THERMOCHEMISTRY

1. INTRODUCTION

Thermochemistry deals with the energy changes involved in chemical reaction.

2. TYPES OF REACTIONS

(i) Exothermic reactions :

These are the chemical reactions involving release of heat.

Examples :- Neutralisation reactions, combustion reactions, slaking of lime, etc.

(ii) Endothermic reactions :

These are the chemical reactions involving absorption of heat.

Examples :- Decomposition reactions, elemination reaction, etc.

(iii) Thermo neutral reactions :

These are chemical reaction in which heat is neither absorbed nor released.

e.g. $\frac{1}{2}H_2(g) + aq. \rightarrow H^+(aq.)$; $\Delta H^\circ = 0$

$$AgClO_2(s) \longrightarrow Ag(s) + \frac{1}{2}Cl_2(g) + O_2(g) \; ; \; \Delta H^\circ = 0$$

The reason behind release or absorption of heat in the reaction may be defined as difference in internal energy, bond energy, enthalpy, etc.

For exothermic reaction :

(i) $\sum U_{Reactant} > \sum U_{Product}$

(ii) $\sum H_{Reactant} > \sum H_{Product}$

(iii) $\sum (BE)_{Reactant} < \sum (BE)_{Product}$

3. REPRESENTATION OF HEAT INVOLVED IN REACTIONS

(i) Old convention :

Reactants $\longrightarrow$ Products $\quad \overset{\text{Exo}}{\underset{\text{Endo}}{\pm Q}}$ [Q = heat lost]

(ii) Modern convention :

Reactants $\longrightarrow$ Products $\quad \Delta H = \overset{\text{Endo}}{\underset{\text{Exo}}{\pm Q}}$ [Q = heat gained]

4. THERMO CHEMICAL EQUATION

It represents a balanced chemical reaction in which the physical state along with allotropic form of all the reaction components as well as heat involved in reaction, are given.

$C_2H_5OH(\ell) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O)(\ell)$; $\Delta_rH° = -1367$ kJ/mol

The above equation decribes the combustion of liquid ethanol at constant temperature and pressure. The negative sign of enthalpy change indicates that this is an exothermic reaction.

The coefficients in a balanced thermochemical equation refer to the number of moles (never molecules) of reactants and products in the reaction. Per mole of $\Delta_rH°$ defines the mole of reaction. For above reaction per mole means per mole of $C_2H_5OH(\ell)$, per 3 moles of $O_2(g)$, per 2 moles of $CO_2(g)$ and per 3 moles of $H_2O(\ell)$.

5. ENTHALPY CHANGE OF REACTION OR REACTION ENTHALPY (Δ_rH)

Enthalpy of reaction is defined as the quantity of heat evolved or absorbed when molar quantities of substances react completely in amounts represented by chemical equation, all components being maintained at same pressure and same temperature conditions.

For example : $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$; $\Delta_rH = -183.92$ kJ

Thus, when one mole of gaseous hydrogen reacts completely with one mole of gaseous chlorine, 183.92 kJ of heat is evolved.

$\Delta_rH = \Sigma H_{products} - \Sigma H_{reactants} = [2 \times H_m(HCl, g)] - [1 \times H_m(H_2, g) + 1 \times H_m(Cl, g)]$

where H_m = molar enthalpy

5.1 FACTORS AFFECTING HEAT OR ENTHALPY OF REACTION :

The enthalpy change of reaction (ΔH) depends upon the following factors :

(i) Physical state of the reactants and the products : The ΔH of a reaction depends upon the physical states of reactants and products. For example, when hydrogen and oxygen gases combine to give liquid water, the heat of reaction is different than when they combine to form gaseous water at the same temperature and pressure.

$H_2(g) + O_2(g) \rightarrow H_2O(\ell)$; $\Delta H = -285.83$ kJ

$H_2(g) + O_2(g) \rightarrow H_2O(g)$; $\Delta H = -241.82$ kJ

(ii) Quantities of reaction components : The amount of heat evolved or absorbed depends upon the amount of components involved in the reaction. For example, the heat of combustion of 2 moles of carbon is double than heat of combustion of 1 mole of carbon.

(iii) Allotropic forms : The amount of heat evolved or absorbed for different forms of the same substance are different. For example,

$C(\text{diamond}) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -395.41$ kJ

$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -393.51$ kJ

(iv) Temperature :The heat of reaction depends upon the temperature of reactants and products.

$H_2O(\ell) \rightarrow H_2O(g)$ $\Delta H =$ x kcal at 298K

$H_2O(\ell) \rightarrow H_2O(g)$ $\Delta H =$ y kcal at 373K

The dependence of reaction enthalpy on temperature is given by Kirchoff's equation :

$$\Delta_r H_2 - \Delta_r H_1 = \int_{T_1}^{T_2} \Delta_r (C_P) \cdot dT$$

and $$\Delta_r U_2 - \Delta_r U_1 = \int_{T_1}^{T_2} \Delta_r (C_V) \cdot dT$$

However, $\Delta_r H$ and $\Delta_r U$ do not change significantly on changing the temperature.

(v) Measurement at constant pressure or volume : The heat of reaction depends upon the conditions of measurement of heat at constant pressure or volume, as,

$\Delta_r H = \Delta_r U + \Delta_r (PV)$

ΔH may be equal, greater than or less than $\Delta_r U$.

For reaction involving gaseous components,

$\Delta_r H = \Delta_r U + \Delta_r n_g \cdot RT$

(vi) Pressure : Enthalpy of any component may depend on pressure and $\Delta_r H$ may change on changing the pressure. As, the enthalpy of an ideal gas is independent from the change in pressure, for the reactions involving ideal gases, $\Delta_r H$ is pressure independent.

EXERCISE-I

1. Consider the reaction : $N_2 + 3H_2 \longrightarrow 2NH_3$ carried out at constant temperature and pressure, if ΔH and ΔU are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ? **[AIEEE-2005]**

(A) $\Delta H = \Delta U$ (B) $\Delta H = 0$ (C) $\Delta H > \Delta U$ (D) $\Delta H < \Delta U$

2. For which reaction will $\Delta H = \Delta U$?

(A) $H_2(g) + Br_2(g) \rightarrow 2\ HBr(g)$ (B) $C(s) + 2\ H_2O(g) \rightarrow 2H_2(g) + CO_2(g)$

(C) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$ (D) $2CO(g) + O_2(g) \rightarrow 2\ CO_2(g)$

3. For which of the following change $\Delta H \neq \Delta U$?

(A) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$

(B) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(\ell)$

(C) $C(s) + O_2(g) \longrightarrow CO_2(g)$

(D) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

4. A mixture of 2 moles of carbon monoxide and one mole of oxygen in a closed vessel is ignited to get carbon dioxide. If ΔH is the enthalpy change and ΔU is the change in internal energy, then :-

(A) $\Delta H > \Delta U$ (B) $\Delta H < \Delta U$ (C) $\Delta H = \Delta U$ (D) Not definite

5. For the reaction : $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, ΔH is -

(A) $\Delta U + 2RT$ (B) $\Delta U - 2RT$ (C) $\Delta U + RT$ (D) $\Delta U - RT$

6. When the following reaction was carried out in a bomb calorimeter, ΔU is found to be –742.7 kJ/mol of $NH_2CN(s)$ at 300 K.

