CHAPTER # 11

THERMOCHEMISTRY

Q1. Define thermodynamic and thermochemistry.

Ans: Thermodynamic:

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

Thermochemistry:

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

Note: Every process in this universe whether it occurs in living cells or in test tubes. or in the atmosphere or in water etc. is accompanied by an energy change. Some processes release energy, other require energy. However, in all these cases total amount of energy in the universe remains constant.

Q2. Explain the role of energy in chemical reactions.

Ans: Role of Energy in Chemical Reactions:

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

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

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

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

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

Thus in chemical reactions energy is exchanged with the surroundings.

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

Ans: Definitions of Terms Used in Thermodynamics

1. System:

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

Surroundings:

The part of the universe except system is called surroundings

Boundary:

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

State Function:

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

Examples:

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

3. Heat:

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

4. Heat Capacity:

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

5. Internal Energy:

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

6. Work:

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

7. Enthalpy of a Substance (H):

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

$$H = E + PV$$

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

Ans: System:

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

Surroundings:

The remaining part of the universe is called surroundings.

Boundary:

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

Examples:

i. In the study of reaction between limestone and hydrochloric acid solution in a test tube, limestone and hydrochloric acid solution form a system. The test tube and everything around the test tube is surroundings.

ii. In the study of thermal decomposition of a compound, the sample of the compound would be the system. Whereas the beaker, the source of heat and everything else would be surroundings.

5. Explain thermochemical reactions and also give its types.

Ans: Thermochemical Reactions:

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

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

There are two types of thermochemical reactions -

(1) Exothermic Reactions:

(2) Endothermic Reactions:

Explanation:

When a chemical change takes place, energy is exchanged between system and its surroundings Energy has many forms such as heat, light, work etc. A chemical reaction which proceeds with the evolution or absorption of heat is called a thermochemical reaction.

Classify the following processes as exothermic or endothermic.

(a) Freezing of water

(b) Combustion of methane

(c) Sublimation of dry ice

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

(e) decomposition of limestone.

Solution:

Note: "Lighter →Denser

Energy is given out. Exothermic reaction

ΔH - Negative

Denser → Lighter

Energy is taken in Endothermic reaction

ΔH = Positive

Exothermic process:

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

Endothermic process:

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

(a) Freezing of water:

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

(b) Combustion of methane:

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

(C) Sublimation of dry ice:

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

(d) $H_2O(g) \rightarrow H_2O(l)$
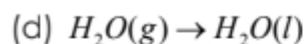
Gas molecules have high energy when they convert into liquid energy is released because the liquid molecules have low energy as compare to gas molecules. Thus, it is an exothermic process.

(e) Decomposition of limestone.

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

Q6. Briefly describe the heat of reaction with the help of example.
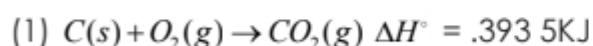
Ans: Heat of Reaction:

The amount of heat evolved or absorbed in a chemical reaction, when molar quantities of reactants and product are same as shown in a chemical reaction is called heat of reaction.
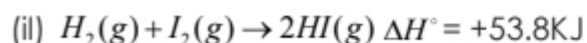
Enthalpy change:

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

Examples:

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$ ΔH° = .393 5KJ

This equation shows that 1 mole of solid carbon (12g) reacts with 1 mole of oxygen gas (32g) to give 1 mole of CO_2 gas (44g) at 25°C and 1 atmospheric pressure and 393.5 KJ heat is evolved

(il) $H_2(g) + I_2(g) \rightarrow 2HI(g)$ ΔH° = +53.8KJ

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

Note: If a reaction is exothermic when going in one direction, it will be endothermic in the reverse direction. When a reaction is reversed, the magnitude of $\Delta H°$ remains the same but its sign changes.

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

$CO_2(g) \rightarrow C(s) + O_2(g)$ $\Delta H°$ = +393 5KJ

$2HI(g) \rightarrow H_2(g) + I_2(g)$ $\Delta H°$ = -53.8KJ
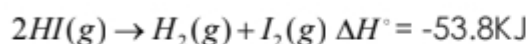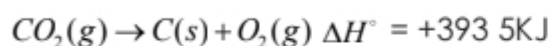
Q7. Briefly explain thermodynamics with the help of examples.

Ans: Thermodynamics:

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

Motion of automobile:

When gasoline burns in an automobile engine energy is released. A part of this energy is converted into heat which heats up the engine. The rest of the energy moves piston which turns a crankshaft and the crankshaft does work to move the automobile. Thus chemical energy released when gasoline burns is converted into heat and work.

Industrial products:

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

Fertilizers:

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

Batteries:

Batteries produce electric energy from chemical reaction.

Conclusion:

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

Q8. Define the following terms.

i. State of the system

ii. Initial state final state

iii. Open system

iv. Close system and Isolated system.

Ans: i. State of the system

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

The condition of a system when various properties like temperature, pressure. volume, number of moles etc of system have definite values is called state of the system.

Initial state:

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

Final state:

The final state of a system is its state after the change has occurred in a chemical reaction, the description of the products defines the final state. There are three types of systems, open system, closed system and isolated system.

Open system:

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

Close system:

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

Isolated system:

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

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

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

OR

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

Change in any property of a system is determined by the difference in the value of that property in the final state and the value of the same property in the initial state.

Explanation:

Variables such as pressure, temperature, volume and energy depend only on the state of the system. A change in any of these variables depends only on the difference between initial and final conditions, but does not depend on the path followed. Such variables are called state functions or state variables.

For example:

Let V_1 is the initial volume of Ha gas confined in a cylinder at temperature T. and pressure P_1 When temperature is increased from T_1. to T_2 its volume becomes V_2 and pressure changes to P_2. The changes in volume (ΔV) is given by the following equation.

$\Delta V = V_2 - V_1$

Similarly change in temperature ΔT and change pressure ΔP are given by the equations.

$\Delta T = T_2 - T_1$

$\Delta P = P_2 - P_1$

Q10. Differentiate between Spontaneous and non-spontaneous reactions.

Ans:

Spontaneous reactions	Non-spontaneous reactions
i. The reactions which processed on their own and do not need any external energy to proceed are called spontaneous reactions	i. The reactions which required external energy to proceed are called non spontaneous reactions
ii. For example emission of rays from radioactive elements, burning of methane and coal	ii. For example reaction of nitrogen and oxygen to make nitric oxide, thermal decomposition of P205

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

Ans: Internal Energy:

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

It is denoted by E

Absolute value of internal energy of a system cannot be measured. However change in internal energy (ΔE) of a system can be measured. The internal energy is a state function and depends only on the initial and final states of the system

Mathematically:

$$\Delta E = E_2 - E_1$$

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

Explanation:

i. in every chemical process energy is transformed from one form to another. The amount of energy transformed depends upon the energy contents of reactants and products.

ii. Every system has definite amount of energy present in it. This energy is due to kinetic as well as potential energies of the particles present in the system

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

iv. The potential energy is due to all types of attractive forces present between the particles. These attractive forces include all types of bonds and Van der Waal's forces.

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

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

Chemical reactors occur at constant pressure, we can equate the heat change in these reactors to the change in enthalpy.

This means we can define heat of a reaction as the change in enthalpy (ΔH). as the difference between the enthalpies of the products (final estate) and the enthalpies of the reactants (initial state).

Mathematically:

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

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

Exothermic:

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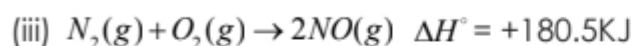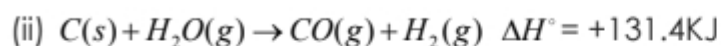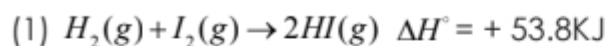
Examples of exothermic reactions:

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H° = -393.5KJ$

(ii) $2H_2(g) + O_2(g) \rightarrow H_2O(l)$ $\Delta H° = -571\ 6KJ$

(III). $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ $\Delta H° = -110.5KJ$
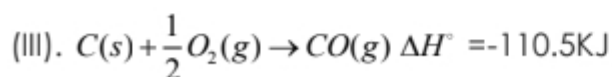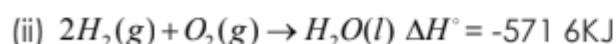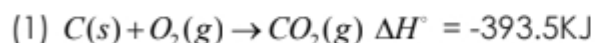
Endothermic:

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

ΔH is positive.

