CHEMISTRY (XI)

Chapter 7

Thermochemistry

Short Questions

1. Define thermochemistry.

Ans: The study of heat changes accompanying a chemical reaction is known as thermochemistry.

2. What is thermochemical equation? Give two examples.

Ans: A balanced chemical equation which shows not only the reactants and products but also the amount of heat energy absorbed or released is known as a thermochemical equation.

Examples: $C(s) + O_2(g) \rightarrow CO_2(g) \quad (\Delta H = -393.5\ KJmol^{-1})$

$N_2(s) + O_2(g) \rightleftharpoons 2NO(g) \quad (\Delta H = +180.5\ KJmol^{-1})$

3. What are thermochemical reactions? Give their types.

Ans: The chemical reactions which involve heat changes are called as thermodynamic reactions. Most chemical reactions are thermochemical reactions because energy of reactants is never equal to that of products and difference is either released to surrounding or absorbed from surrounding. There are two types of such reactions:

- ✓ Exothermic reactions: Exo means out and therm means heat. It is a reaction in whichheat energy is released.
- ✓ Endothermic reactions: Endo means in and therm means heat. It is a reaction in which heat energy is absorbed.

4. What information thermochemical equations convey?

Ans: The important information that can be drawn from thermochemical equations is:

- Nature of reaction is predicted, whether it is endothermic or exothermic.
- Exact amount of net heat released or absorbed in the reaction.

5. What is spontaneous process? Give two examples.

Ans: The process which takes place on its own without any outside assistance and moves from a non-equilibrium state towards an equilibrium state is termed as spontaneous process.

Example:

1. Evaporation of water

   $H_2O\ (l) \rightleftharpoons H_2O\ (g) \qquad \Delta H = +44\ KJ\ mol^{-1}$

2. Dilution of NH_4Cl in water

$NH_4Cl\ (s) + H_2O \rightleftharpoons NH_4^+\ (aq) + Cl^-\ (aq) \qquad \Delta H° = +16.2\ KJ\ mol^{-1}$

6. What is the difference between a spontaneous and a non-spontaneous reaction?

Ans:

Spontaneous reaction

A process which takes place on its own without any outside assistance and moves from a non-equilibrium state towards an equilibrium state is termed as spontaneous process or natural process. It is unidirectional, irreversible and a real process. Some examples of spontaneous processes are given below:

(i) Water flows from higher level to the lower level. The flow cannot be reversed without some external aid.

(ii) Neutralization of a strong acid with a strong base is a spontaneous acid-base reaction.

$$NaOH\,(aq) + HCl\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)$$

Non-spontaneous reaction

Non-spontaneous process is the reverse of the spontaneous process. It does not take place on its own and does not occur in nature. Reversible processes constitute a limiting case between spontaneous and non-spontaneous processes. Some non-spontaneous processes can be made to take place by supplying energy to the system from external source. Some examples of non-spontaneous processes are given below:

(i) Pumping of water uphill.

(ii) Transfer of heat from cold interior part of the refrigerator to the hot surroundings.

(iii) When nitrogen reacts with oxygen, nitric oxide is formed. This reaction takes place by the absorbance of heat. Although, N_2 and O_2 are present in air, but they do not react chemically at ordinary conditions. The reaction takes place when the energy is provided by lightening.

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$$

7. What are endothermic and exothermic reactions? Give examples.

Ans:

Exothermic Reactions

In this reaction reactants are at higher energy in the beginning of a reaction and products obtained are at lower energy after reaction. The difference in the energy of products and reactants appears in the form of heat released by the system in the surroundings.

$$C(s) + O_2\,(g) \rightarrow CO_2(g) \qquad (\Delta H = -393.5\ KJ.mol-1)$$

$$H_2\,(g) + \tfrac{1}{2}O_2\,(g) \rightarrow H_2O\,(l) \qquad (\Delta H = -285.8\ KJ.mol-1)$$

Endothermic Reactions

In this reaction reactants are at lower energy before reaction starts and products obtained are at higher energy after reaction stops. The difference in the energy of products and reactants appears in the form of heat absorbed by the system from the surroundings.

