{\text{hydration}}$$

6. Process can be:

Exothermic: Releases heat (like NaOH in water, $\Delta H = -44.5 \text{ kJ/mol}$).

Endothermic: Absorbs heat (like NH_4NO_3 in water, $\Delta H = +25.7 \text{ kJ/mol}$).

Examples

Negative ΔH (exothermic): LiCl (-37.0 kJ/mol), AlCl_3 (-321.0 kJ/mol).

Positive ΔH (endothermic): NaCl ($+2.98 \text{ kJ/mol}$), NH_4NO_3 ($+25.7 \text{ kJ/mol}$).

Factors Affecting Enthalpy of Hydration

1. **Ionic Charge**

Higher ionic charge = more exothermic hydration enthalpy.

Example: MgO (Mg^{2+} , O^{2-}) > NaCl (Na^+ , Cl^-).

2. **Ionic Radius**

Smaller ions = more exothermic hydration enthalpy.

Example: MgSO_4 > CaSO_4 because Mg^{2+} is smaller than Ca^{2+} .

Concept Assessment Exercise 6.8

LiF vs NaF: LiF has higher hydration enthalpy because Li^+ is smaller than Na^+ .

NaNO_3 vs KNO_3 : NaNO_3 has higher hydration enthalpy because Na^+ is smaller than K^+ .

ENTROPY

What is entropy?: Measure of disorder/randomness in a system (denoted by "S").

Entropy changes:

System goes from ordered $\rightarrow$ disordered = entropy increases ($\Delta S > 0$).

Example: Ice melting.

System goes from disordered $\rightarrow$ ordered = entropy decreases ($\Delta S < 0$).

Example: Water vapor condensing.

Calculating entropy change: $\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$

EXERCISE

Q1. Choose the correct Answer:

- (i) Which of the following substances have zero value for their standard enthalpy of formation?
(a) O_3 (b) H_2O (c) ZnO (d) None of these
- (ii) Calorie is equivalent to
(a) 4.18J (b) 4.18 kJ (c) 0.418J (d) 0.418 kJ.
- (iii) Enthalpy of neutralization of all the strong acids and strong basis has the same value due to
(a) The formation of salt and water (b) The formation of salt
(c) The complete ionization of acids and bases
(d) The combination of H^+ and OH^- ions to form water.
- (iv) Total heat content of a system is called
(a) Enthalpy (b) Internal energy (c) Heat (d) State function
- (v) Heat of _____ of a substance is always negative
(a) Formation (b) Combustion (c) Decomposition (d) Solution
- (vi) A balloon filled with oxygen is placed in a freezer. Identify system
(a) Balloon (b) Oxygen (c) Freezer (d) All of these
- (vii) A bomb calorimeter is used in _____ calorimetry:
(a) Constant volume (b) Constant pressure
(c) Both a and b (d) Constant temperature
- (viii) Boron Haber cycle is used to determine lattice energies of
(a) Molecular solids (b) Ionic solids (c) Covalent solids (d) Metallic solids
- (ix) Enthalpy of combustion for C is $-393.5 \text{ kJmol}^{-1}$
 $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H_{\text{Combustion}} = -393.5 \text{ kJmol}^{-1}$
Enthalpy of formation of CO_2 would be
(a) $+393.5 \text{ kJ}$ (b) -393.5 kJ
(c) Zero (d) Cannot be predicted from the given equation.
- (x) Which of the following is not a state function of a system?
(a) Thermal energy at constant pressure (b) Enthalpy

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- (c) Internal energy (d) Work done
- (xi) For writing a thermochemical equation for enthalpy of combustion of an element requires,
- (a) 1 mole of element as reactant
 - (b) 1 mole of oxide of element as product
 - (c) Standard states of all the substances
 - (d) Balanced equation of 1 mole of element
1. (a) 2. (a), (b) 3. (a), (c), (d) 4. (a), (b), (c), (d)

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ANSWERS

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

=====

SHORT QUESTIONS/ANSWERS

Q.2 Name and define units of thermal energy

Ans. Units of thermal energy

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

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

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

$$1 \text{ Calorie} = 4.18 \text{ Joules}$$

Q.3 Define the following terms system, surroundings and boundary.

Ans:

- **System:** The part of the universe on which we wish to focus attention is called a system.
- **Surroundings:** The part of the universe except system is called surroundings.
- **Boundary:** The real or imaginary surface separating the system from surroundings is called boundary.
- **STATE FUNCTION:** A property of a system that is determined by the state of the system regardless of how that condition was achieved is called state function.
- **HEAT:** Heat is the transfer of thermal energy between two bodies that are at different temperature.
- **HEAT CAPACITY:** The amount of heat required to raise the temperature of the given quantity of a substance by one Kelvin is called heat capacity.