Examples of endothermic reactions:

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

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

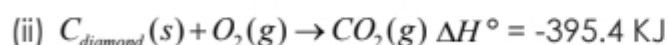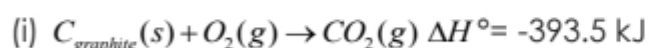(iii) $N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\Delta H^\circ = +180.5KJ$

Q13. Why we cannot measure the value of AH for the conversion of graphite to diamond in a calorimeter?
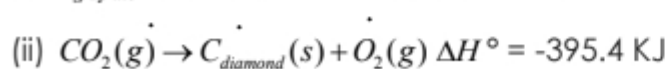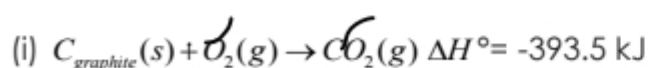
Ans: Standard States and Standard Enthalpy Changes:

We can measure enthalpy change for a chemical reaction at constant pressure using a calorimeter. However, it is not only very difficult but also impossible in many cases. This is because some reactions are too slow.
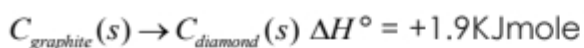
The value of ΔH for the conversion of graphite to diamond cannot be measured in a calorimeter because reaction is very slow under normal conditions.

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

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

(i) $C_{graphite}(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^\circ = -393.5$ kJ

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

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

(i) $C_{graphite}(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^\circ = -393.5$ kJ

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

$$C_{graphite}(s) \rightarrow C_{diamond}(s) \; \Delta H° = +1.9KJmole$$

Conclusion:

Thus the enthalpy of diamond is 1.9 kJ/mole greater than graphite at 25°C and one atm pressure.
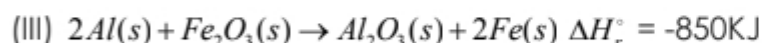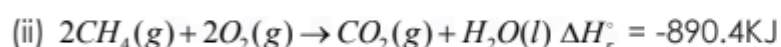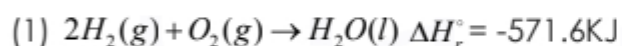
Therefore, thermodynamic properties of two substances can be properly compared by using a common reference state (standard state).

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

Ans: Standard Enthalpy of Reaction $\Delta H_r°$

The enthalpy change in a chemical reaction when reactants and products are in their standard states and their molar quantities are same as shown by the balanced chemical equator is called standard enthalpy of reaction.

Examples:

(1) $2H_2(g) + O_2(g) \rightarrow H_2O(l) \; \Delta H_r° = -571.6KJ$

(ii) $2CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + H_2O(l) \; \Delta H_r° = -890.4KJ$

(III) $2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(s) \; \Delta H_r° = -850KJ$

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

Ans: Standard Enthalpy of Formation $\Delta H_f°$

It is defined as the enthalpy change that accompanies the formation of one mole of a compound from its elements with all substances in their standard states. Standard enthalpies of formation of some compounds are shown in table.

Table: Standard enthalpies of formation of some compounds in KJ $mole^{-1}$

$H_2O(g)$	-245.1	$Fe_2O_3(s)$	-824.2	$Na^+(aq)$	-240.1

$H_2O(l)$	-285.8	$Fe_2O_3(s)$	-824.2	$Na^+(aq)$	-240.1
$H_2O_2(l)$	-187.8	$SiO_3(s)$	-910.9	$K^+(aq)$	-252.4
$NH_3(g)$	-46.1	$CaCO_3(s)$	-1207	$Mg_2^+(aq)$	-466.9
$NH_3(g)$	-80.3	$BaCO_3(s)$	-1219	$Ca_2^+(aq)$	-542.8
$NH_3(aq)$	-80.3	NaOH(s)	-425.6	$Al_3^+(aq)$	-524.7
$N_2N_4(l)$	50.6	KOH(s)	-424.8	C(s, diamond)	1.9
HF(g)	-271.1	$HONO_2(l)$	-174.1	$CH_4(g)$	-74.8

HCl(g)	-92.3	$HONO_2(aq)$	-207.4	$C_2H_2(g)$	226.7
HCl(aq)	-167.2	$(HO)_2SO_2(l)$	-814.0	$C_2H_4(g)$	52.3
HBr(g)	-36.4	$(HO)_2SO_2(aq)$	-909.3	$C_2H_6(g)$	-84.7
HI(g)	26.5	$NH_4Cl(s)$	-314.4	$C_3H_8(g)$	-103.9
$H_2S(g)$	-20.6	NaCl(s)	-411.2	$C_4H_{10}(g)$	-126.2
CO(g)	-110.5	NaBr(s)	-361.1	$C_6H_6(l)$	49.0
$CO_2(g)$	-393.5	NaI(s)	-287.8	$C_6H_5CH_3(l)$	12.1
NO(g)	90.3	KCl(s)	-436.8	$C_8H_{18}(l)$	-249.9

$NO_2(g)$	33.2	KBr(s)	-393.8	$CH_3OH(l)$	-238.7
$N_2O_4(g)$	9.2	KI(s)	327.9	$C_2H_5OH(l)$	-277.7
$SO_2(g)$	-296.8	AgCl(s)	-127.1	$CH_3CHO(l)$	-192.3
$SO_3(g)$	-395.7	$CaCl_2(s)$	-795.8	$CH_3COCH_3(l)$	-248.1
MgO(s)	-601.7	$AlCl_3(s)$	-704.2	$CH_3COOH(l)$	-484.5
CaO(s)	-635.1				

Method to write thermochemical equation for enthalpy of formation:

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

ii. Show standard states of all the substances

iii. Finally balance the atoms

Example:

Write thermochemical equation for the formation of H_2O, SO_3 **and** H_2O_2 **Use data given**

in table

(i) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ ΔH_f° = -285.8 KJ mole

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

(iii) $H_2(g) + O_2(g) \rightarrow H_2O_2(l)$ ΔH_f° = -191.2 KJ mole
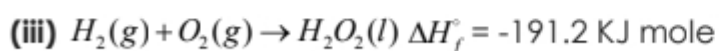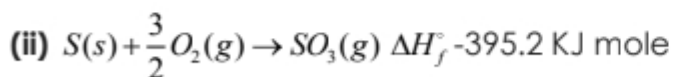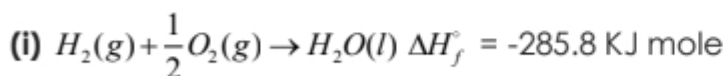
Standard enthalpies of formation of some substances are shown in table.

Q17. Define standard enthalpy of combustion and how can we write

thermochemical equation for standard enthalpy of combustion?

Ans: Standard Enthalpy of Combustion ΔH_c°

The enthalpy change when one mole of a substance is completely burnt in excess of oxygen under standard conditions is called standard enthalpy of combustion. Standard enthalpies of combustion of some substances are shown in table.