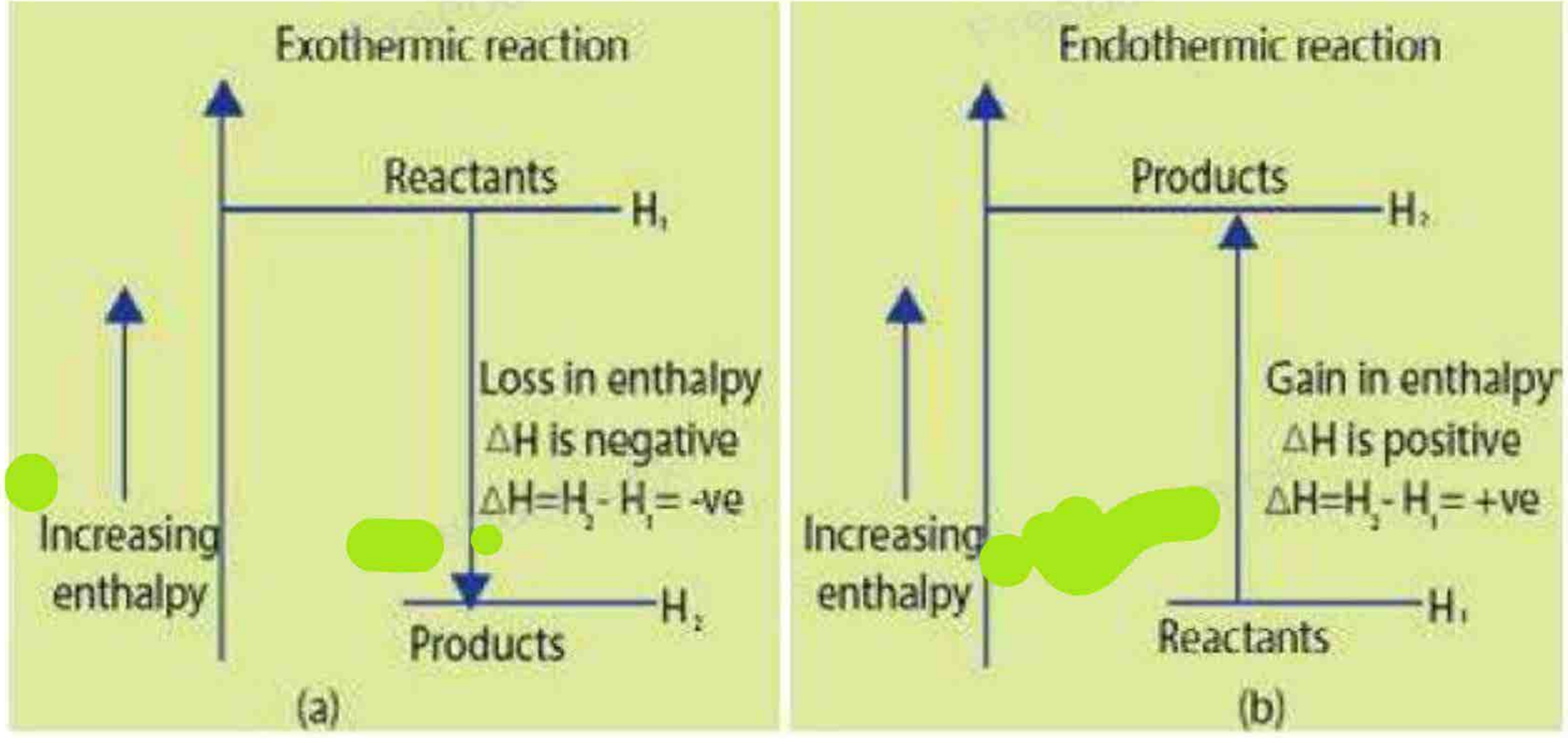
$N_2(s) + O_2(g) \quad 2NO(g) \rightleftharpoons (\Delta H = +180.5\ kJ.mol^{-1})$

$C(s) + 2S(s) \rightarrow CS_2(l) \qquad (\Delta H = +92.0\ kJ.mol^{-1})$

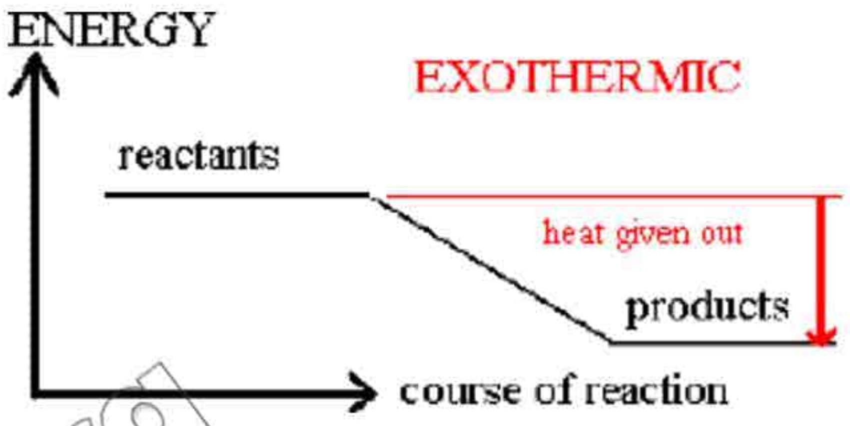
8. Differentiate between endothermic and exothermic reactions.

Ans: Following are the differences between exothermic and endothermic reactions:

Sr No	Exothermic reactions	Endothermic reactions
1	In this reaction reactants are at higher energy in the beginning of a reaction and products obtained are at lower energy after reaction. The difference in the energy of products and reactants appears in the form of heat released by the system in the surroundings.	In this reaction reactants are at lower energy before reaction starts and products obtained are at higher energy after reaction stops. The difference in the energy of products and reactants appears in the form of heat absorbed by the system from the surroundings.
2	The reactions in which heat energy is evolved	The reactions in which heat energy is absorbed
3	The enthalpy change is shown with a negative sign	The enthalpy change is shown with a positive sign
4	Example $C(s) + O_2(g) \longrightarrow$ $CO_2(g)\ \Delta H = -393.7\ kJ/mol$	Example $N_2(g) + O_2(g) \longrightarrow$ $2NO(g)\ \Delta H = +180.51\ kJ/mol$



9. Why heat energy is released in exothermic reactions?



Ans: In exothermic reactions the energy content of products is lesser than that of reactants. Therefore, during reaction heat is released from system to surroundings.