$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(l)$$

Calculate ΔH_{300K} for the reaction. (R = 8 J/mole-K).

7. For the reaction : $2A(g) + 3B(g) \longrightarrow 4C(g) + D(\ell)$; $\Delta H = -20$ KJ/mole

Find the heat exchanged when 0.4 mole of A reacts with excess of B in a closed rigid container. The temperature is constant at 300 K. [R=8.3 J/K mole]

5.2 MEASUREMENT OF ΔU AND ΔH : CALORIMETRY :

We can measure energy changes associated with chemical or physical processes by an experimental technique called calorimetry. In calorimetry, the process is carried out in a vessel called calorimeter, which is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved in the process by measuring temperature changes. Measurements are made under two different conditions:

(i) at constant volume, q_V

(ii) at constant pressure, q_p

(a) ΔU measurements : For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter (Figure). Here, a steel vessel (the bomb) is immersed in a water bath. The whole device is called calorimeter. The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume. Under these conditions, no work is

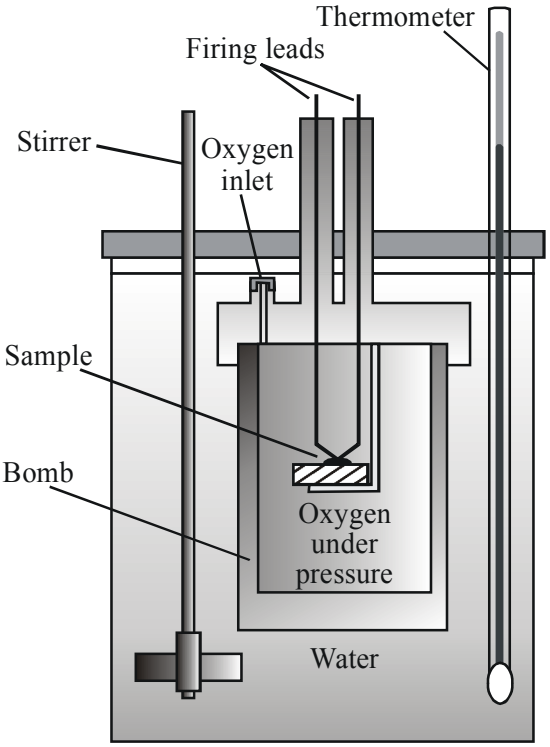


Figure : Bomb calorimeter

done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as $\Delta V = 0$. Temperature change of the calorimeter produced by the completed reaction is then converted to q_V, by using the known heat capacity of the calorimeter with the help of equation 6.11.

(b) **ΔH measurements :** Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter shown in figure. We know that $\Delta H = q_p$ (at constant p) and, therefore, heat absorbed or evolved, q_p at constant pressure is also called the heat of reaction or enthalpy of reaction, $\Delta_r H$.

In an exothermic reaction, heat is evolved, and system loses heat to the surroundings. Therefore, q_p will be negative and $\Delta_r H$ will also be negative. Similarly in an endothermic reaction, heat is absorbed, q_p is positive and $\Delta_r H$ will be positive.

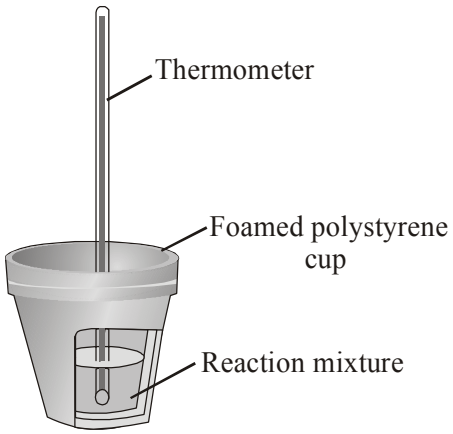


Figure : Calorimeter for measuring heat changes at constant pressure (atmospheric pressure)

Ex.1. *1g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation*

$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g)$

During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm?

Sol. : *Suppose q is the quantity of heat from the reaction mixture and C_V is the heat capacity of the calorimeter, then the quantity of heat absorbed by the calorimeter.*

$q = C_V\ \Delta T$

Quantity of heat from the reaction will have the same magnitude but opposite sign because the heat lost by the system (reaction mixture) is equal to the heat gained by the calorimeter.

$q = -C_V \times \Delta T = -20.7\ kJ/K \times (299 - 298)K = -20.7\ kJ$

(Here, negative sign indicates the exothermic nature of the reaction)

Thus, ΔU for the combustion of the 1g of graphite = –20.7 kJ

For combustion of 1 mol of graphite,

$$\Delta H = \Delta U = \frac{12.0\text{g mol}^{-1} \times (-20.7\text{kJ})}{1\text{g}} = -2.48 \times 10^2\ \text{kJ.mol}^{-1}, \quad \textit{Since } \Delta n_g = 0$$

EXERCISE-II

8. One gm sample of NH_4NO_3 (s) is decomposed in a bomb calorimeter (constant volume). The temperature of the calorimeter system falls by 6K. If the heat capacity of system is 1.25 kJ/K, what is the molar enthalpy of decomposition of NH_4NO_3(s) at 300 K. [R = 8.3 $JK^{-1}\ mol^{-1}$].
$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(l)$.

9. 0.16 g of methane was subjected to combustion at 27° C in a bomb Calorimeter . The temperature of Calorimeter system (including water) was found to rise by 0.5° C . Calculate the heat of combustion of methane at
(i) constant volume (ii) constant pressure .
The thermal capacity of Calorimeter system is 17.7 kJ K^{-1} . (R = 8.313 $mol^{-1}\ K^{-1}$)

10. If 1.22 gm of benzoic acid gives off 31.723 J of energy when burned in bomb calorimeter in the presence of excess oxygen at an initial temperature of 24.6°C. Calculate, W and ΔU for the given amount of benzoic acid in the calorimeter, assuming ideal gas behaviour.