Table: <mark>Standard enthalpies of combustion in KJ</mark> $mole^{-1}$

$H_2(g)$	-285.8	$CH_4(g)$	-890.4	$C_6H_6(l)$	-3268
C(graphite)	-393.5	$C_2H_6(g)$	-1560	$C_2H_5OH(l)$	-1367
C(diamond)	-395.4	$C_8H_{18}(l)$	-5512	$CH_3CHO(l)$	-1167
S(rhombic)	-296.9	$C_2H_4(g)$	-1411	$CH_3COOH(l)$	-875
S(monoclinic)	-297.2	$C_2H_2(g)$	-1300	$C_6H_{12}O_6$ (s) (glucose)	-2802

Method to write Thermochemical equation for enthalpy of combustion:

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

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

iii. Show standard states of all the substances.

iv. Finally, balance the atoms

Example:

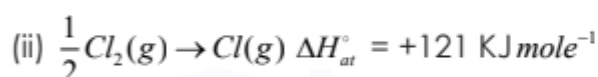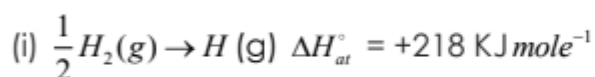**Write thermochemical equation for the combustion of, C, CH, and H. Use data given in above table.**

<mark>Solution:</mark>

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$ ΔH_c° = -393.5 KJ $mole^{-1}$

(ii) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ ΔH_c° -890.4 KJ $mole^{-1}$

(iii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ ΔH_c° = -285.8 KJ $mole^{-1}$
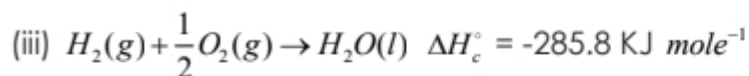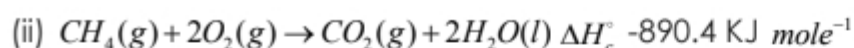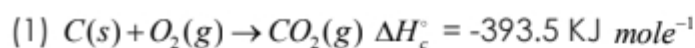
Q18. Define standard enthalpy of atomization and also give its examples.

Ans: Standard Enthalpy of Atomization (ΔH_{at}°)

The enthalpy change when one mole of gaseous atoms are formed from its element under standard conditions is called standard enthalpy of atomization, eg.

(i) $\frac{1}{2}H_2(g) \rightarrow H$ (g) ΔH_{at}° = +218 KJ $mole^{-1}$

(ii) $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ ΔH_{at}° = +121 KJ $mole^{-1}$

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

Ans: Standard Enthalpy of Neutralization ΔH_n°

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

NaOH (aq) + HCl (aq) — NaCl(aq) + H_2O (l) ΔH_n° = - 57.4KJ $mole^{-1}$
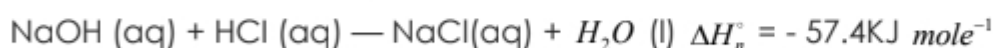
Strong acids and bases ionize completely in their aqueous solutions. Thus, when solutions of NaOH and HCl are mixed together, the only change which occurs formation of water. Na' and Cl ions remain in solution. Thus heat of neutralization is due to the formation of water from H and OH ions.
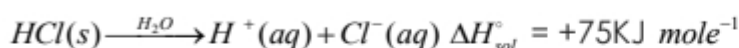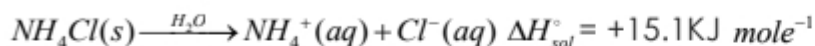
$Na^+(aq) + OH^-(aq) + H^+(aq) + Cl^-(aq) \rightarrow$ ΔH_n°= - 57.4KJ $mole^{-1}$
$Na^+(aq) + Cl^-(aq) + H_2O(l)$

or $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ ΔH_n° = . 57.4KJ $mole^{-1}$
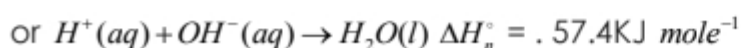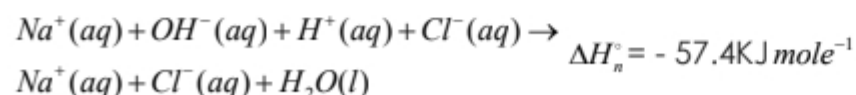
Q20. Define standard enthalpy of solution and also give its examples.

Ans: 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.

e.g.

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

$$HCl(s)\xrightarrow{H_2O} H^+(aq)+Cl^-(aq)\ \Delta H^\circ_{sol} = +75KJ\ mole^{-1}$$

SELF-CHECK EXERCISE 11.2

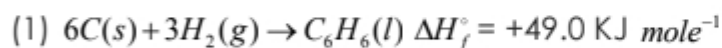**1. Write thermochemical equation form the given information.**

(I) Standard enthalpy of formation of benzene (I) is +49.0kj $mole^{-1}$

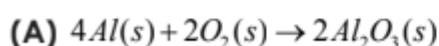**(II) Standard enthalpy of formation of ethanol (I) is -277.7 kj $mole^{-1}$**

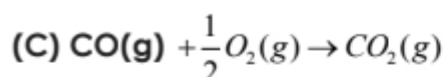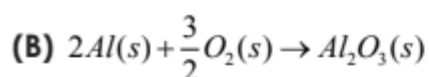**(III) Standard enthalpy of combustion of acetic acid(I) is -876 kj $mole^{-1}$**

(IV) When ethanol is burned in air -1367 KJ $mole^{-1}$ energy is released at 1 atm and 25°c.

Solution:

(1) $6C(s)+3H_2(g)\rightarrow C_6H_6(l)\ \Delta H^\circ_f = +49.0\ KJ\ mole^{-1}$

(ii) $2C(s)+3H_2(g)+\dfrac{1}{2}O_2(g)\rightarrow C_2H_5OH(l)\quad \Delta H^\circ_f = -277.7\ KJ\,mole^{-1}$

(iii) $CH_3COOH(l)+2O_2(g)\rightarrow CO_2(g)+2H_2O(l)\quad \Delta H^\circ_f = -876\ KJ\,mole^{-1}$

(iv) $C_2H_5OH(l)+3O_2(g)\rightarrow 2CO_2(g)+3H_2O(l)\quad \Delta H^\circ_f = -1367\ KJ\,mole^{-1}$
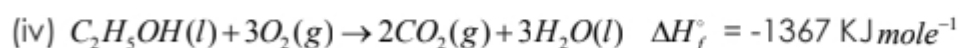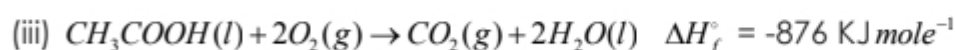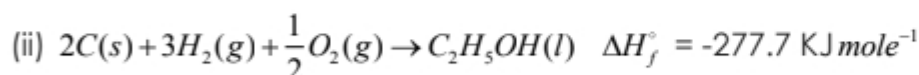
2. Which of the following equations describe a reaction for which ΔH° is equal to the enthalpy of formation of a compound, ΔH°_f

(A) $4Al(s)+2O_2(s)\rightarrow 2Al_2O_3(s)$

(B) $2Al(s) + \frac{3}{2}O_2(s) \rightarrow Al_2O_3(s)$

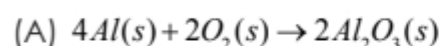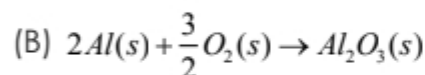**(C)** $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

Solution:

Condition:

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

Show standard states of all the substances.

Finally balance the atoms.

(A) $4Al(s) + 2O_2(s) \rightarrow 2Al_2O_3(s)$

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

(B) $2Al(s) + \frac{3}{2}O_2(s) \rightarrow Al_2O_3(s)$

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

C. $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$
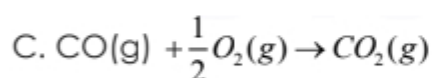
As the reactant (CO) is not an element thus this reaction does not represent the enthalpy of formation of CO_2

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

Ans: Band Dissociation Energy:

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

Bond Energy:

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

Nature of reaction:

When a chemical reaction occurs, old bonds break and new bonds form. Bond breaking always requires energy and bond formation always releases energy The difference between bond dissociation energy and bond energy determines whether the reaction absorbs or releases energy overall.