10. Define system, surrounding, boundary, state and state function.

***Ans:* System**

The term system is used for anything (materials) under test in the laboratory or under consideration in the classroom for the purpose of argument.

Surrounding

The remaining portion of the universe other than the system is known as its surroundings.

Boundary

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

Example

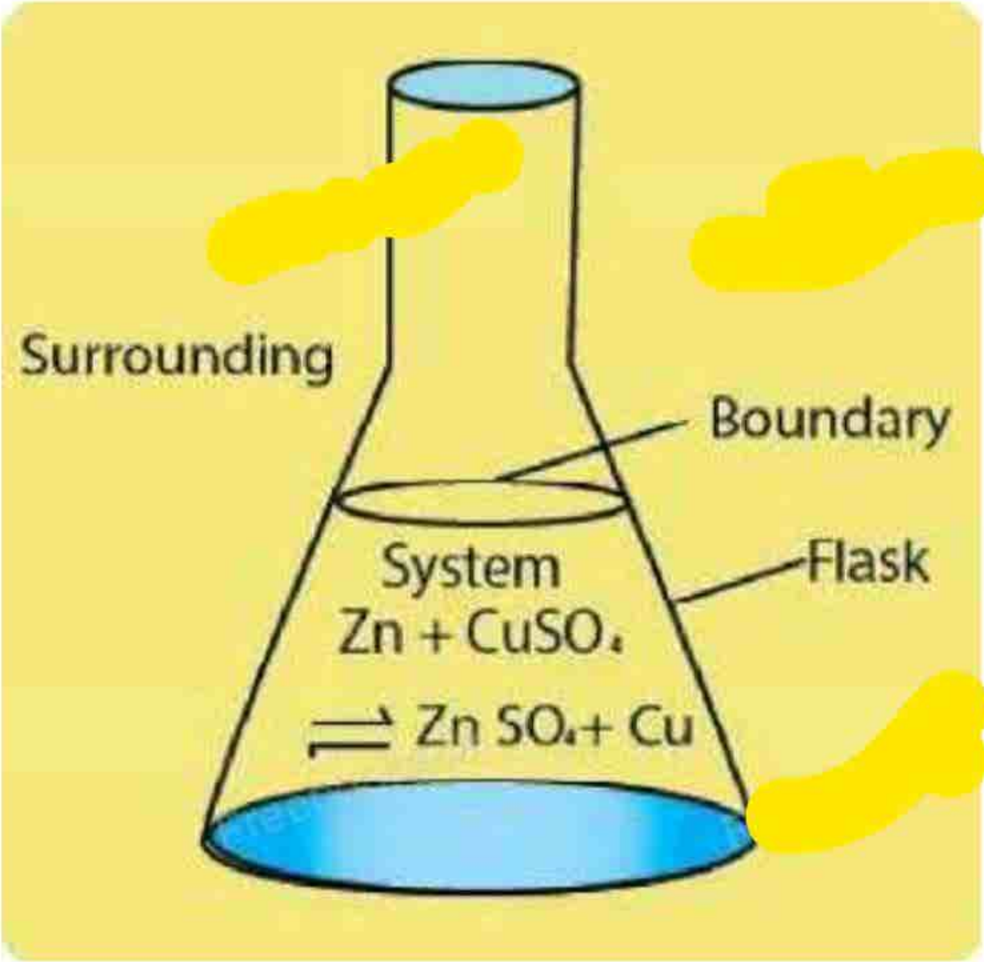


Diagram for system, surrounding and boundary

State

The state of a system is the condition of a system.

There are two states

1. Initial state 2. Final state

Example: Initial temperature T_1 and final temperature T_2

State Function

A state function is a macroscopic property of a system which has some definite values for initial and final states and which is independent of the path adopted to bring about a change. By convention, we use capital letters as symbols for a state function, e.g. pressure (P), temperature (T), volume (V), internal energy (E) and enthalpy (H) are all state functions.

11. Define internal energy.

Ans: The total of all the possible kinds of energies of the system i.e kinetic energy and potential energy is called its internal energy, E.

Mathematically

$E = \Sigma$ kinetic energy $+ \Sigma$ potential energy

12. Define heat and work.

Ans:

Heat

Heat is not a property of a system. It is therefore not a state function. It is defined as the quantity of energy that flows across the boundary of a system during a change in its state due to the difference in temperature between the system and the surroundings. Heat evolved or absorbed by the system is represented by a symbol **q**.

The sign of **q** is positive when heat is absorbed by the system from surroundings and it is negative when heat is absorbed by the surroundings from the system.

Work

Work is also a form in which energy is transferred from one system to another. It is defined as the product of force and distance i.e.

$$W = F \times S$$

Work is measured in **Joules in SI units**.