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

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

- **Enthalpy of substance:**

Sum of internal energy and product of pressure, volume is known as enthalpy.

Q.4 Classify reactions as exothermic or endothermic.

Ans. See notes

Q.5 Define bond dissociation energy.

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

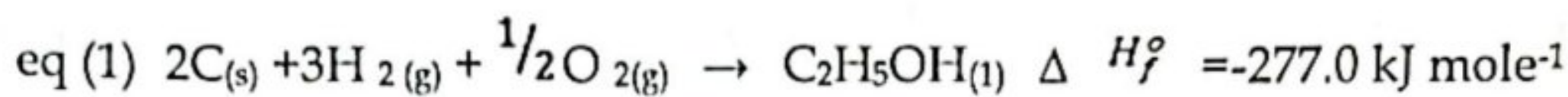
Q.6 When ethanol burns in oxygen, carbon dioxide and water are formed

- (a) Write the equation which describes this reaction.
- (b) Using the following data, calculate the enthalpy of combustion for ethanol C_2H_5OH .

$$\Delta H_f^\circ \text{ for ethanol}(l) = -277.0 \text{ KJmole}^{-1}$$

$$\Delta H_f^\circ \text{CO}_2(\text{g}) = -393.5 \text{ KJ mole}^{-1}, \Delta H_f^\circ \text{water}(\text{l}) = -285.8 \text{ KJ mole}^{-1}$$

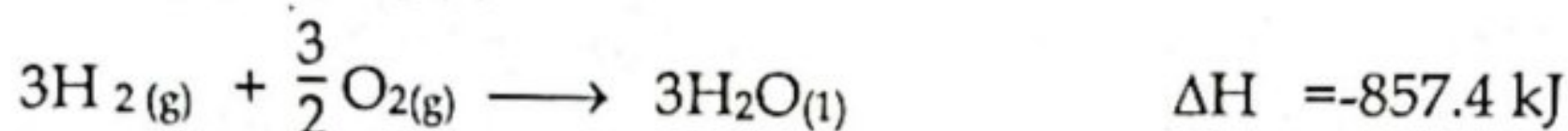
Ans.



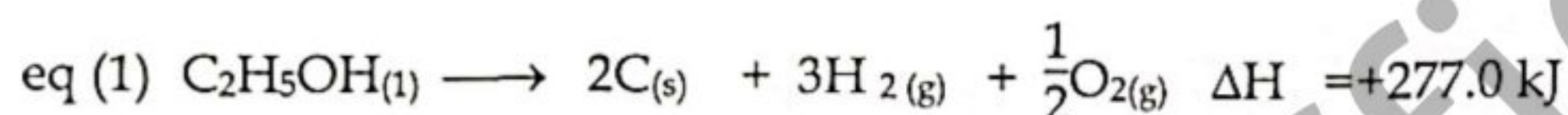
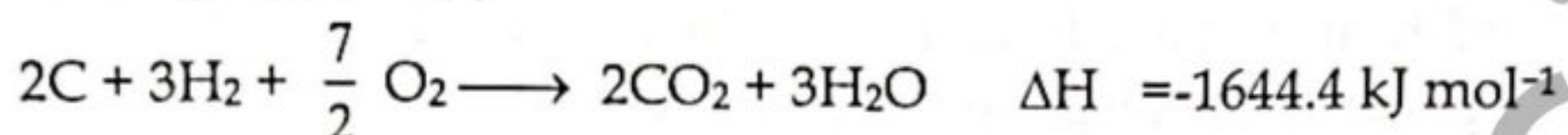
Multiplying eq (2) with '2'



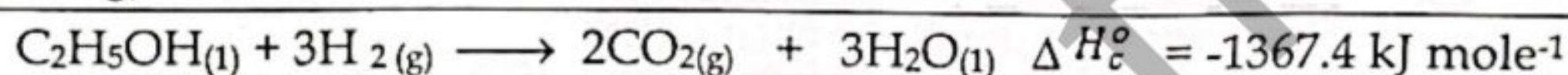
Multiplying eq (3) with '3'



Adding eq (4) & (5)



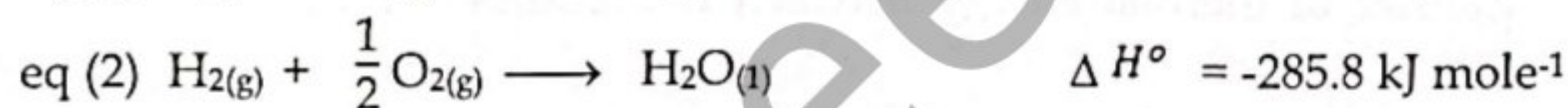
(subtracting)



Q.7 Calculate from the data in table 11.1 and 11.2 the enthalpy changes of the following reactions at standard conditions.