Mathematically:

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

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

For reaction between H_2 and O_2 to produce H_2O

$$H_2(g) + O_2(g) \rightarrow H_2O(l) \quad \Delta H^\circ = ?$$
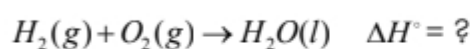
ΔH_f° = 2 x B D.E of H_2 (g) + B.D.E of O_2 (g) - 4 x B.E of O-H bonds

= 2 x (+436KJ) + 493.6KJ -4 (460KJ)

= 1365 KJ - 1840KJ

ΔH_f° =.474.4 KJ.

Conclusion:

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

Q22. Differentiate between Heat and temperature.

Ans:

heat	temperature
i. Heat involves the transfer of energy between TWO objects due to measure temperature difference. It is the degree of hotness or coldness of a system	i. Temperature is defined as the measure of average kinetic energy of the molecules of a substance

ii. We use calorimeter for its measurement	ii. We use thermometer for its measurement
iii. It is not a state function	iii. It is a state function
iv. Its unit is kJ.	iv. Its units are °C. K °F
v. It is mass dependent.	v. It is independent of mass.

Q23. Define heat capacity.

Ans: Heat Capacity:

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

Unit:

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

Explanation:

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

$q \alpha \Delta T$

$q = C \times \Delta T$

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

Mathematically:

Heat Capacity $= \dfrac{heat}{\Delta T}$

Q24. Define specific heat capacity.

Ans: Heat capacity:

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

It is expressed in Joules per gram per Kelvin,

Mathematically:

Specific heat Capacity = $\dfrac{heat}{gram \times \Delta T}$

Q25. Define molar heat capacity.

Ans: Molar heat capacity:

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

Unit:

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

Mathematically:

Molar heat capacity= $\dfrac{heat}{moles \times \Delta T}$

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

Ans: If the quantity of heat is absorbed by n moles of the substance and its temperature raises from T_1 to T_2. its molar heat capacity C is given by the expression.

$$C = \dfrac{q}{n(T_2 - T_1)}$$

Since heat absorbed by a substance at constant pressure is equal to ΔH

$q = \Delta H$

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

$$C_P = \dfrac{\Delta H}{n(\Delta T)}$$

or

$$C_p n(\Delta T) = \Delta H$$

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

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

Ans: When neat is absorbed by a substance at constant volume, then 4, - AE.

And

$$C_v = \frac{q_v}{n\Delta t}$$

$$C_v = \frac{\Delta E}{n\Delta t}$$

$$\Delta E = nC_v \Delta t$$

Where C_v is molar heat capacity of the substance at constant volume

Example:

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

Molar heat Capacity of Cu=0.387 x 63.54

= 24.59 J $K^{-1}mole^{-1}$

Knowing specific heat capacity of a substance, ils mass and temperature change of substance being heated or cooled, we can determine heat absorb or released

Note:

Re-arranging equation (i) we get,

q=C x m x ΔT

Similarly, if we know mole of the substance then.

q=CXNX ΔT

q= nxC X ΔT

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

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

2. Calculate the heat involved when an Al pan weighing 200g is cooled from 100°C to 25°C at constant pressure capacity of Al is 0.9 Jg. K^{-1}

Solution:

Mass of Al pan = 200 g

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

$T_1 = 100\ °C$

$T_2 = 25°C$

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

$\Delta T = 100 - 25 = 75°C$

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

$\Delta T = 75°C$

q = ?

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

$q = 200 \times 0.9 \times 75$

$q = 13500 \ J$

Q28. Explain calorimetry and also give its types.

Ans: Calorimetry:

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

A device that measures heat flow is called calorimeter.

Calorimeters measure the heat released from a system either at constant pressure

($q_o = \Delta H$) or constant volume ($q_o = \Delta E$)

Thus there are two types of calorimetry.

i.   **Constant Pressure Calorimetry:**

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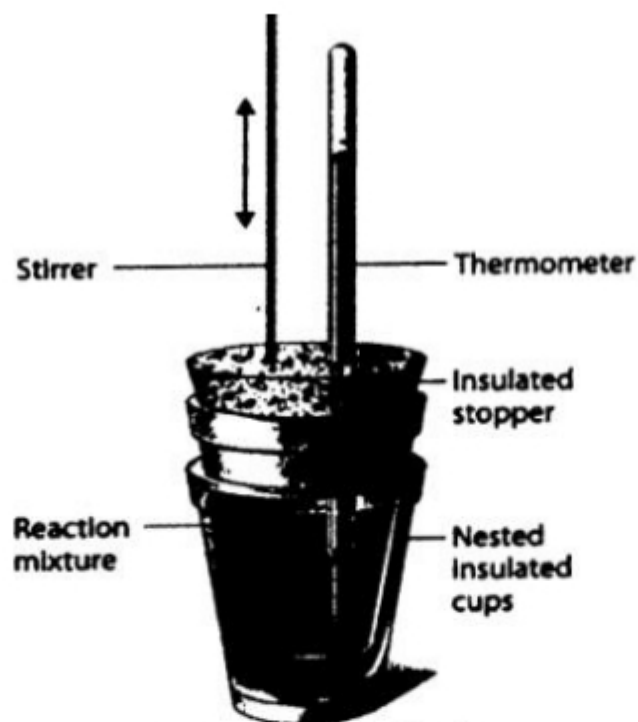
Coffee cup calorimeter

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

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

ii. **Constant volume Calorimetry:**

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

ii. A bomb calorimeter is used for this purpose. Chemical reaction in a bomb calorimeter takes palce 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
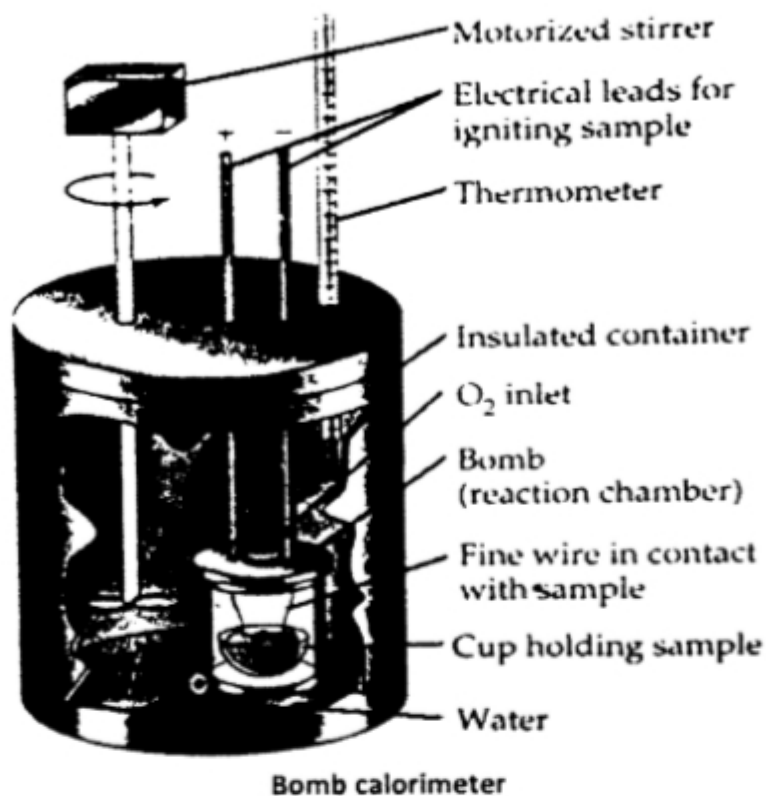
Estimation oh Heat of Reaction from Experimental Data:

This process can be understood by the following example.

In a reaction $50\,cm^3$ of 1.0M NaOH neutralizes $50\,cm^3$ of 1.0M HCl at 25°C. use this experimental data to calculate the heat of reaction (neutralization) using a calorimeter. Specific heat of water is 4.2 $Jg^{-1}K^{-1}$.