Work is not a state function. The sign of W is positive when work is done on the system and it is negative when work is done by the system.

13. State first law of thermodynamics.

Ans: The first law of thermodynamics, also called the law of conservation of energy, states that energy can neither be created nor destroyed, but can be changed from one form to another. In other words, a system cannot destroy or create energy. However, it can exchange energy with its surroundings in the form of heat and work.

14. Prove that ΔE=q_v

Ans: Consider a gas enclosed in a cylinder having a frictionless piston. When a quantity of heat **q** is supplied to the system, its internal energy E_1 changes to E_2 and piston moves upwards. The change in internal energy ΔE is given by the following equation.

$$\Delta E = E_2 - E_1 = q + w$$

$$\Delta E = q + w$$

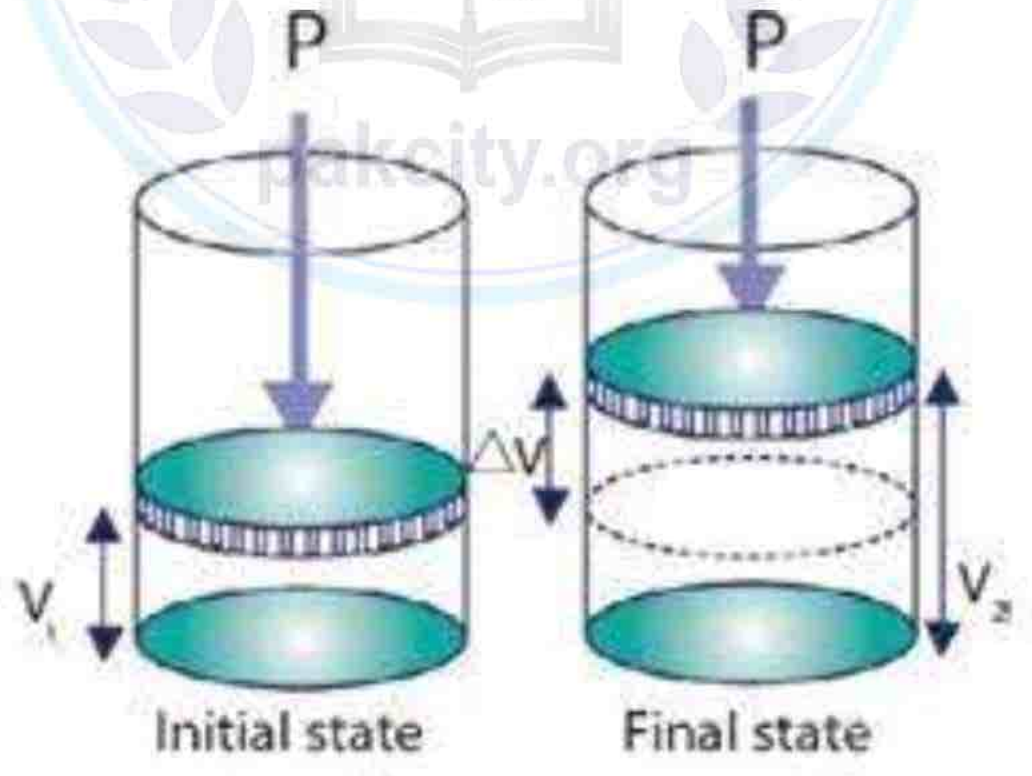
In this equation **q** represents the amount of heat absorbed by the system and V is the work done by the system in moving the piston up. If **w** is pressure-volume work then the above expression assumes the following form:

$$\Delta E = q - P\Delta V \qquad (1)$$

When the piston is kept in its original position or the volume of the gas is not allowed to change then ΔV = 0 will take the following form:

$$\Delta E = q_v \qquad (2)$$

This eq (2) shows that a change in internal energy of a system at constant volume is equal to heat absorbed by the system (q_v).



15. Define enthalpy.

Ans: To take account of increase in internal energy and accompanying work done by the gas, there is a property of the system called enthalpy or heat content. It is represented by H. In general, enthalpy is equal to the internal energy E plus the product of pressure and volume (PV).

$$H = E + PV$$

Enthalpy is a state function. It is measured in joules.

16. Prove that $\Delta H = q_p$

Ans: Enthalpy is equal to the internal energy, E plus the product of pressure and volume (PV).

$$H = E + PV$$

Enthalpy is a state function. It is measured in joules. It is not possible, to measure the enthalpy of a system in a given state. However, change in enthalpy (ΔH) can be measured for a change in the state of system. A change in enthalpy of a system can be written as:

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

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

Since the gas is kept at constant pressure = 0

Hence

$$\Delta H = \Delta E + P\Delta V \text{..........} (1)$$

17. In case of liquids and solids, the changes in state do not cause significant volume change i.e. $\Delta V = 0$. For such process, ΔH and ΔE are approximately the same i.e. $\Delta H \approx \Delta E$

Ans: According to first law of thermodynamics:

$$\Delta E = q + w$$

If w is pressure - volume work done by the system, then:

$$w = - P\Delta V$$

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

Putting the value of ΔE in equation (1) we get:

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

$$\Delta H = q$$

Since the pressure is constant, therefore,

$$\Delta H = q_p$$

This shows that change in enthalpy is equal to heat of reaction at constant pressure.