6. STANDARD ENTHALPY OF REACTION, $\Delta H^{\ominus}$

Enthalpy of a reaction depends on the conditions under which a reaction is carried out. It is, therefore, necessary that we must specify some standard conditions. **The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.**

The standard state of a substance at a specified temperature is its pure form at 1 bar. For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1 bar; standard state of solid iron at 500 K is pure iron at 1 bar. Usually data are taken at 298 K.

Standard conditions are denoted by adding the superscript $\ominus$ to the symbol ΔH, e.g., $\Delta H^{\ominus}$

7. SOME DIFFERENT KINDS OF $\Delta_r H^{\ominus}$:

7.1 STANDARD ENTHALPY OF FORMATION, $\Delta_f H^{\ominus}$:

The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. The reference state of an element is its most stable state of aggregation at 25° C and 1 bar pressure. For example, the reference state of dihydrogen is H_2 gas and those of dioxygen, carbon and sulphur are O_2 gas, $C_{graphite}$ and $S_{rhombic}$ respectively. Some reactions with standard molar enthalpies of formation are given below.

$H_2(g) + O_2(g) \rightarrow H_2O(A)$; $\Delta_f H^{\ominus} = -285.8 \text{ kJ mol}^{-1}$

$C \text{ (graphite, s)} + 2H_2(g) \rightarrow CH_4(g)$; $\Delta_f H^{\ominus} = -74.81 \text{ kJ mol}^{-1}$

$2C \text{ (graphite,s)} + 3H_2(g) + O_2(g) \rightarrow C_2H_5OH(A)$; $\Delta_f H^{\ominus} = -277.7 \text{ kJ mol}^{-1}$

It is important to understand that a standard molar enthalpy of formation, $\Delta_f H^{\ominus}$, is just a special case of $\Delta_r H^{\ominus}$, where one mole of a compound is formed from its constituent elements, as in the above three equations, where 1 mol of each, water, methane and ethanol is formed. In contrast, the enthalpy change for an exothermic reaction:

$CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$; $\Delta_r H^{\ominus} = -178.3 \text{kJ mol}^{-1}$

is not an enthalpy of formation of calcium carbonate, since calcium carbonate has been formed from other compounds, and not from its constituent elements. Also, for the reaction given below, enthalpy change is not standard enthalpy of formation, $\Delta_f H^{\ominus}$ for HBr(g).

$H_2(g) + Br_2(l) \rightarrow 2HBr(g)$; $\Delta_f H^{\ominus} = -72.8 \text{ kJ mol}^{-1}$

Here two moles, instead of one mole of the product is formed from the elements, i.e.,

$\Delta_r H^{\ominus} = 2\Delta_f H^{\ominus}$

Therefore, by dividing all coefficients in the balanced equation by 2, expression for enthalpy of formation of HBr (g) is written as

$H_2(g) + Br_2(A) \rightarrow HBr(g)$; $\Delta_f H^{\ominus} = -36.4$ kJ mol^{-1}

(i) $\Delta_f H° = 0$ for all the elements in their reference state.

(ii) **Standard enthalpy of reaction from standard enthalpy of formation :** The knowledge of standard enthalpy of formation of various substances can be used to calculate the standard enthalpy of reactions under standard conditions. The standard enthalpy of any reaction ($\Delta H°$) is equal to the difference between the $\Delta_f H°$ of all the products and the reactants.

$\Delta H°$ = Sum of the standard enthalpy of formation of products - Sum of the standard enthalpy of formation of reactants.

i.e., $\mathbf{\Delta_r H^o = \Sigma \Delta_f H^o_{(products)} - \Sigma \Delta_f H^o_{(reactants)}}$

For a reaction, $aA + bB \rightarrow cC + dD$

$\Delta_r H° = \Sigma \Delta_f H^o_{(products)} - \Sigma \Delta_f H^o_{(reactants)}$

$= [c\Delta_f H^o(C) + d\Delta_f H^o(D)] - [a\Delta_f H^o(A) + b\Delta_f H^o(B)]$

Ex.2. *Standard enthalpies of formation of $CO(g)$, $CO_2(g)$, $N_2O(g)$ and $N_2O_4(g)$ are –110, –393, –81 and 10 kJ/moe, respectively. Find the $\Delta_r H°$ for the reaction :*

$N_2O_4(g) + 3CO \longrightarrow N_2O(g) + 3CO_2(g)$

Sol. : $\Delta_r H^o = \Sigma \Delta_f H^o_{(products)} - \Sigma \Delta_f H^o_{(reactants)}$

$= \left[\Delta_f H°_{N_2O(g)} + 3 \times \Delta_f H°_{CO_2(g)}\right] - \left[\Delta_f H°_{N_2O_4(g)} + 3 \times \Delta_f H°_{CO(g)}\right]$

$= [81 + 3 \times (-3393)] - [10 + 3 \times (-110)] = -778$ kJ/mol.

7.2 STANDARD ENTHALPY OF COMBUSTION, $\Delta_C H^{\oplus}$:

Standard enthalpy of combustion is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the **reactants and products** being in their standard states at the specified temperature.

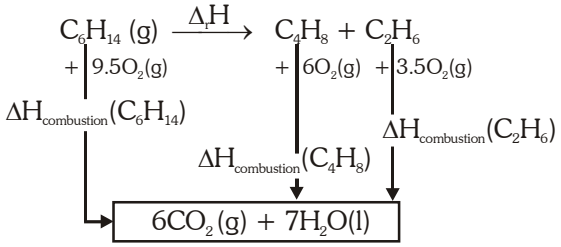
For example, the standard enthalpy of combustion of methane at 298.15 K is –890.36 kJ mol^{-1}. This implies the following reaction :

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$; $\Delta H° = -890.36$ kJ mol^{-1}

The standard enthalpy of combustion of methane at 298.15 K may be writen as

$\Delta_c H°(CH_4, g, 298.15\ K) = -890.36$ kJ mol^{-1}

7.2.1 Application of enthalpy of combustion : Consider a reaction of decompostion of C_6H_{14} into C_4H_8 and C_2H_6. The following diagram show how enthalpy of combustions can be used to estimate enthalpy of reaction.