Activity

Since neutralization reaction is carried out at constant pressure. We will use coffee cup calorimeter (shown in figure 11.2) to calculate the heat of neutralization in the above example. For this purpose take two nested Styrofoam cups. The outer cup will provide extra thermal insulation. Place $50\,cm^3$ of 1.0M NaOH in the inner Styrofoam cup and 50 cm^3 of 1.0M HCl at 25°C in a beaker. Keep the two solutions for some time to let them

acquire room temperature. Suppose room temperature is 25°C. now add slowly the acid solution into the NaOH in the inner cup. The temperature of the solution will rise due to the evolution of heat during the neutralization process. Note down this temperature (suppose it is 31.9°C). Calculate the amount of heat evolved by the following equation.

$Q = m \times C \times \triangle T$

Volume of NaOH = $50\,cm^3$

Volume of HCl = $50\,cm^3$

Total volume of reaction mixture = $50\,cm^3 + 50\,cm^3 = 100\,cm^3$

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

Total mass of reaction mixture (m) = $100\,cm^3 + 1g\,cm^{-3} = 100g$

Raise in temperature = 6.9°C

Or = 6.9K

Now

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

$q = 100g \times 4.2\,Jg^{-1}K^{-1} \times 6.9K$
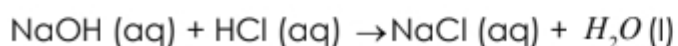
$q = 2.9 \times 10^3\,J$

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

$= \dfrac{1 \times 50}{1000} = 0.5$

Similarly, no of moles of HCl = $= \dfrac{1 \times 50}{1000} = 0.5$

Considering, chemical equation.

NaOH (aq) + HCl (aq) $\rightarrow$ NaCl (aq) + H_2O (l)

1 mole   1 mole   1 mole

0.05mole   0.05mole   0.05mole

Thus formation of 0.05 moles of water release heat = 2.9×10^3 J

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

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

$$= 58.0 \, kJ \; mole^{-1}$$

Since heat is evolved at constant pressure.

$$q_p = \Delta H_n^{\circ} = -58.0 KJmole^{-1}$$

SELF-CHECK EXERCISE 11.4

Experimental data shows that when 87.5 cm^3 of a 0.10M HCI solution is mixed with 25.0 cm^3 of 0.35M NaOH in a calorimeter, complete neutralization occurs. The temperature of the calorimeter changes from 25°C to 26.07°C. use this data to determine heat of neutralization for the reaction.

Solution:

Volume of NaOH = 25 cm^3

Volume of HCI = 87.5 cm^3

Total volume of reaction mixture = 25 cm^3 + 87.5 cm^3 = 112.5 cm^3

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

Total mass of reaction mixture (m) = 112.5 cm^3 + 1g cm^{-3} = 112.5g

Raise in temperature = ΔT 26.07 ...

$q = m \times \triangle T$

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

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

$= \dfrac{0.35 \times 25}{1000} = 0.00875$ moles

Similarly, no of moles of HCl = $= \dfrac{0.1 \times 87.5}{1000} = 0.00875$ moles

NaOH (aq) + HCl (aq) $\rightarrow$ NaCl (aq) + H_2O (l)
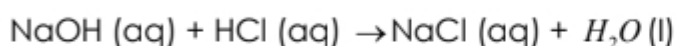
1 mole   1 mole   1 mole

0.00875 mole 0.00875 mole   0.00875 mole

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

Heat release during the formation of 1 mole of water = $\dfrac{505.575}{0.00875}$

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

$= 57.8$ kJ $mole^{-1}$

at constant pressure.

$\Delta H_n^\circ = -57.8 KJ mole^{-1}$

Q.29: How can we measure energy available from food

Ans: estimate of energy available from food:

Human beings require three major classes of food.

    (1)   Carbohydrates.

    (2)   Protein.

    (3)   Fats.

Most human energy derived from carbohydrates and fats. Carbohydrates are the source of quickest energy.

Glucose is the simpler carbohydrate, also known as blood sugar. It is soluble in blood and is transported by the blood to all the tissues.

In tissues it is oxidized to form CO_2 and H_2O and energy.

We can measure energy available from glucose by determining its heat of combustion. the bomb calorimeter shown in figure is used for measuring the energy available from food, which is just the enthalpy of combustion.

Activity

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

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

$\qquad$ = 6.52°C

Heat evolved = Δt x total heat capacity of calorimeter

$\qquad$ =6.52 x 4.321 KjK^{-1}

$\qquad$ = 28.1729 KJ

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

   = 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 = $\dfrac{28.1729g}{0.01mole^{-1}}$ = 2817.29 KJ $mole^{-1}$

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

SELF-CHECK EXERCISE 11.5

Fats and oils are a rich source of energy. They provide more energy as compare to carbohydrates and proteins. When 1.0g of a typical fat glycerol trioleate, $C_{57}H_{104}O_6$

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

Rise in temperature = ΔT = 8.77°C =877K

total heat capacity of calorimeter = 4.321 KjK^{-1}

Heat evolved = ?

Heat evolved = ΔT x total heat capacity of calorimeter

   =8.77 x 4.321 KjK^{-1}

   = 37.895 KJ

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

   = 0.001131 moles

Heat produce by 0.0011 moles of glyceryl trioleate = 37.895KJ

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

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

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

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

Ans. HESS'S law:

GH. Hess stated this law in 1840.

It states that the enthalpy change in chemical reaction is same whether the reaction takes place in a single step in several steps.

Explanation:

Enthalpy is a state function therefore, enthalpy change in a chemical reaction in going from some initial state to some final state is independent of the path followed by the reaction.

Thus in going from a particular set of reactant to a particular set of products, the change in enthalpy is the same whether the reaction takes lace in one step or in many steps. this principle is known as Hess's law.

Mathematically:

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

Example:

Suppose a reactant A changes into the product B in one step and enthalpy change in

ΔH

this step is $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$. Now suppose this change take place in three steps,

$\Delta H_1^{\circ} + \Delta H_2^{\circ} = 68KJ$

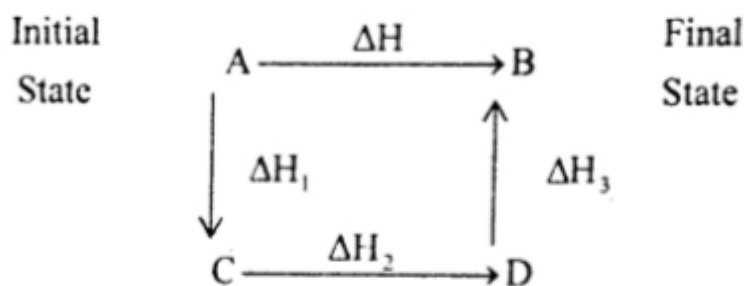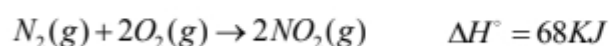involving a change from A to C, C to D as shown below:

Fig. 11.4

If ΔH_1, ΔH_2 and ΔH_3 are enthalpy changes in these steps, as shown in the figure. Then according to the Hess's Law.
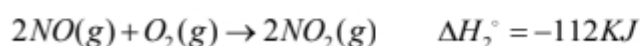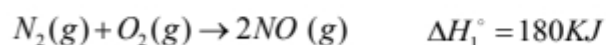
$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$
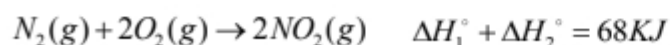
HESS'S law to construct simple energy cycle:

Example;

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

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

This reaction can be carried out in two steps.

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

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

NET reaction

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

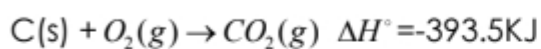Notice that the sum of two steps gives the net reaction and $\Delta H^\circ = \Delta H_1^\circ + \Delta H_2^\circ = 68KJ$

For energy cycle see fig.11.4
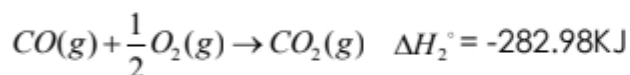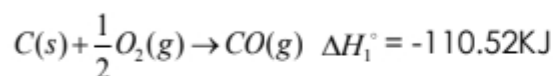
Example:

Combustion of C to CO_2 evolves 393.5 KJ of energy.