18. Define enthalpy of a reaction. Give an example.

Ans: The standard enthalpy of a reaction ΔH^o is the enthalpy change which occurs when the certain number of moles of reactants as indicated by the balanced chemical equation, react together completely to give the products under standard conditions, i.e 25 °C (298K) and one atmosphere pressure. All the reactants and products must be in their standard physical states. Its units are $kJmol^{-1}$.

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)} \qquad \Delta H^\circ = -285.8 kJmol^{-1}$$

19. Define enthalpy of formation. Give an example.

Ans: The standard enthalpy of formation of a compound is the amount of heat absorbed or evolved when one mole of the compound is formed from its elements. It is denoted by ΔH°_f. All the substances involved are in their standard physical states and the reaction is carried out under standard conditions i.e. at 25 °C (298 K) and one atm. pressure. Its units are kJ mol^{-1}.

$$Mg_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow MgO_{(s)} \qquad \Delta H^\circ_f = -692 kJ\ mol^{-1}$$

20. Define enthalpy of atomization. Give an example.

Ans: The standard enthalpy of atomization of an element is defined as the amount of heat absorbed when one mole of gaseous atoms is formed from the element under standard conditions. It is denoted by ΔH^o_{at} For example, the standard enthalpy of atomization of hydrogen is given below:

$$\frac{1}{2}H_{2(g)} \rightarrow H_{(g)} \qquad \Delta H^o_{at} = 218 kJ\ mol^{-1}$$

21. Define enthalpy of neutralization. Which instrument is used to measure it?

Ans: The standard enthalpy of neutralization is the amount of heat evolved when one mole of hydrogen ions $[H^+]$ from an acid react with one mole of hydroxide ions $[OH^-]$ from a base to form one mole of water. For example, the enthalpy of neutralization of sodium hydroxide by hydrochloric acid is -57.4 kJ mol^{-1}. A strong acid HCl and a strong base, NaOH, ionize completely in dilute solutions as follows:

$$HCl\,(aq) \longrightarrow H^+\,(aq) + Cl^-\,(aq)$$

$$NaOH \longrightarrow Na^+\,(aq) + OH^-\,(aq)$$

It is measured by using glass calorimeter. Formula applied is

$$\mathbf{q = m \times s \times \Delta T}$$

22. The enthalpy of neutralization is merely the heat of formation of one mole of liquid water from its ionic components. Justify.

Ans: When strong acid strong base solutions are mixed together during the process of neutralization, the only change that actually occurs is the formation of water molecules leaving the sodium ions and the chloride ions as free ions in solution. Thus, the enthalpy of neutralization is merely the heat of formation of one mole of liquid water from its ionic components.

$$H^+\,(aq) + Cl^-\,(aq) + Na^+\,(aq) + OH^-\,(aq) \longrightarrow Na^+\,(aq) + Cl^-(aq) + H_2O\,(l)$$

$$H+\,(aq) + OH-\,(aq) \longrightarrow H_2O\,(l)\ \Delta H_n = -57.4\ kJ/mol$$

23. Define enthalpy of combustion. Give an example.

Ans: The standard enthalpy of combustion of the substance is the amount of heat evolved when one mole of the substance is completely burnt in excess of oxygen under standard conditions. It is denoted by ΔH^o_c.

$$C_2H_5OH(\ell) + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(\ell)} \qquad \Delta H^o_c = -1368 \text{kJ mol}^{-1}$$

24. Define enthalpy of solution. Give an example.

Ans: The standard enthalpy of a solution is the amount of heat absorbed or evolved when one mole of a substance is dissolved in so much solvent that further dilution results in no detectable heat change. For example, enthalpy of solution (ΔH^o_{sol}) of ammonium chloride is +16.2 kJmol^{-1} and that of sodium carbonate is -25.0 kJmol^{-1}.

25. What is the purpose of bomb calorimeter?

Ans: A bomb calorimeter is usually used for the accurate determination of the enthalpy of combustion for food, fuel and other compounds.