From the inspection of the above diagram, it is clear that

$$\Delta H_{reaction} = \Delta H_{combustion}(C_6H_{14}) - \Delta H_{combustion}(C_4H_8) - \Delta H_{combustion}(C_2H_6)$$

Hence $\mathbf{\Delta_r H = \Sigma\Delta_c H(Reactants) - \Sigma\Delta_c H(Products)}$

Ex.3. *Calculate the standard enthalpy of formation of carbon disulphide (ℓ). Given that the standard enthalpies of combustion of carbon (s) sulphur (s) and carbon disulphide (ℓ) are 393.3, –293.72 and –1108.76kJ mol^{-1} respectively.*

Sol : $C(s) + 2S(s) \longrightarrow CS_2(\ell)$; $\Delta_f H^\circ_{(CS_2(\ell))} = ?$

Now, $\Delta_r H^o = \Sigma\Delta_c H^o_{(Reactants)} - \Sigma\Delta_c H^o_{(Products)}$

$= \left[\Delta_c H^\circ_{C(s)} + 2\times\Delta_c H^\circ_{S(s)}\right] - \left[\Delta_c H^\circ_{CS_2(\ell)}\right]$

$= [(-393.3) + 2 \times (-293.72] - [-1108.76]$

$= -128.02$ kJ/mol

EXERCISE-III

11. On the basis of the following thermochemical data :

$H_2O(\ell) \rightarrow H^+(aq) + OH^-(aq)$; $\Delta H = 57.32$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell)$; $\Delta H = -286.20$ kJ

The value of enthalpy of formation of OH^- ion at 25°C is :- **[AIEEE-2009]**

(A) +228.88 kJ (B) –343.52 kJ (C) –22.88 kJ (D) –228.88 kJ

12 The enthalpies of combustion of carbon and carbon monoxide are –393.5 and –283 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide per mole :- **[AIEEE-2004]**

(A) 110.5 kJ (B) 676.5 kJ (C) –676.5 kJ (D) –110.5 kJ

13. For which species $\Delta H_{formation} \neq 0$

(A) $H^+_{(aq.)}$ (B) $Br_{2(g)}$ (C) $I_{2(s)}$ (D) $C_{(graphite)}$

14. Which of the following equations represents a reaction that provides the enthalpy of formation of $CH_3Cl(g)$?

(A) $C(s) + HCl(g) + H_2(g) \rightarrow CH_3Cl(g)$ (B) $C(s) + 3/2\ H_2(g) + 1/2\ Cl_2(g) \rightarrow CH_3Cl(g)$

(C) $C(s) + 3\ H(g) + Cl(g) \rightarrow CH_3Cl(g)$ (D) $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$

15 Use the given standard enthalpies of formation to determine the enthalpy of reaction of the following reaction:

$TiCl_4(g) + 2\ H_2O(g) \rightarrow TiO_2(g) + 4\ HCl(g)$

$\Delta H^o_f\ TiCl_4(g) = -763.2$ kJ/mole $\Delta H^o_f\ TiO_2(g) = -944.7$ kJ/mole

$\Delta H^o_f\ H_2O(g) = -241.8$ kJ/mole $\Delta H^o_f\ HCl(g) = -92.3$ kJ/mole

(A) – 278.1 kJ (B) + 369.2 kJ (C) + 67.1 kJ (D) – 67.1kJ

16. Using the following information calculate the enthalpy of formation of CH_4.

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$; $\Delta H^o = -890.4$ kJ

$\Delta H^o_f\ CO_2(g) = -393.5$ kJ/mole $\Delta H^o_f\ H_2O(l) = -285.9$ kJ/mole

(A) – 98.6 kJ/mole (B) – 65.5 kJ/mole (C) – 74.9 kJ/mole (D) – 43.5 kJ/mole

Q.17 The heats of formation of $CO_2(g)$ and $H_2O(l)$ are –394 kJ/mole and –285.8 kJ/mole respectively Using the data for the following combustion reaction, calculate the heat of formation of $C_2H_2(g)$.
$2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$; $\Delta H^o = -2601$ kJ
(A) – 238.6 kJ/mole (B) 253.2 kJ/mole (C) 238.7 kJ/mole (D) 226.7 kJ/mole

Q.18 The heats of formation of $CO_2(g)$ and $H_2O(l)$ are –394 kJ/mole and –285.8 kJ/mole respectively & $\Delta H^o_{Combustion}\ [C_3H_8(g)] = -2221.6$ kJ. Then the heat of formation of $C_3H_8(g)$ is -
(A) 212.2 kJ/mole (B) – 143.3 kJ/mole (C) 185.4 kJ/mole (D) – 103.6 kJ/mole

Q.19 The standard enthalpy of formation of ammonia gas is -

Given : $N_2H_4(g) + H_2(g) \longrightarrow 2NH_3(g)$; $\Delta H_r^\circ = -40 kJ/mol$

$\Delta H_f^\circ[N_2H_4(g)] = -120 kJ/mol$

(A) –60 kJ/mol (B) –180 kJ/mol (C) 40 kJ/mol (D) –80 kJ/mol

Q.20 Calculate standard enthalpy of formation of carbon–di–sulphide (*l*) . Given the standard enthalpy of combustion of carbon (s) , sulphur (s) & carbon–di–sulphide (*l*) are : – 393, – 293 and – 1108 kJ mol^{-1} respectively.

Q.21 The enthalpy change for the reaction $C_3H_8(g) + H_2(g) \longrightarrow C_2H_6(g) + CH_4(g)$ at 25° C is – 55.7 kJ/mol. Calculate the enthalpy of combustion of $C_2H_6(g)$. The enthalpy of combustion of H_2, C_3H_8 & CH_4 are –285.8, – 2220 & –890.0 kJ/mol respectively.

7.3 BOND ENTHALPY, $\Delta_{bond}H^\ominus$:

Chemical reactions involve the breaking and making of chemical bonds. Energy is required to break a bond and energy is released when a bond is formed. It is possible to relate heat of reaction to changes in energy associated with breaking and making of chemical bonds. With reference to the enthalpy changes associated with chemical bonds, two different terms are used in thermodynamics.

(i) Bond dissociation enthalpy
(ii) Mean bond enthalpy

Let us discuss these terms with reference to diatomic and polyatomic molecules.

Diatomic Molecules: Consider the following process in which the bonds in one mole of dihydrogen gas (H_2) are broken:

$H_2(g) \rightarrow 2H(g)$; $\Delta_{H-H}H^\ominus = 435.0$ kJ mol^{-1}

The enthalpy change involved in this process is the bond dissociation enthalpy of H–H bond. The bond dissociation enthalpy is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase.

Note that it is the same as the enthalpy of atomization of dihydrogen. This is true for all diatomic molecules. For example:

$Cl_2g) \rightarrow 2Cl(g)$; $\Delta_{Cl-Cl}H^\ominus = 242$ kJ mol^{-1}

$O_2(g) \rightarrow 2O(g)$; $\Delta_{O=O}H^\ominus = 428$ kJ mol^{-1}

In the case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule.