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

This reaction may takes place in two steps.

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

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

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

Energy cycles:

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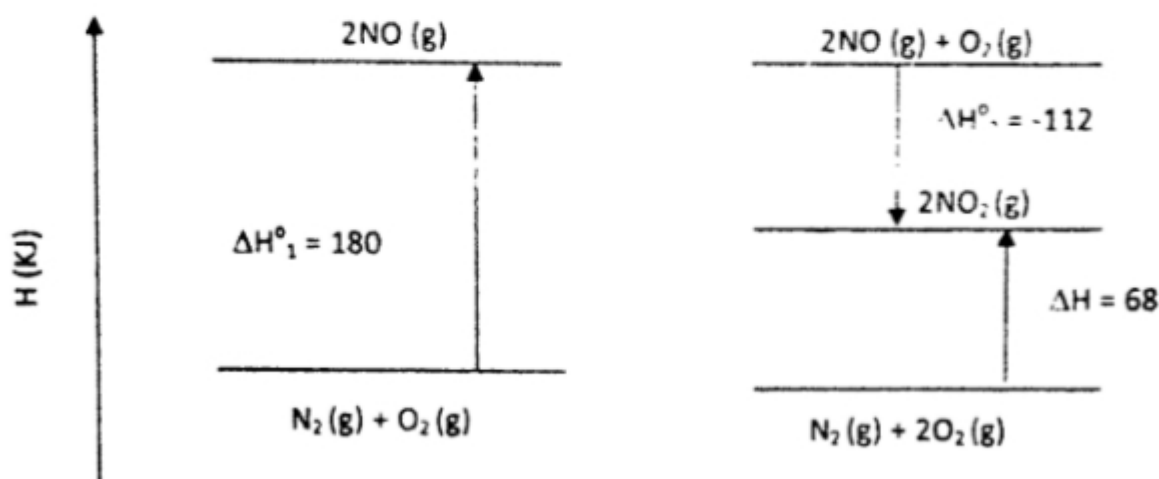

Fig: energy cycle for the reaction between N_2 (g) and O_2 (g) produce NO_2 (g)
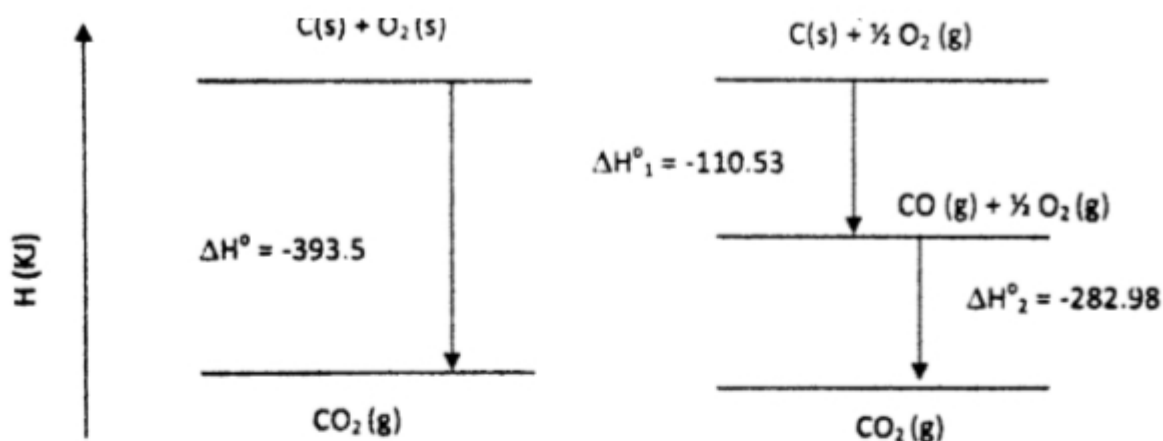
Fig: energy cycle for the reaction between C(g) and $O_2(g)$ produce $CO_2(g)$

Applications:

There are many compounds which cannot be prepared directly from their elements. Some of these compounds cannot be decomposed into their constituent elements. E.g. CCl_4.
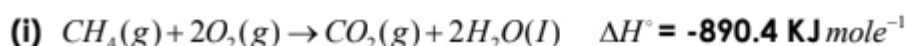
Some elements do not burn completely due to the formation of a protective covering on their surface. Such as Al, B etc.
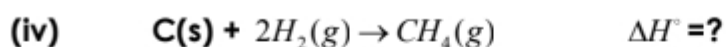
Thus enthalpies of formation of CCl_4, Al_2O_3, B_2O_3 etc cannot be determined directly by calorimeter.

Hess's law is particularly useful for determining enthalpies of formation of such compounds.
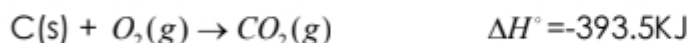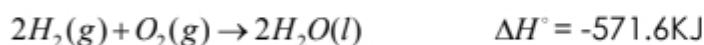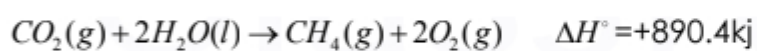
Example 11.5:

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

(i) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H° = $ **-890.4 KJ** $mole^{-1}$

(ii) $H_2(g) + \frac{1}{2}O_2(g)$ ... $\Delta H° =$ **-2855 KJ** $mole^{-1}$

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

(iv)   **C(s)** + $2H_2(g) \rightarrow CH_4(g)$ $\Delta H° = ?$

To obtain $\Delta H°$ for the required reaction we must somehow combine equations i, ii and to produce that reaction and add the corresponding $\Delta H°$ values. This can be done by focusing on reactants and products of the requires reaction. The reactants are C(s) and $2H_2(g)$ and the product is $CH_4(g)$. How can we obtain the correct equation? Reaction (iii) has C(s) as reactant which is needed in the required equation. thus equation (iii) will be used equation (ii) has $H_2(g)$ as reactant but the required equation needs $2H_2(g)$, thus equation (ii) will be used after multiplying by 2. Equation (i) has $CH_4(g)$ as reactant, but this is needed as product in the required equation. Thus reaction (i) must be reversed and the sign of $\Delta H°$ changed according. Adding the equations and deleting the species that occur on both sides we get.

$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$ $\Delta H° = +890.4kj$

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

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

$C(s) + 2H_2(g) \rightarrow CH_4$ $\Delta H° = -74.6KJ\, mole^{-1}$

This gives the required equation and its enthalpy.

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

Ans: enthalpies of reactions from enthalpies of formation:

It is often convenient to calculate the $\Delta H°$ values for a reaction from values for the standard enthalpies of formation $\Delta H_f°$ of the reactants and products. For a given reaction.

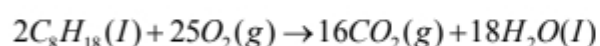$$\Delta H° = \sum \text{coeff} \Delta H_f° \dots \text{(products)} - \sum \text{coeff} \Delta H_f° \dots \text{(reactants)}$$

Where coeff = coefficient

Elements in their standard states are not included in the $\Delta H°$ reaction calculations i.e $\Delta H_f°$ for an element in its standard state is zero. When balanced equation for a reaction is multiplied by an integer the value of $\Delta H°$ for that reaction should be multiplied by the same integer.