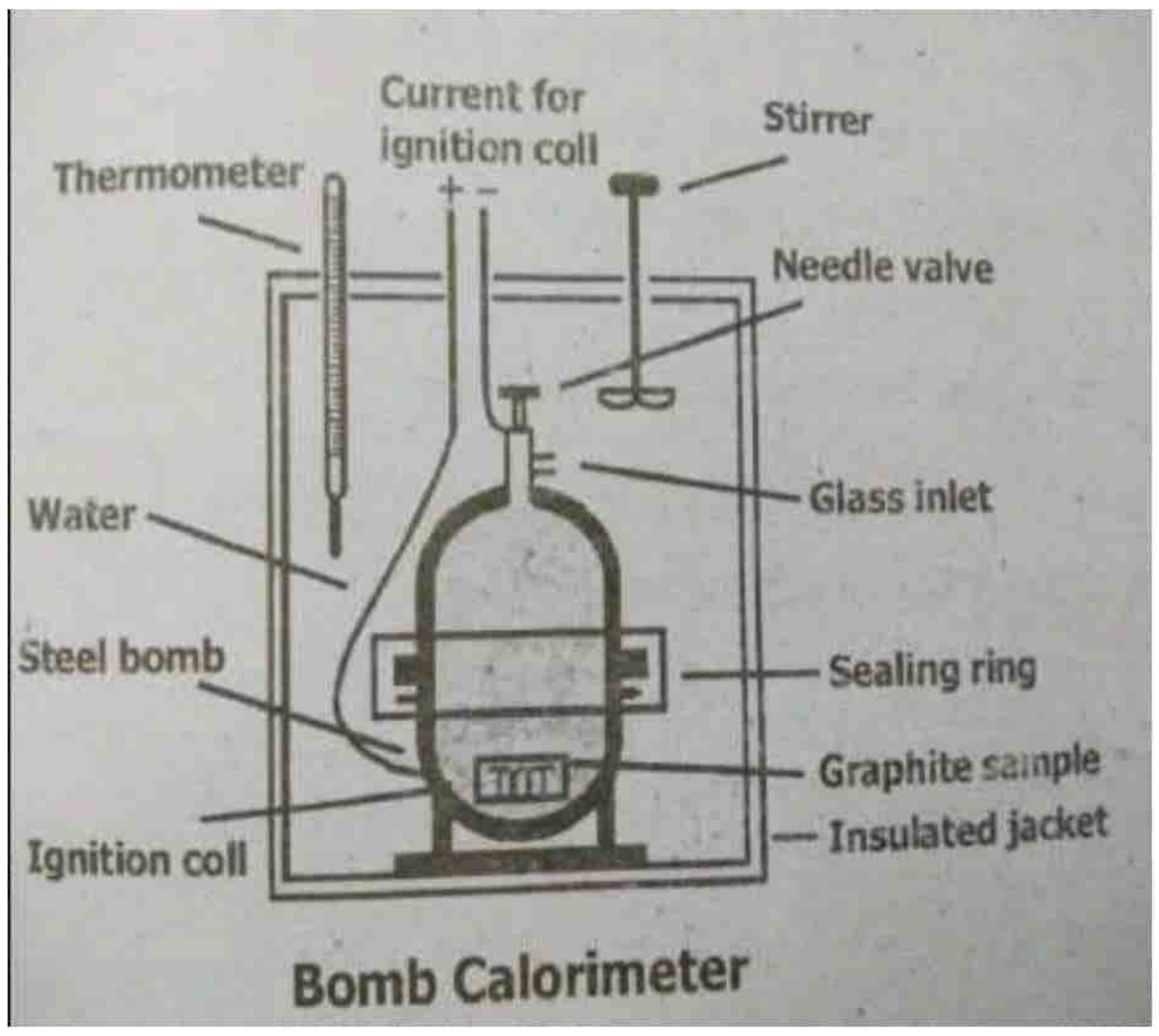
26. Define heat capacity.

Ans: The heat capacity 'c' of a body or a system is defined as the quantity of heat required to change its temperature by 1 kelvin.

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

27. Draw a labeled diagram of Bomb Calorimeter.

Ans:



28. State Hess's law. Give an example.

Ans: If a chemical change takes place by several different routes, the overall energy change is the same, regardless of the route by which the chemical change occurs, provided the initial and final conditions are the same.

Example: Formation of CO_2 is explained in direct and indirect ways below,

Direct route:

$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.5\ KJ.mol^{-1}$

Indirect route:

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad \Delta H_1 = -283.7\ KJ\ mol^{-1}$

$C(g) + \frac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta H_2 = -110 KJ\ mol^{-1}$