Polyatomic Molecules: Let us now consider a polyatomic molecule like methane, CH_4. The overall thermochemical equation for its atomization reaction is given below:

$CH_4(g) \rightarrow C(g) + 4H(g)$; $\Delta_a H^\ominus = 1665$ kJ mol^{-1}

In methane, all the four C – H bonds are identical in bond length and energy. However, the energies required to break the individual C – H bonds in each successive step differ :

$CH_4(g) \rightarrow CH_3(g) + Hl(g)$; $\Delta_{bond} H^\ominus = +427$ kJ mol^{-1}

$CH_3(g) \rightarrow CH_2(g) + H(g)$; $\Delta_{bond} H^\ominus = +439$ kJ mol^{-1}

$CH_2(g) \rightarrow CH(g) + H(g)$; $\Delta_{bond} H^\ominus = +452$ kJ mol^{-1}

$CH(g) \rightarrow C(g) + H(g)$; $\Delta_{bond} H^\ominus = +347$ kJ mol^{-1}

Therefore,

$CH_4(g) \rightarrow C(g) + 4H(g)$; $\Delta_a H^\ominus = 1665$ kJ mol^{-1}

In such cases we use **mean bond enthalpy of C – H bond.**

For example in CH_4, $\Delta_{C-H} H^\ominus$ is calculated as:

$$\Delta_{C-H} H^\ominus = \frac{1}{4} (\Delta_a H^\ominus) = \frac{1}{4} (1665 \text{ kJ mol}^{-1}) = 416 \text{ kJ mol}^{-1}$$

We find that mean C–H bond enthalpy in methane is 416 kJ/mol. It has been found that mean C–H bond enthalpies differ slightly from compound to compound, as in CH_3CH_2Cl, CH_3NO_2, etc, but it does not differ in a great deal. Using Hess's law, bond enthalpies can be calculated.

(i) Mean bond enthalpy may be used to calculate $\Delta_r H$ of gaseous reaction :
Reactants (R, g) $\longrightarrow$ Products (P, g), as

$R(g) \rightarrow$ gaseous atoms A(g) ; $\sum \Delta_{Bond} H_R = H_A - H_R$

$P(g) \rightarrow A(g)$; $\sum \Delta_{Bond} H_p = H_A - H_P$

$$\Delta_r H = H_P - H_R = \sum \Delta_{bond} H_R - \sum \Delta_{bond} H_P$$

$$\boxed{\Delta_r H = \sum \Delta_{bond} H_{Reactants} - \sum \Delta_{bond} H_{Poroducts}}$$

(ii) If physical state of any component is different than gaseous, then it should be converted into gaseous atom.

(iii) ΔH calculated from bond enthalpy give $\Delta_r H_{theo}$ because mean enthalphies are used in place of bond dissociation enthalpies. Normally it remain very close to experimental $\Delta_r H$ but if any reaction component is more or less stable by any effect like resonance, hyperconjugation, strain, etc, the value differs largely. The difference is called energy or enthalpy of the kind responsible for the difference like resonance energy, strain energy, etc. It is given by

$$\Delta_r H_{exp} - \Delta_r H_{theo} = \Delta H_{effect}$$

Ex.4. *If E_{C-C} is 344 kJ mol^{-1} and E_{C-H} is 415 kJ mol^{-1}, calculate the enthalpy of formation of propane. The enthalpies of atomization of carbon(s) and hydrogen (g) are 716 kJ mole^{-1} and 433 kJ mole^{-1} respectively.*

Sol. : *The enthalpy of formation is the sum of the atomization and bond energies. For propane, the enthalpies of atomization are*

$$3C(s) \longrightarrow 3C(g) \; ; \; \Delta H = 3 \times 716 = 2148 \text{ kJ}$$

$4H_2(g) \longrightarrow 8H(g)$; $\Delta H = 4 \times 433 = 1732$ kJ

The bond enthalpies are

$2E_{C-C} = 2 \times -344 = -688$ kJ

$8E_{C-H} = 8 \times -415 = -3320$ kJ

Adding

$3C + 4H_2 \longrightarrow C_3H_8$; $\Delta H_f = 2148 + 1732 - 688 - 3320 = -128$ kJ mole^{-1}

EXERISE-IV

21 The enthalpy change for the following reaction is 513 kJ. Calculate the average Cl – F bond energy.

$ClF_3(g) \rightarrow Cl(g) + 3\,F(g)$

(A) 1542 kJ/mole (B) 88 kJ/mole (C) 171 kJ/mole (D) 514 kJ/mole

22 Using bond enthalpy data, calculate enthalpy of formation of gaseous isoprene .

$$5\,C(s) + 4\,H_2(g) \longrightarrow H_2C = \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} - \underset{\displaystyle H}{\overset{\displaystyle |}{C}} = CH_2(g)$$

Given : C — H = 98.8 kcal/mol ; H — H = 104 kcal/mol ;

C — C = 83 kcal/mol ; C = C = 147 kcal/mol &

$C(s) \rightarrow C(g) = 171$ kcal/mol.

30 For the reaction : $N_2H_4(g) \rightarrow N_2H_2(g) + H_2(g)$; $\Delta_r H° = 109$ kJ /mol

Calculate the bond enthalpy of N = N.

Given : B.E. (N – N) = 163 kJ/mol, B.E. (N–H) = 391 kJ/mol, B.E. (H–H) = 436 kJ/mol

24 Using the bond enthalpy data given below, calculate the enthalpy change for the reaction.

$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

Bond	C–C	C = C	C–H	H–H
Bond Enthalpy	336 kJ/mol	606 kJ/mol	410 kJ/mol	431 kJ/mol

25. If at 298 K the bond energies of C–H, C–C, C=C and H–H bonds are respectively 414, 347, 615 and435 kJ mol^{-1}, the value of enthalpy change for the reaction : **[AIEEE-2003]**

$H_2C=CH_2(g) + H_2(g) \longrightarrow H_3C–CH_3(g)$ at 298 K

will be :-

(A) +125 kJ (B) –125 kJ (C) +250 kJ (D)–250 kJ

26. The standard enthalphy of formation of NH_3 is –46.0 kJ mol^{-1}. If the enthalpy of formation of H_2 from its atoms is –436 kJ mol^{-1} and that of N_2 is –712kJ mol^{-1}, the average bond enthalpy of N–H bond in NH_3 is :- **[AIEEE-2010]**

(A) –1102 kJ mol^{-1} (B) –964 kJ mol^{-1} (C) + 352 kJ mol^{-1} (D) +1056 kJ mol^{-1}

27. If the bond dissociation energies of XY, X_2 and Y_2 (all gaseous diatomic molecules) are in the ratio of 1 : 1 : 0.5 and $\Delta_f H$ for the formation of XY is –200 kJ mol^{-1}. The bond dissociation energy of X_2 will be **[AIEEE-2005]**

(A) 200 kJ mol^{-1} (B) 100 kJ mol^{-1} (C) 800 kJ mol^{-1} (D) 300 kJ mol^{-1}

28 The enthalpy of atomization of $PH_3(g)$ is 954 kJ mol^{-1} and that of $P_2H_4(g)$ is 1485 kJ mol^{-1}. What is the bond enthalpy of the P–P bond?