Example 1:

Calculate ΔH of reaction for the following reaction, which take place when gasoline burns in internal combustion engines where the values of $\Delta H_f°$ are -269Kj, 0Kj, -393.5Kj for $C_8H_{18}(l)$, $O_2(g)$, $CO_2(g)$ and $H_2O(l)$ recpectively

$$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$$

Solution:

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

$= [16 \times \Delta H_f° \text{ for } CO_2(g) + 18 \times \Delta H_f° \ H_2O(l)] - [2 \times \Delta H_f° \text{ for } C_8H_{18}(l) + 25 \times \Delta H_f° \text{ for } O_2(g)]$

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

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

$=$ -11440.4KJ+ 538KJ

$=$ -10902.4KJ

$$= -1.09 \times 10^4 KJ$$

Example 2:

Calculate $\Delta H°_{reaction}$ for the following reaction. This reaction take place in the tissues of the living organisms where the values of $\Delta H_f°$ are -1258.18Kj, 0Kj, -393.5Kj and -285Kj for $C_6H_{12}O_6$ (s), O_2 (g), CO_2 (g) and $H_2O(I)$ respectively

$$2C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(I)$$
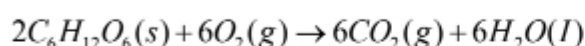
Solution:

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

$$\Delta H°_{reaction} = [6 \wedge H_f° \ CO_2 (g) + 6 \wedge H_f° \ H_2O(I)] - [\wedge H_f° \ C_6H_{12}O_6(s) + 6 \wedge H_f° \ O_2(g)]$$

$$= [6(-393.5KJ) + 6(-285.8KJ] - [-1258.18KJ + 6 \times 0]$$

$$= [-2361.0KJ - 1714.8KJ] - [-1258.18KJ]$$

$$= -4075.8KJ + 1258.18KJ$$

$$= -2817.62KJ$$

this means one mole (180g) of glucose provides 2818.82KJ energy. Therefore energy provided by one gam of glucose will be $\dfrac{2817.62 KJmole^{-1}}{180 gmole^{-1}} = 15.65KJ.$

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

Ans: Born Haber Cycle:

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

Lattice Energy:

the change in energy that takes place when separated gaseous ions are packed together to form one mole of an ionic solid is called lattice energy.

$$M^+(g) + X^-(g) \rightarrow MX(s)$$
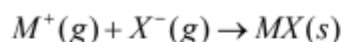
Lattice energy cannot be determined directly. However it can be determined indirectly by means of born Haber cycle. Consider the case of NaCl. Its standard enthalpy of formation (ΔH_f°) is -411 $KJmole^{-1}$

Cycle:

The formation reaction can be considered as taking place in several steps, one of which is the formation of lattice. This complete sequence of reaction is called a cycle (Fig. 11.6)

Step-I: sublimation of solid sodium. The energy of sublimation for Na(s) is 180 $KJmole^{-1}$

$$Na(s) \rightarrow Na(g) \qquad\qquad \Delta H_s^\circ = +108 KJmole^{-1}$$

Step-II: Ionization of Na(g) atom to form Na^+ (g) ion. This process corresponds to the first ionization energy for Na.

$$Na(s) \rightarrow Na^+(g) + 1e \qquad\qquad \Delta H_{IE}^\circ = +496 KJmole^{-1}$$
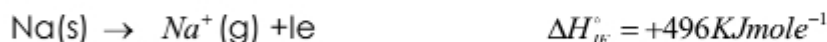
Step-III dissociation of Cl_2 molecules. We need to form one mole of Cl atoms by breaking the Cl-Cl bond in $\frac{1}{2}$ mole of Cl_2 molecules. The energy required to break this bond is 121 KJ/mole and is known as enthalpy of atomization for Cl_2.

$$\frac{1}{2} Cl_2(g) \rightarrow Cl(g) \qquad\qquad \Delta H_{at}^\circ = +121 KJmole^{-1}$$

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

Steps-4: formation of Cl(g) ion. Energy is released in this step equal to the electron affinity for Cl.

$$Cl\,(g) + 1e \rightarrow Cl^- \,(g) \qquad\qquad \Delta H_{EA}^{\circ} = -349 KJmole^{-1}$$

Step-5: formation of solid NaCl from the gaseous Na^+ and Cl^- ions. This corresponds to the lattice energy (ΔH_l) for NaCl(s) which is to be calculated.

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \qquad \Delta H_l^{\circ} = ?$$
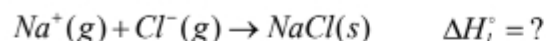
Calculation of lattice energy of NaCl:

Since the sum of these five steps gives the overall reaction desired, the sum of the individual energy changes give the overall give the overall energy change. Thus
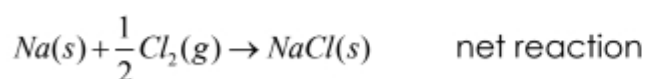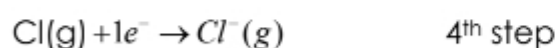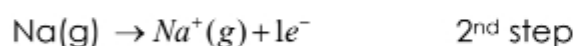
$$\Delta H_f^{\circ} = \Delta H_s^{\circ} + \Delta H_{I\,E}^{\circ} + \Delta H_{at}^{\circ} + \Delta H_{E\,A}^{\circ} + \Delta H_l^{\circ}$$

411KJ = +108KJ +496KJ +121KJ + (-349KJ) + ΔH_l°

ΔH_l° = -411KJ -(108KJ +4961KJ +121KJ – 349KJ)

ΔH_l° = -787 $KJmole^{-1}$

Thus lattice energy of NaCl is 787 KJ/mole.

Na(s) → Na(g)   1st step

$Na(g) \rightarrow Na^+(g) + 1e^-$ 2nd step

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ 3rd step

$Cl(g) + 1e^- \rightarrow Cl^-(g)$ 4th step

$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ 5th step

―――――――――――――――――――――――――――――――

$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$ net reaction

Electron affinities of atoms are usually calculated from born-haber cycle because it is difficult to determine electron affinities directly.

Born-Haber Cycle for the formation of NaCl(s):

Na$^+$(g) + e$^-$ + Cl(g)

121 KJ

Na$^+$(g) + e$^-$ + $\frac{1}{2}$Cl$_2$(g)

Na$^+$(g) + Cl$^-$(g)

496KJ

-349KJ

108KJ

Na(g) + $\frac{1}{2}$ Cl$_2$(g)

Na(s) + $\frac{1}{2}$ Cl$_2$(g)

-411KJ   NaCl(s)

ΔH°
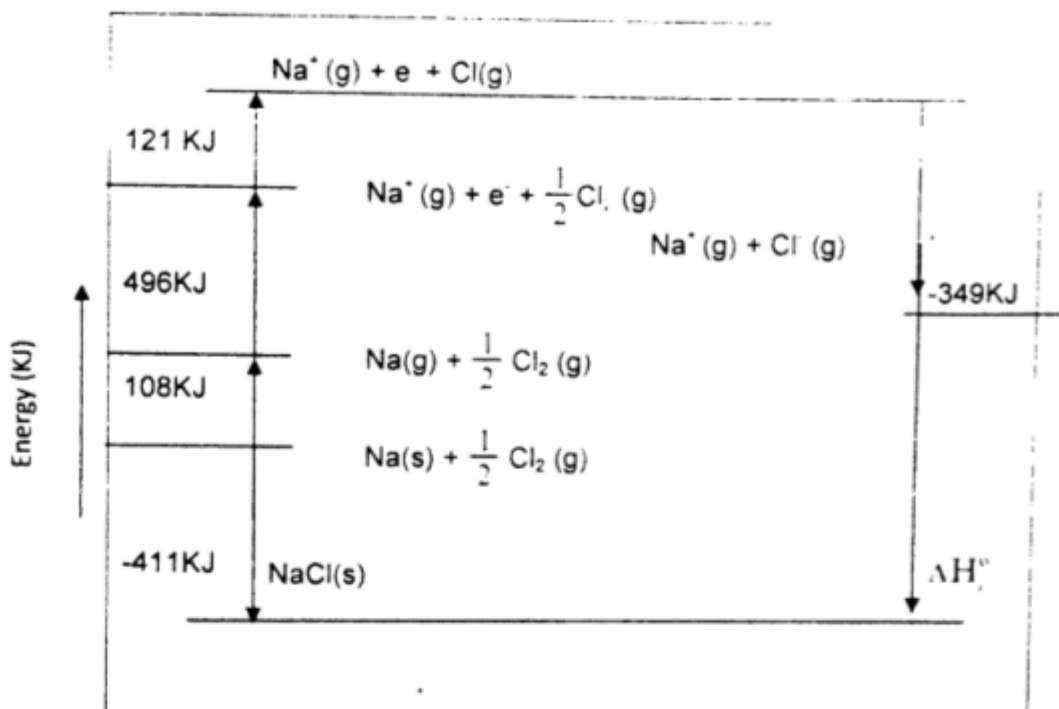
Energy (KJ)