According to Hess's law

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

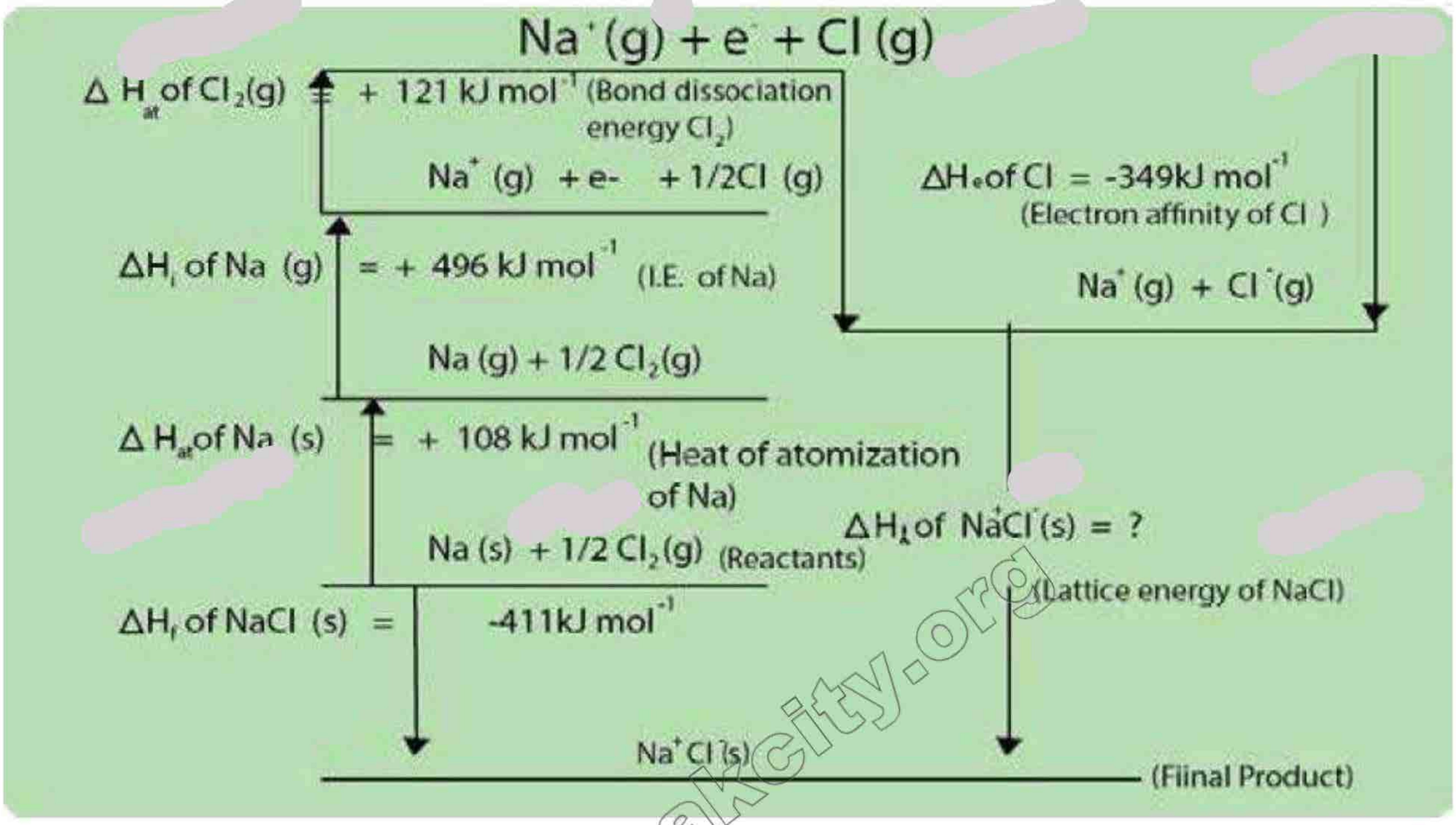
$-393.7 = -283.7 + (-110)$

$-393.7 = -393.7$

29. State Born Haber cycle.

Ans: It states that energy change in a cyclic process is always zero. It enables us to calculate the lattice energies of binary ionic compounds such as M^+X^-.

30. Draw Born Haber cycle for sodium chloride.



Ans:

Lattice energy of NaCl= -787 kJ/mol

31. Define lattice energy. Give an example.

Ans: The lattice energy of an ionic crystal is the enthalpy of formation of one mole of the ionic compound from gaseous ions under standard conditions.

$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow Na^+Cl^-_{(s)} \qquad \Delta H^\circ_{Latt} = -787\ kJ\ mol^{-1}$$

32. Why it is necessary to mention the physical states of reactants and products in the thermochemical equation?

Ans: Thermochemical equation tells about heat change and heat change is always accompanied by a physical change. For example,

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad (\Delta H = -285.8\ KJ.mol^{-1})$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \qquad (\Delta H = -241.8\ KJ.mol^{-1})$$

The two values of formation of water are due to different physical states of water. Therefore, it is necessary to mention physical states of reactants and products in a thermochemical equation.

33. Burning of a candle is a spontaneous process. Justify it.

Ans: There are two types of spontaneous processes:

- Those which start and proceed on their own.
- Those which are once started (by giving some energy) then proceed on their own.

Burning of candle is the example of second type of reactions which are once started with some amount of energy but afterwards proceed and complete on their own

34. Differentiate between Law of conservation of energy and Hess's Law.

Ans: The law of conservation of energy is a physical law that states energy cannot be created or destroyed but can be changed from one form to another.

Hess's law is defined as if a chemical change takes place by several different routes the overall energy change is the same regardless of the route by which the chemical change occurs, provided the initial and final conditions are the same.

35. Is it true that ΔH and ΔE have the same values for the reaction taking place in solution state?

Ans: In case of solids and liquids the change in volume is negligibly small. Therefore, in equation

$\Delta H = \Delta E + P\Delta V$ the factor becomes $\Delta V = 0$ and we are left with

$\Delta E \approx \Delta H$

Hence, it is true that ΔH and ΔE have the same values for the reactions taking place in solution state.

36. Mention the various units of energy.

Ans: The various units of energy are Joule, KiloJoule and Calorie.