29. The enthalpy changes for the following processes are listed below : **[AIEEE-2006]**

$Cl_2(g) = 2Cl(g)$, 242.3 kJ mol^{-1}
$I_2(g) = 2I(g)$ 151.0 kJ mol^{-1}
$ICl(g) = I(g) + Cl(g)$, 211.3 kJ mol^{-1}
$I_2(s) = I_2(g)$, 62.76 kJ mol^{-1}

Given that the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation for ICl(g) is :-

(A) –16.8 kJ mol^{-1} (B) +16.8 kJ mol^{-1} (C) +244.8 kJ mol^{-1} (D) –14.6 kJ mol^{-1}

30. The standard enthlapy of formation ($\Delta_f H°$) at 298K for methane, $CH_4(g)$, is –74.8 kJ mol^{-1}. The additional information required to determine the average energy for C–H bond formation would be:-

(A) Latent heat of vapourization of methane **[AIEEE-2006]**
(B) The first four ionization energies of carbon and electron gain enthalpy of hydrogen
(C) The dissociation energy of hydrogen molecule H_2
(D) The dissociation energy of H_2 and enthalpy of sublimation of carbon

31 $XeF_2(g) + H_2(g) \rightarrow 2HF(g) + Xe(g)$; $\Delta H° = -430$ kJ
using the following bond energies: H–H = 435 kJ/mol, H–F = 565 kJ/mol
Calculate the average bond energy of Xe-F in XeF_2 .

32 Using the given data calculate enthalpy of formation of acetone (g) . [All values in kJ mol^{-1}]
Bond enthalpy of :

C — H = 415 ; C — C = 350 ; (C = O) = 730
(O = O) = 495.0 ; H — H = 435 ; $\Delta_{sub}H$ of C = 720

7.4 ENTHALPY OF NEUTRALISATION, $\Delta_{neut}H^{\ominus}$:

The reaction in which an acid and a base react to give a salt and water is called neutralization reaction. Neutralization reactions are exothermic in nature. The enthalpy change when one gram equivalent of an acid and one gram equivalent of a base neutralise each other completely in dilute aqueous solution, is called enthalpy of neutralization.

For examples :

(i) Neutralization of HCl with NaOH
$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(\ell)$; $\Delta_{neut.}H = -57.1$ kJ

(ii) Neutralization of CH_3COOH with NaOH
$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa + H_2O(\ell)$; $\Delta_{neut.}H = -55.9$ kJ

It is important to note that the term gram equivalent is used in the definition of heat of neutralization. This is because neutralization involves 1 mole of H^+ ions and 1 mole of OH^- ions to form 1mole of water and 57.1 kJ of heat is liberated.

$H^+(aq) + OH^- \longrightarrow H_2O(\ell)$; $\Delta_{neut.}H = -57.1$kJ

Now, one gram equivalent of various acids on complete dissociation liberates one mole of H^+ ions. But one mole of the acid may produce more than one mole of H^+ ions in solution depending

upon its basicity; for example 1mol of H_2SO_4 gives 2 mol of H^+ ions and 1mol of H_3PO_4 gives 3 mol of H^+ ions on complete dissociation. But 1gram equivalent of both (H_2SO_4 or H_3PO_4) produces only 1 mol of H^+ ions.Thus, it is more appropriate to use the term gram equivalent in the definition of enthalpy of neutralization.

The average enthalpy of neutralization of any strong acid by a strong base is found to be –57.1 kJ/eq. This is because strong acids and strong bases are completely ionized in aqueous solutions. The aqueous solution of one gram equivalent of all strong acids contain the same number of H^+ ions. Similarly, aqueous solution of one gram equivalent of all strong bases also contain same number of OH^-. The neutralization reactions between strong acids and strong bases in aqueous solutions involve simply the combination of H^+ ions (from an acid) and OH^- ions (from a base) to form unionized water molecules. For example, the reaction between hydrochloric acid and sodium hydroxide. The neutralization can be represented as :

$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq)\ Cl^-(aq) + H_2O(\ell)$; $\Delta H = -57.1$ kJ

Cancelling common ions :

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell)$; $\Delta H = -57.1$ kJ

(i) $\Delta_{neut}H$ for any strong acid by any strong base is almost constant.

$\Delta_{neut}\Delta(H^+/OH^-) = -57.1$ kJ/mole^{-1} $= -13.7$ kcal mol^{-1}

It is due to the only enthalpy change occuring in such process which is

$H^+(aq.) + OH^-(aq) \rightarrow H_2O(l)$; $\Delta H° = -13.7$ kcal/eq.

(ii) If any of the acid or base is weak, the numerical value of $\Delta_{neut}H$ decreases from 13.7 kcal by enthalpy of ionization for the weak component. **The weak component is assumed completely unionised in solution.**

Ex5. *The acids HA, HB & HC are neutralised seperately by NaOH. If $\Delta_{neut}H$ are –12.1, –3.9 & –7.2 kcal/eq. Arrange the acids in the increasing order of their acidic strength.*

Sol: *A > C > B*

Ex.6. *$\Delta_{neut}H$ of $H_2C_2O_4$ by NaOH is –8.7 kcal/mol, $\Delta_{ion}H$ of oxalic acid is*

Sol : *$-27.4 + H_{ion} = -8.7$*

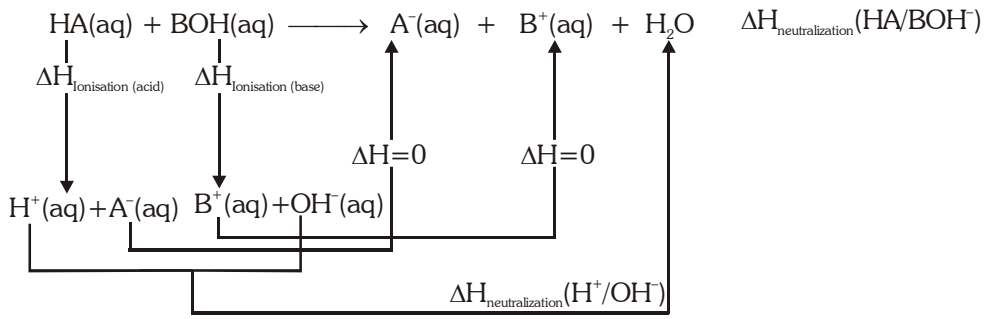
$\therefore\ \Delta_{ion}H = +18.7$ kcal/mol

7.4.1 The enthalpy of neutralization of weak acid and weak base : Consider the neutralisation of weak acid HA with weak base BOH.