SELF-CHECK EXERCISE 11.6

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

i) Standard enthalpy of formation of MgO = -602 $KJmole^{-1}$

ii) Standard enthalpy of formation of Mg = 150 $KJmole^{-1}$

iii) Ionization energy of Mg(g) to form Mg^{+2} (g) is 2180 $KJmole^{-1}$

iv) Standard enthalpy of atomization of O_2 = 247 $KJmole^{-1}$

v) Electron affinity of O(g) to form O^{-1}(g) = -141 $KJmole^{-1}$

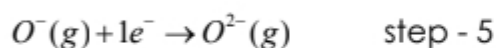vi) Electron affinity of O^{-1}(g) to form O^{-2}(g)= 878 $KJmole^{-1}$

(Ans: -1367.4KJ)

Solution: $\Delta H^\circ_f = \Delta H^\circ_s + \Delta H^\circ_{IE} + \Delta H^\circ_{at} + \Delta H^\circ_{EA} + \Delta H^\circ_l$

-602KJ= +150KJ +2180KJ +247KJ + (-141KJ) +878KJ + ΔH_l°

ΔH_l° = -602KJ – (+150KJ+2180KJ+247KJ-141KJ+878KJ)

ΔH_l° =-602kj-3314kj = -3916 $KJmole^{-1}$

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

$Mg(s) \rightarrow Mg(g)$ step – 1

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

$\dfrac{1}{2}O_2(g) \rightarrow O(g)$ step - 3

$O(g) + 1e^- \rightarrow O^-(g)$ step – 4

$O^-(g) + 1e^- \rightarrow O^{2-}(g)$ step - 5

$Mg^{2+}(g) + O^{2-}(g) \rightarrow MgO(s)$ step - 6

$Mg(s) + \dfrac{1}{2}O_2(g) \rightarrow MgO(s)$
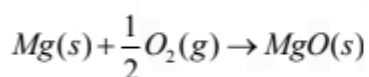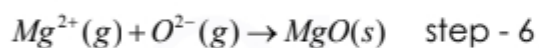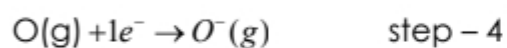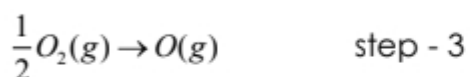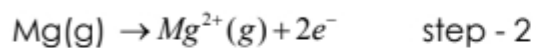
The sum of these steps gives the overall desired reaction.

The Born-Haber for MgO lattice energy is

$$Mg^{2+}(g) + O^{2-}(g)$$
_____

$$Mg^{2+}(g) + 2e^- + O(g)$$
_____

$$878 \text{ kJ mole}^{-1}$$ ↑

$$247 \text{ kJ mole}^{-1}$$ ↑ $$-141 \text{ kJ mole}^{-1}$$

↓ $$Mg^{2+}(g) + 1e^- + O^-(g)$$
_____

$$Mg^{2+}(g) + 2e^- + \tfrac{1}{2} O_2(g)$$
_____

$$2180 \text{ kJ mole}^{-1}$$ ↑

$$\Delta H\theta$$

$$Mg(g) + \tfrac{1}{2} O_2(g)$$
_____

$$150 \text{ kJ mole}^{-1}$$ ↑

$$Mg(s) + \tfrac{1}{2} O_2(g)$$
_____

$$-602 \text{ kJ mole}^{-1}$$ ↓

$$MgO(s)$$
_____
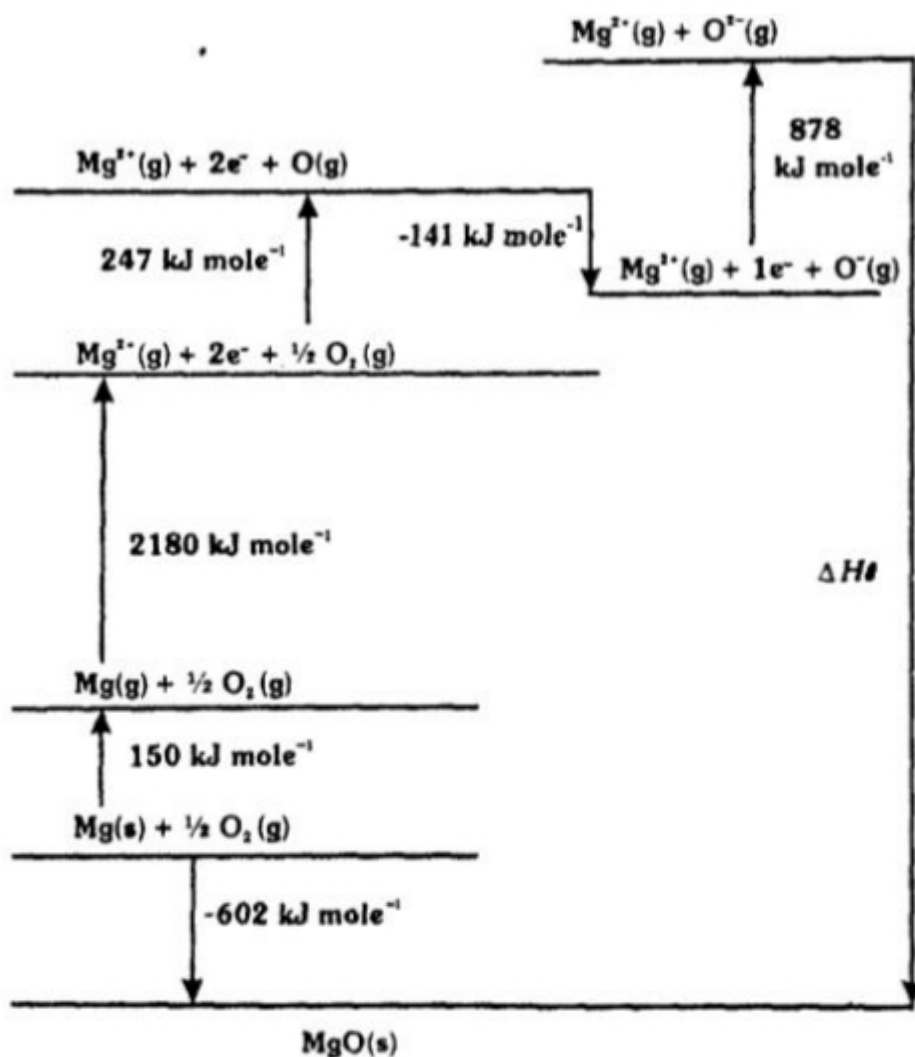
SUMMARY OF KEY TERMS

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

- A chemical reaction that proceeds with the evolution of heat is called an exothermic reaction.

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

- The amount of heat evolved or absorbed in a chemical reaction, when molar quantities of reactants and product are same as shown in a chemical reaction is called heat of reaction.
- The study of all types of energy changes associated with chemical and physical changes is known as thermodynamics.
- The condition of a system when various properties like temperature, pressure, volume, number of moles etc of system have definite values is called state of the system.
- The properties that are determined by the state of the system regardless of how that condition was achieved are called state functions.
- The sum of all kinds of energies of the particles of the system is called as internal energy.
- Thus, enthalpy of a substance is defined as the system's internal energy plus the product of its pressure and volume (H=E+PV).
- The amount of heat required to raise the temperature of given amount of a substance by 1kelvin is called heat capacity.
- A device that measures heat flow is called calorimeter.
- Hess's law states that the enthalpy change in a chemical reaction is same whether the reaction takes place in a single step or in several steps.