Ans.



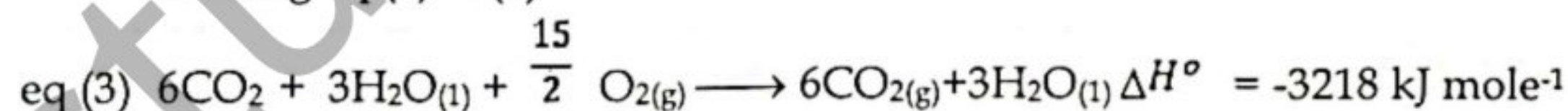
Multiplying eq (1) with '6'



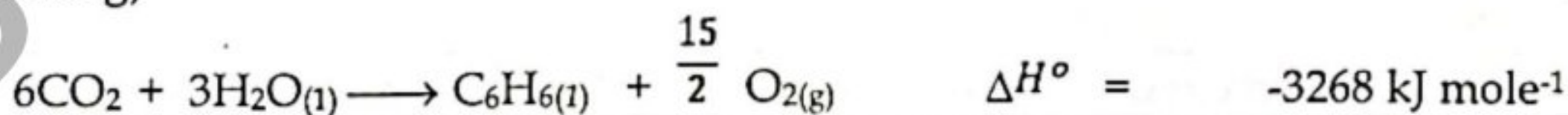
Multiply Eq. (3) by 3 and reverse the equation,



Adding eq (4) & (5)

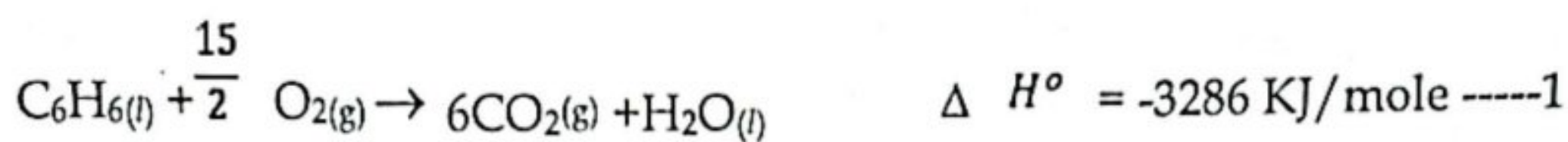


(subtracting)



Q.8 The heat of combustion of liquid benzene, C_6H_6 to form H_2O and CO_2 at 1 atm and 25°C is $-3268 \text{ KJ mole}^{-1}$ of benzene. What is the heat of formation of liquid benzene under these conditions?

Ans. Heat of combustion of liquid benzene $\text{C}_6\text{H}_6(\text{l})$



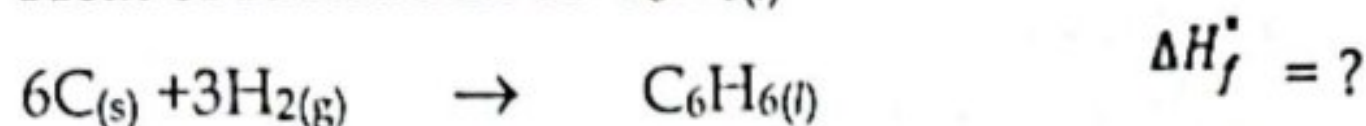
Heat of formation of gaseous $\text{CO}_2(g)$