37. Differentiate between Internal energy and enthalpy.

Ans:

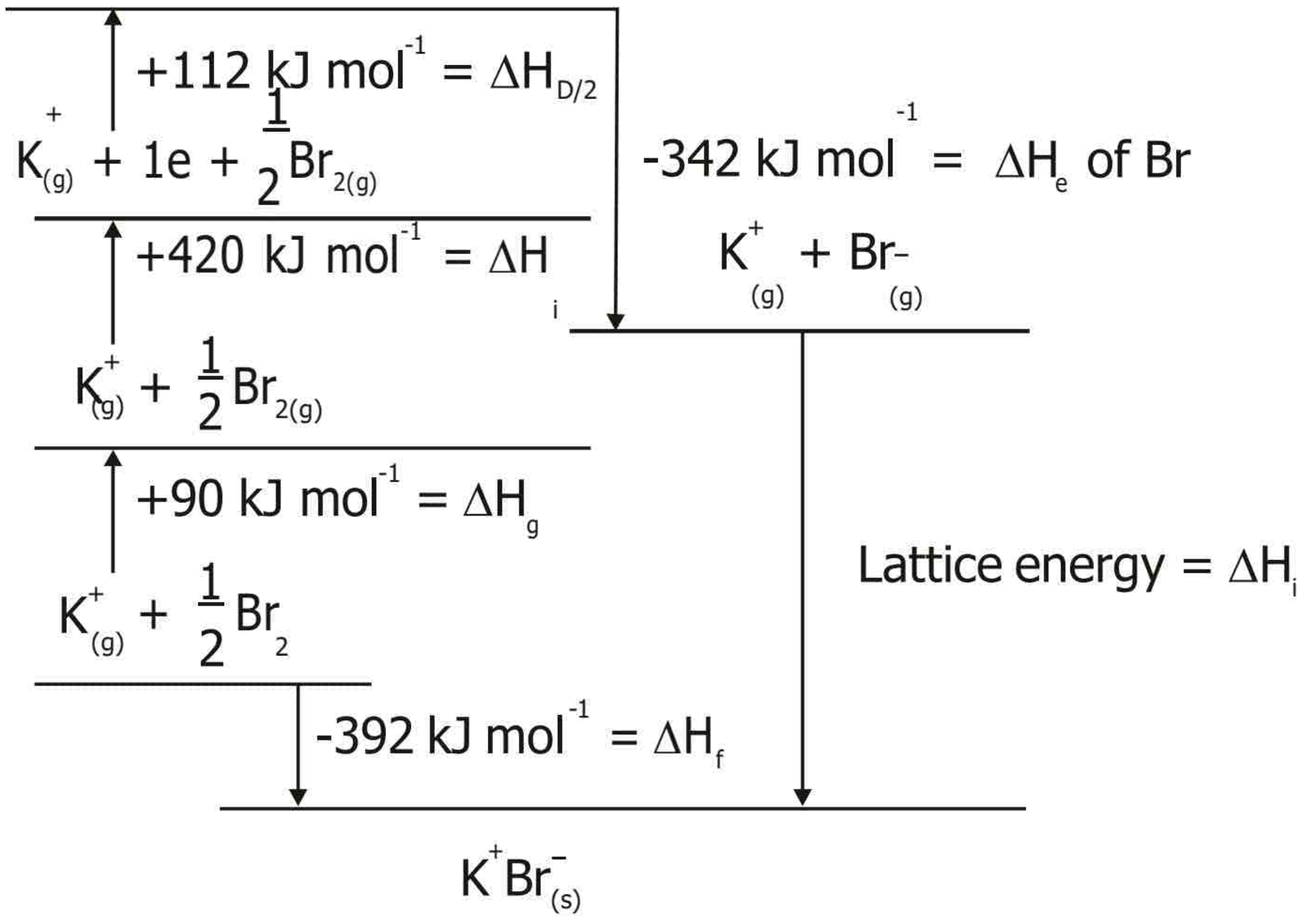
Internal Energy(E)	**Enthalpy(H)**
The total energy of a system including all forms of kinetic and potential energies is known as Internal Energy	The sum of internal energy change and work done is known as Enthalpy or Heat content. **OR** The heat absorbed by system at constant pressure is known as Enthalpy.
Mathematically it is E = Total kinetic energy + total potential energy	Mathematically it is H = E + PV

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

Ans: No, it is not true that non-spontaneous process never happens in the universe. A non-spontaneous process occurs but it needs energy to take place. For example, water cannot flow from the ground to the top of the hill on its own. However, pumping of water uphill can be made possible with the help of devices like motor pumps, which consume electrical energy.

39. Draw a complete fully labeled Born-Haber Cycle for the formation of Potassium bromide.

Ans:



Requirement:	$\Delta H_l = ?$
$K^+_{(g)} + Br^-_{(g)} \rightarrow KBr_{(g)}$	Lattice energy of KBr

Calculation and Result:

According to Born-Haber cycle,

$$\Delta H_s + \Delta H_i + \Delta H_s + \Delta H_e + \Delta H_l = \Delta H_f$$

Putting the values

$$+90 + 420 + 112 - 342 + \Delta H_l = -392$$

$$\Delta H_l = -392 - 90 - 420 - 112 + 392$$

$$= -1014 + 392$$

$$\Delta H_l = \mathbf{-672\ KJ\ mol^{-1}}$$