Where, $\Delta H_{ionisation}$ (HA) = Enthalpy of ionization of acid HA = Enthalpy to ionize 1 mole of weak acid in aq. soln.

$\Delta H_{ionisation}$ (BOH) = Enthalpy of ionization of base BOH

$\Delta H_{neutralisation}$ (H^+/OH) = Enthalpy change for the reaction of H^+ and OH^- to form water.



Thus for weak acid :

$$\Delta H_{neut}\,(BOH/HA) = \Delta H_{ion.}\,(HA) + \Delta H_{ion}\,(BOH) + \Delta H_{neut}\,(H^+/\,OH^-)$$

EXERCISE-V

33 Calculate the enthalpy of ionisation of weak acid $H_2A(H_2A \rightarrow 2H^+ + A^{2-})$ in Kcal/ mol, if enthalpies of neutralisation of HCl and H_2A by a strong base are –14 Kcal/eq and –11 Kcal/eq respectively.

34 Enthalpy of neutralization of H_3PO_3 acid is -106.68 kJ/mol using NaOH. If enthalpy of neutralization of HCl by NaOH is –55.84 kJ/mol. Calculate $\Delta H_{ionization}$ of H_3PO_3 into its ions

(A) 50.84 kJ/mol (B) 5 kJ/mol (C) 2.5 kJ/mol (D) 60.84 kJ/mol

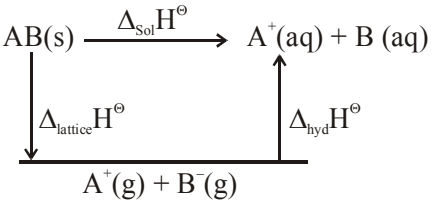
7.5 ENTHALPY OF SOLUTION, $\Delta_{sol}H^{\ominus}$:

When a solute is dissolved in a solvent, a solution is formed. During dissolution of a solute in any solvent, a certain amount of heat is either absorbed or evolved. The change in enthalpy when one mole of a solute is dissolved in a specified quantity of a solvent at a given temperature is called enthalpy of solution. To avoid the amount of solvent, enthalpy of solution is usually defined for an infinite dilute solution. Thus, enthalpy of solution at infinite dilution is the enthalpy change when one mole of a substance is dissolved in such a large quantity of solvent so that further dilution does not give any further enthalpy change.

$KCl(s) + aq. \longrightarrow KCl(aq)$; $\Delta_{sol}H = +18.6 kJ\ mol^{-1}$

$CaCl_2(s) + aq. \longrightarrow KCl(aq)$; $\Delta_{sol}H = -75.3 kJ\ mol^{-1}$

When an ionic compound dissolves in a solvent, the ions leave their ordered positions on the crystal lattice. These are now more free in solution. But solvation of these ions (hydration in case solvent is water) also occurs at the same time. This is shown diagrammatically, for an ionic compound, AB (s)



The enthalpy of solution of AB(s), $\Delta_{sol}H^{\ominus}$, in water is, therefore, determined by the selective values of the lattice enthalpy, $\Delta_{lattice}H^{\ominus}$ and enthalpy of hydration of ions, $\Delta_{hyd}H^{\ominus}$ as

$$\Delta_{sol}H^{\ominus} = \Delta_{lattice}H^{\ominus} + \Delta_{hyd}H^{\ominus}$$

For most of the ionic compounds, $\Delta_{sol}\,H^0$ is positive and the dissociation process is endothermic. Therefore the solubility of most salts in water increases with rise of temperature.

7.6 ENTHALPY OF HYDRATION, $\Delta_{Hyd}H$:

This is defined as the enthalpy change (evolved or absorbed) when one mole of the anhydrous salt combines with the required number of moles of water to form the specific hydrated salt.

$$CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4.5H_2O(s) \; ; \quad \Delta H_{Hydration} = -78.21 \text{ kJ mol}^{-1}$$

Hydration is generally exothermic change.

If enthalpy of solution of the hydrated and anhydrous salt is known, then heat of hydration can be calculated.

For example :

(a) $CuSO_4(s) + aq. \longrightarrow CuSO_4\,(aq.) \; ; \; \Delta_{sol}H = -66.50$ kJ

(b) $CuSO_4.5H_2O(s) + aq. \longrightarrow CuSO_4\,(aq.) \; ; \; \Delta_{sol}H = 11.71$ kJ

Thus, (a – b) gives

$$CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4.5H_2O(s) \; ; \; \Delta H_{Hydration} = -78.21 \text{ kJ}$$

Ex.7. *Calculate the enthalpy change when infinitely dilute solutions of $CaCl_2$ and Na_2CO_3 mixed. ΔH_f^0 for $Ca^{2+}(aq.)$, $CO_3^{2-}(aq.)$ and $CaCO_3(s)$ are –129.80, –161.65,–288.5 kcal mole^{-1} respectively.*

Sol : *On mixing $CaCl_2(aq.)$ and Na_2CO_3*

$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaCl$

Solutions are very dilute and thus 100% dissociation occurs.

$$Ca^{2+}(aq.) + 2Cl^-(aq.) + 2Na^+(aq.) + CO_3^{2-}(aq.) \longrightarrow CaCO_3\downarrow + 2Na^+(aq.) + 2Cl^-(aq.)$$

or $$Ca^{2+}(aq.) + CO_3^{2-}(aq.) \longrightarrow CaCO_3(s)$$

$\therefore$ $$\Delta H = \sum H^0_{products} - \sum H^0_{reactants}$$

or $$\Delta H = H^0_{f\,CaCO_3} - \left[H^0_{f\,Ca^{2+}} + H^0_{f\,CO_3^{2-}}\right]$$

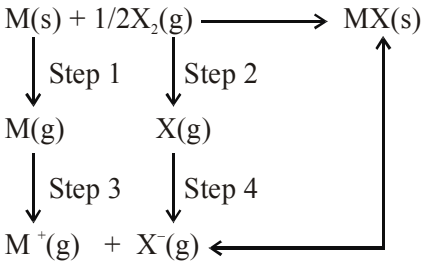
$\because$ *$\Delta H°$ of a compound = $\Delta H°$ formation = –288.5 – (–129.8 – 161.65) = 2.95 kcal*

7.7 LATTICE ENTHALPY ($\Delta_{lattice}H$) :

The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state under conditions of constant temperature and pressure.

$$Na^+Cl^-(s) \longrightarrow Na^+(g) + Cl^-(g) \; ; \qquad \Delta_{lattice}H = +788 \text{ kJ mol}^{-1}$$

7.7.1 Determination of lattic energy (Born-Haber cycle) : Since, it is impossible to find the lattice enthalpies by direct experiment, it is generally calculated by indirect method known as **Born-Haber cycle.**



Born-Haber cycle

The change in enthalpy that occurs when 1 mole of a solid crystalline substance is formed from its gaseous ions.