Heat of formation of liquid $\text{H}_2\text{O}(l)$



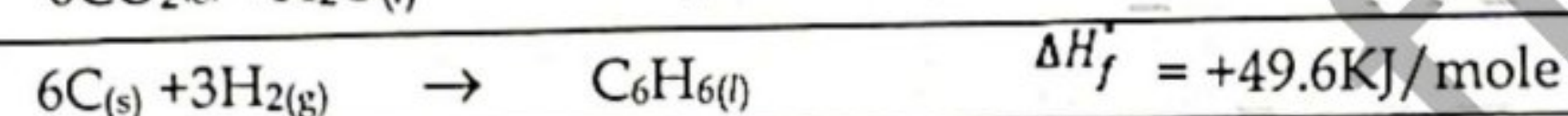
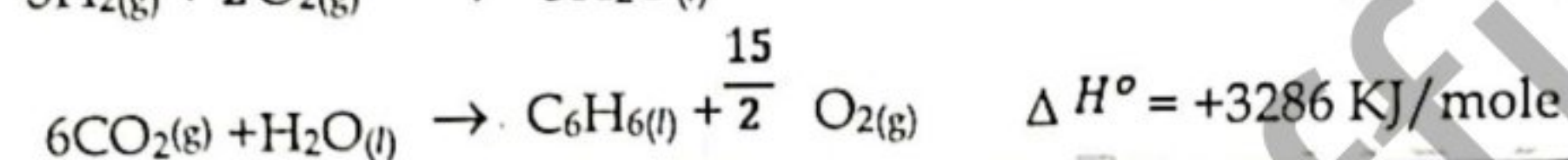
Heat of formation of $\text{C}_6\text{H}_6(l)$



Multiply eq.2 by 6

Multiply eq.3 by 3 and reverse eq.1

Then add all the resulting equation, we get



Q.10 Camphor ($\text{C}_{10}\text{H}_{16}\text{O}$) has a heat of combustion of 5903.6 KJ/mole. A sample of camphor having mass of 0.1204g is burned in a bomb calorimeter. The temperature increases by 2.28°C . Calculate heat capacity of the calorimeter.

Ans. Mass of camphor $m = 0.1204\text{g}$

Temperature $\Delta T = 2.28^\circ\text{C}$ OR 2.28K

Enthalpy of combustion = $\Delta H_c^\circ = 5903.6 \text{ KJ/mole}$

Molar mass of camphor ($\text{C}_{10}\text{H}_{16}\text{O}$) = $120 + 16 + 16 = 152 \text{ g/mole}$

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

1 mole of camphor produces heat = 5903.6 KJ

$7.92 \times 10^{-4} \text{ moles}$ of camphor produce heat = $5903.6 \times 7.92 \times 10^{-4}$
 $= 4.675 \text{ KJ}$

In a bomb calorimeter, heat evolved = $\Delta T \times \text{Heat capacity of calorimeter}$

$4.675 = 2.28 \times \text{Heat capacity of calorimeter}$

Heat capacity of calorimeter = $\frac{4.675}{2.28} = 2.05 \text{ KJK}^{-1}$

Q.11 In a coffee-cup calorimeter 100cm^3 of 1.0M HCl and 100cm^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 $4.18 \text{ J/g}^\circ\text{C}$.

Ans. Volume of NaOH = 100cm^3

Volume of HCl = 100cm^3

Total volume of reaction mixture = $100\text{cm}^3 + 100\text{cm}^3 = 200\text{g}$

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

Total mass of reaction mixture (m) = $200\text{cm}^3 \times 1\text{g cm}^{-3} = 200\text{g}$

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Rise in temperature $\Delta T = 6.9^\circ\text{C}$

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

Now

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

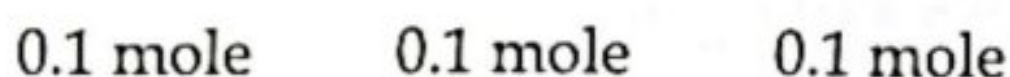
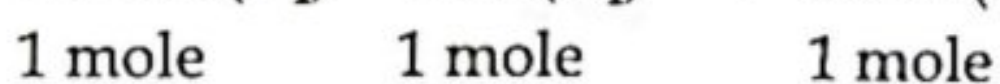
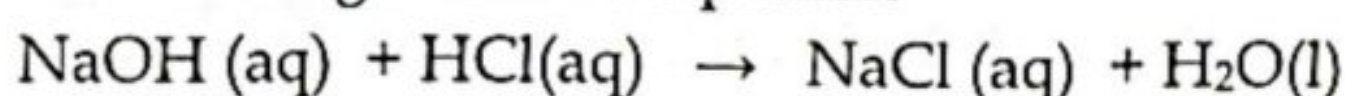
$$q = 200\text{g} \times 4.2 \text{ J g}^{-1}\text{C}^{-1} \times 6.9^\circ\text{C}$$

$$q = 5.796 \times 10^3 \text{ J}$$

$$\text{No. Of moles of NaOH} = \frac{M \times \text{Vol of solution (cm}^3\text{)}}{1000}$$
$$= \frac{1 \times 100}{1000} = 0.10 \text{ moles}$$

$$\text{Similarly, No of moles of HCl} = \frac{1 \times 100}{1000} = 0.10 \text{ moles}$$

Considering chemical equation



Thus formation of 0.1 moles of water release heat $= 5.796 \times 10^3 \text{ J}$

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

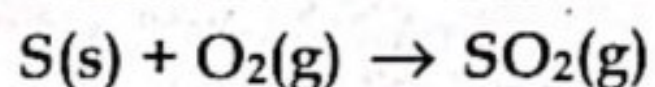
$$= 5.796 \times 10^4 \text{ J mole}^{-1}$$

$$= 57.96 \text{ kJ mole}^{-1}$$

Since heat is evolved at constant pressure,

$$q_p = \Delta H_p^\circ = -57.96 \text{ kJ mole}^{-1}$$

Q.12 Calculate ΔH° for the reaction

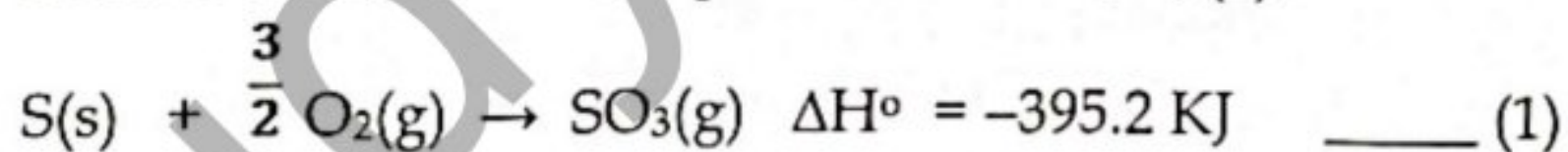


from the following data

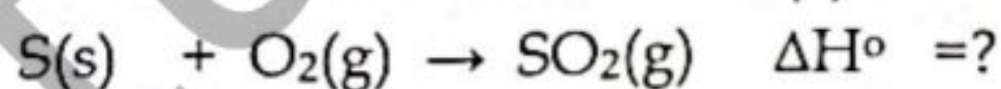


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Ans. Heat of combustion of liquid benzene C_6H_6 (l)



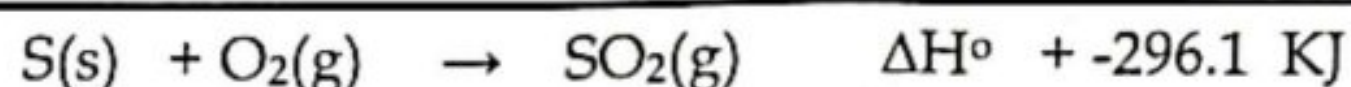
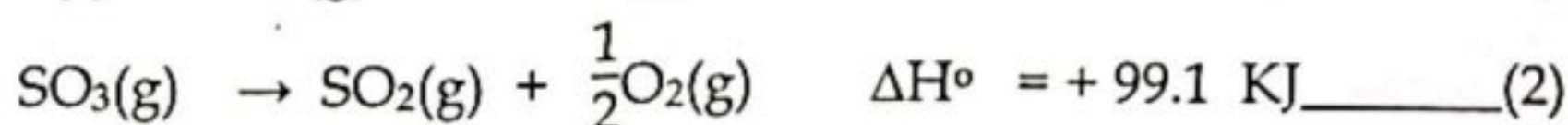
Heat of formation of C_6H_6 (l)



Divide Eq. (2) by 2,

Take Eq. As such

Then add all the resulting equation. We get



Q.13 An aluminum 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 $24.35 \text{ J mole}^{-1} \text{ K}^{-1}$

Ans. Mass of aluminum frying pan = 745 g
 Atomic mass of aluminum frying pan = 27 g mole⁻¹

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

 Initial temperature = $T_1 = 25^\circ\text{C}$
 Final temperature = $T_2 = 205^\circ\text{C}$
 Temperature rise = $\Delta T = 205^\circ\text{C} - 25^\circ\text{C}$

$$= 180^\circ\text{C}$$

 At constant pressure heat capacity of Al = $C_p = 24.35 \text{ J mole}^{-1} \text{ K}^{-1}$
 At constant pressure, the heat released can be determined as

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

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

$$= 120953 \text{ J}$$

$$= 120.953 \text{ kJ}$$

Q.14 Write the balanced equation for the formation reaction of each of the following substances

- | | |
|--|--------------------------------------|
| (i) $\text{C}_4\text{H}_9\text{OH}$ (Butanol) | (ii) Rust, Fe_3O_4 |
| (iii) Acetic acid $\text{CH}_3\text{CO}_2\text{H}$ | (iv) Urea $(\text{NH}_2)_2\text{CO}$ |

Ans. (i) $4\text{C}_{(s)} + 5\text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{C}_4\text{H}_9\text{OH}_{(l)}$
 (ii) $3\text{Fe}_{(s)} + 2\text{O}_{2(g)} \rightarrow \text{Fe}_3\text{O}_{4(s)}$
 (iii) Acetic acid $\text{CH}_3\text{CO}_2\text{H}$
 $2\text{C}_{(s)} + 2\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow \text{CH}_3\text{COOH}_{(l)}$
 (iv) Urea $(\text{NH}_2)_2\text{CO}$
 $\text{C}_{(s)} + \text{N}_{2(g)} + 2\text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow (\text{NH}_2)_2\text{CO}_{(s)}$

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Q.15 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. (a) $\text{C}_6\text{H}_{12}\text{O}_{6(s)} + 6\text{O}_{2(g)} \rightarrow 6\text{CO}_{2(g)} + 6\text{H}_2\text{O}_{(l)} \quad \Delta H_c^\circ = -2817.28 \text{ kJ mole}^{-1}$
 (b) Give mass of glucose = 1.0 g
 Molar mass of camphor ($\text{C}_6\text{H}_{12}\text{O}_6$) = $12 \times 6 + 1 \times 12 + 16 \times 6$

$$= 180 \text{ g mole}^{-1}$$

$$\text{Number of moles of glucose} = \frac{1}{180} = 5.56 \times 10^{-3} \text{ moles}$$

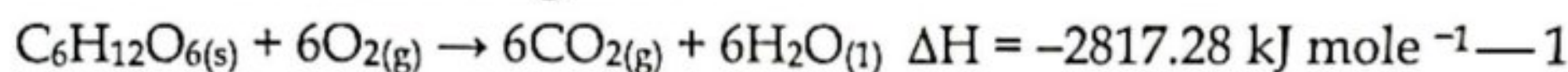
 Given heat produced by glucose = 15.65 kJ
 $5.555 \times 10^{-3} \text{ moles of glucose produce heat} = 15.65 \text{ kJ}$

$$1 \text{ mole of glucose produce heat} = \frac{15.65}{5.555 \times 10^{-3}}$$

$$= -2817.28 \text{ kJ}$$

(c) Heats of combustions of C and H₂ are -393.5 KJmole⁻¹ and -285.8 KJmole⁻¹ respectively. Determine the heat of formation of glucose.

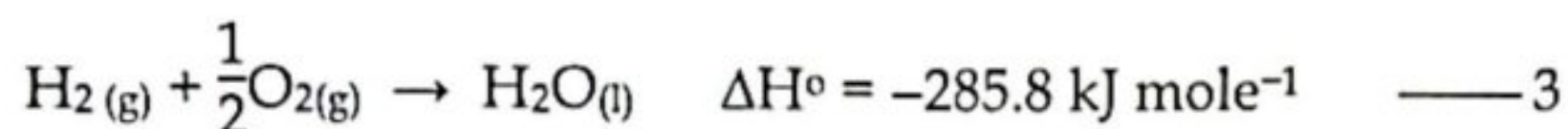
Ans. Heat of combustion of glucose



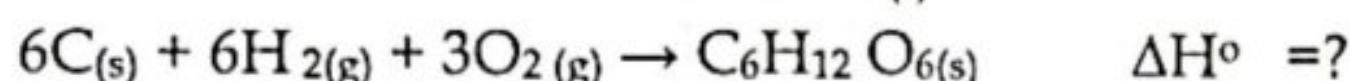
Heat of combustion of C



Heat of combustion of H₂



Heat of combustion of C₆H₁₂O₆(s)

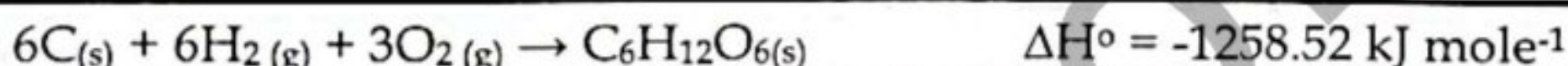


Multiply Eq. (2) by 6,

Multiply Eq. (3) by 6,

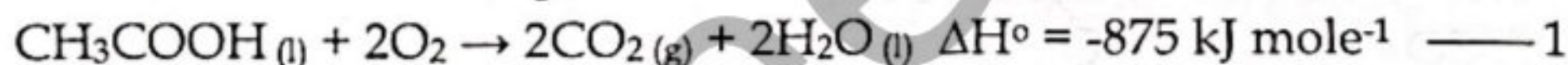
Reverse Eq. (1)

Then add all the resulting equations. We get



Q.16 The standard combustion enthalpies of carbon, hydrogen and acetic acid are -393.5 KJ mole⁻¹, -285.8 KJmole⁻¹ and -875 KJmole⁻¹ respectively. Deduce the value of standard enthalpy of formation of acetic acid, CH₃COOH.

Ans. Heat of combustion of glucose



Heat of combustion of C.



Heat of combustion of H₂.



Heat of combustion of liquid C₂H₃OH (l)

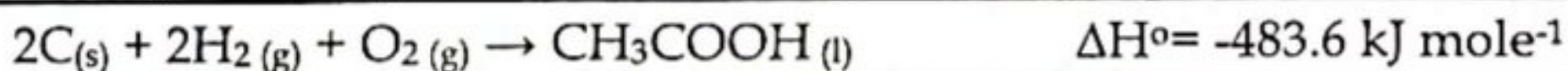


Multiply Eq. (2) by 2

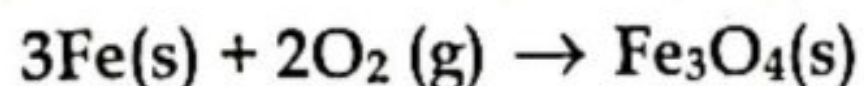
Multiply Eq. (3) by 2,

Multiply Eq. (1)

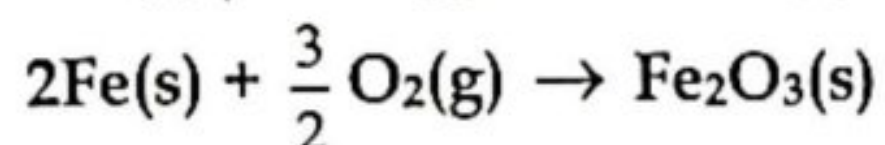
Then add all the resulting equations, we get.



Q.17 Is the conversion of magnetite, Fe₃O₄ to hematite, Fe₂O₃ by oxygen is endothermic or exothermic? Justify your answer.

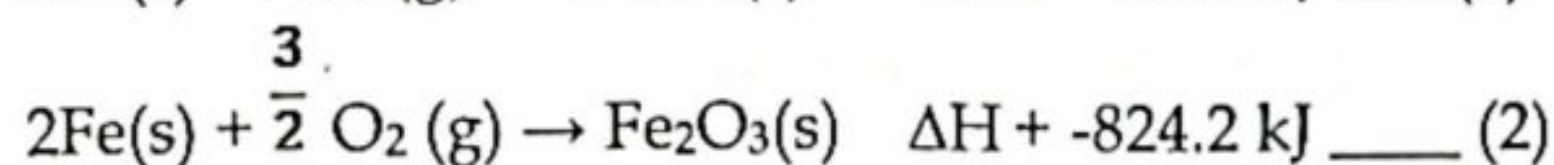
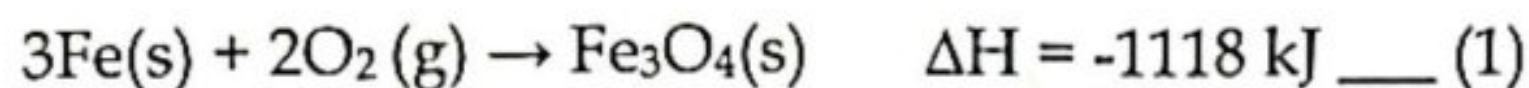


$$\Delta H^\circ = -1118 \text{ KJ}$$

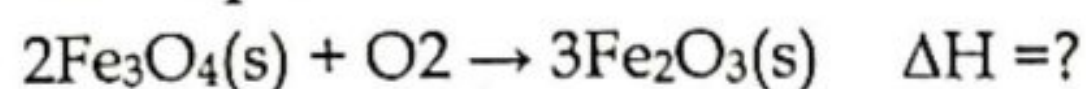


$$\Delta H^\circ = -824.2 \text{ KJ}$$

Ans.



The required conversion is



The standard enthalpy of formation of an element in its pure form is taken as zero.

Thus, according to the relation

$$\begin{aligned} \Delta H_{\text{reaction}}^\circ &= \sum \text{coeff}_p \Delta H_f^\circ (\text{products}) - \sum \text{coeff}_r \Delta H_f^\circ (\text{reactants}) \\ &= [3 \times (-824.2)] - [2 \times (-1118) + (0)] \\ &= (-2472.6) - (-2236) = -2472.6 + 2236 = -236.6 \text{ kJ} \end{aligned}$$

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ADDITIONAL MCQs

IMPORTANT MCQ's

- If an endothermic reaction is allowed to take place very rapidly in the air. The temperature of the surrounding air.
 - remains constant
 - increases
 - decreases
 - remains unchanged
- In endothermic reactions, the heat contents of the
 - products is more than that of reactants.
 - reactants is more than that of products.
 - both (a) and (b)
 - products is equal to reactants
- A chemical change always involve
 - absorption of heat
 - emission of heat
 - either absorption or emission of heat
 - the liberation of heat and light energy
- Spontaneous processes are mostly
 - reversible
 - irreversible
 - endothermic
 - none of these
- Which is not a state function
 - enthalpy
 - entropy
 - pressure
 - heat
- Which of the following statements is contrary to the first law of thermodynamics?
 - Energy can neither be created nor destroyed.
 - One form of energy can be transferred into an equivalent amount of other kind of energy.
 - In an adiabatic process, the work done is independent of its path.
 - Continuous production of mechanical work without supplying equivalent amount of heat is possible.
- For a given process, the heat changes at constant pressure (q_p) and at constant volume (q_v) are related to
 - $q_p = q_v$
 - $q_p < q_v$
 - $q_p > q_v$
 - $q_p = q_v/2$
- First law of thermodynamics is represented as
 - $\Delta E = q + RT$
 - $\Delta E = \Delta H$
 - $\Delta E = q + \Delta p$
 - $\Delta E = q + w$
- The net heat change in a chemical reaction is same whether it is brought about in one or several steps. It is known as

- (a) Henry's law (b) Joule's principle
(c) Hess's law (d) Law of conservation of energy
10. Hess's law of heat summation includes
(a) initial reactants only (b) initial reactants and final products
(c) final products only (d) intermediates only
11. Enthalpy change of which compound cannot be measured directly
(a) CO_2 (b) NO_2 (c) SO_2 (d) CO
12. Born Haber cycle is used to determine the
(a) lattice energy (b) enthalpy of sublimation
(c) enthalpy of vaporization (d) enthalpy of neutralization
13. The smallest Unit of heat energy is
(a) calorie (b) joule (c) erg (d) kilowatt hour
14. Most of the reaction with more stable product are
(a) exothermic (b) endothermic
(c) reaction (d) reaction ionic reaction
15. For the reaction $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ the change in enthalpy is called.
(a) heat of reaction (b) heat of formation
(c) heat of neutralization (d) heat of combustion
16. The change in heat energy of a chemical reaction at constant temperature and pressure is called.
(a) enthalpy change (b) heat of sublimation
(c) bond energy (d) internal energy change
17. One Calorie is equivalent to
(a) 0.418 J (b) 41.84 J (c) 4.184 J (d) 418.4 J
18. 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 strong bases are ionic substances
(c) Acids always give H^+ ions and bases always furnish OH^- ions.
(d) The net chemical change involve the combination of H^+ and OH^- ions to form water
19. Bomb calorimeter cannot measure the enthalpy of formation of:
(a) CO_2 (b) SO_2 (c) MgO (d) All of the above
20. In an endothermic reaction ΔH is
(a) positive (b) negative (c) zero (d) all
21. The enthalpy of an element in standard states is
(a) 1 kJ mol^{-1} (b) zero (c) 298 kJ mol^{-1} (d) always positive
22. The Standard heat of formation is measured at 1 atmosphere and
(a) 0°C (b) 100°C (c) 273°C (d) 25°C
23. The heat contents of the system is known as
(a) entropy (b) enthalpy (c) work (d) free energy
24. The heat of neutralization of given reaction is -57 kJ
 $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
- 19 By using this information, what is the value for heat liberated in the following neutralization reaction.
 $\text{Ba(OH)}_2 + 2\text{HCl} \rightarrow \text{BaCl}_2 + 2\text{H}_2\text{O}$
(a) -57 kJ (b) -76 kJ (c) -114 kJ (d) -228 kJ
25. In a bomb calorimeter, the reactions are carried out at

- (a) constant volume (b) constant pressure
(c) constant temperature (d) a, b and c conditions
26. The enthalpy of combustion is
(a) positive (b) negative
(c) either positive or negative (d) no correlation
27. ΔH for the neutralization reaction NaOH and CH_3COOH is
(a) -57kJ (b) less than -57 kJ (c) greater than -57 kJ (d) zero
28. Which one of the following enthalpies is always an exothermic process
(a) ΔH_c (b) ΔH_s (c) ΔH_{at} (d) ΔH_f

Answer

1.		2.		3.		4.		5.		6.		7.		8.		9.		10.	
11.		12.		13.		14.		15.		16.		17.		18.		19.		20.	
21.		22.		23.		24.		25.		26.		27.		28.					

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