Step 1 : Conversion of metal to gaseous atoms.
$M(s) \longrightarrow M(g)$, ΔH_1 = sublimation energy

Step 2 : Dissociation of X_2 molecules to X atoms
$X_2(g) \longrightarrow 2X(g)$, ΔH_2 = Dissociation energy

Step 3 : Conversion of gaseous metal atom to metal ions by losing electron
$M(g) \longrightarrow M^+(g) + e^-$, ΔH_3 = Ionization enthalpy

Step 4 : X(g) atoms gain an electron to form M^- ions
$X(g) + e^- \longrightarrow X^-(g)$, ΔH_4 = Electron gain enthalpy

Step 5 : M^+ (g) and X^-(g) get together and form the crystal lattice
$M^+(g) + X^-(g) \longrightarrow MX$ (s) , ΔH_5 = Lattice enthalpy
Applying Hess's law we get

$$\Delta H_1 + \frac{1}{2}\Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 = \Delta H_f(MX)$$

On putting the various known values, we can calculate the lattice energy.

Ex.8. *Calculate the proton affinity of $NH_3(g)$ from the following data (in kJ/mole)*

$\Delta H^0_{\text{dissociation}} : H_2(g)$	*= 218*
$\Delta H^0_{\text{formation}} : NH_3(g)$	*= –46*
Lattice energy of NH_4Cl	*= –683*
Ionisation energy of H	*= 1310*
Electron affinity of Cl	*= 348*
Bond dissociation energy $Cl_2(g)$	*= 124*
$\Delta H^0_{\text{formation}} : NH_4Cl(s)$	*= –314*

Sol: *We have to calculate ΔH for the following equation*

$NH_3(g) + H^+(g) \longrightarrow NH_4^+(g)$

Given : $H_2(g) \longrightarrow 2H(g)$: $\Delta H_1 = 218$ kJ/mole

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$: $\Delta H_2 = -46$ kJ/mole

$NH_4Cl(s) \longrightarrow NH_4^+(g) + Cl^-(g)$: $\Delta H_3 = +683$ kJ/mole

$H(g) \longrightarrow H^+(g)$: $\Delta H_4 = 1310$ kJ/mole

$Cl(g) \longrightarrow Cl^-(g)$: $\Delta H_5 = -348$ kJ/mole

$Cl_2(g) \longrightarrow 2Cl(g)$: $\Delta H_6 = 124$ kJ/mole

$$\frac{1}{2}N_2(g)+2H_2(g)+\frac{1}{2}Cl_2(g)\rightarrow NH_4Cl(s) \qquad : \qquad \Delta H_7 = -314\ kJ/mole$$

$$\Delta H=-\frac{1}{2}(\Delta H_1)-\Delta H_2+\Delta H_3-\Delta H_4-\Delta H_5-\frac{1}{2}(\Delta H_6)+\Delta H_7$$

$$=-\frac{1}{2}\times 218+46+683-1310+348-\frac{1}{2}\times 124-314$$

$$= -\ 768\ kJ/mole$$

7.8 IONISATION ENTHALPY, $\Delta_i H$:

Enthalpy change when one mole of gaseous atom is converted into gaseous ion by removing one mole electron from ground state is called ionisation enthalpy.

Example :

$Na(g) \longrightarrow Na^+(g) + e$; $\Delta H_{Ionization}(Na(g))$

$H(g) \longrightarrow H^+(g) + e$; $\Delta H_{Ionization}(H(g))$

$$\mathbf{\Delta_i H = I.E. + \frac{5}{2}RT}$$

7.9 ELECTRON GAIN ENTHALPY, $\Delta_{eg}H$:

Enthalpy change when 1 mole electrons are added to valence shell of gaseous atoms is called electron gain enthalpy.

Example :

$Cl(g) + e \longrightarrow Cl^-(g)$; $\Delta_{eg}H$

$$\mathbf{\Delta_{eg}H = -E_a - \frac{5}{2}RT}$$

7.10 ENTHALPY OF ATOMISATION, $\Delta_a H$:

It is the enthalpy change (always positive) when one mole of a substance is completely dissociated into atoms in the gaseous state, under constant pressure and temperature condition.

For example

$H_2(g) \longrightarrow 2H(g)$; $\Delta_a H = 435.0\ kJ\ mol^{-1}$

$CH_4(g) \longrightarrow C(g) + 4H(g)$; $\Delta_a H = 1665\ kJ\ mol^{-1}$

7.11 ENTHALPY OF TRANSITION (Enthalpy of allotropic form) , $\Delta_{trs}H$:

It is the enthalpy change when one mole of one allotropic form changes to another under conditions of constant temperature and pressure. For example

$C(graphite) \longrightarrow C(diamond)\ \Delta_{trs}H = 1.90\ kJ\ mol^{-1}$

EXERCISE-VI

35. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below:

$$\frac{1}{2}Cl_2(g) \xrightarrow{\frac{1}{2}\Delta_{diss}H^\ominus} Cl(g) \xrightarrow{\Delta_{eg}H^\ominus} Cl^-(g) \xrightarrow{\Delta_{hyd}H^\ominus} Cl^-(aq)$$ **[AIEEE-2008]**

The energy involved in the conversion of $\frac{1}{2}Cl_2(g)$ to $Cl^-(aq)$

(using the data $\Delta_{diss}\ H^\ominus_{Cl_2} = 240$ kJ mol^{-1}, $\Delta_{eg}\ H^\ominus_{Cl} = -349$ kJ mol^{-1}, $\Delta_{hyd}H^\ominus_{Cl^-} = -381$ kJ mol^{-1}) will be:-

(A) –610 kJ mol^{-1} (B) –850 kJ mol^{-1} (C) +120 kJ mol^{-1} (D) +152 kJ mol^{-1}

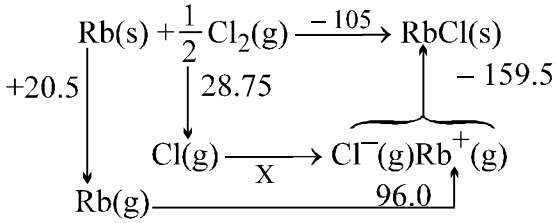
36 The lattice enthalpy of solid NaCl is 772 kJmol^{-1} and enthalpy of solution is 2 kJmol^{-1}. If the hydration enthalpy of Na^+ & Cl^- ions are in the ratio of 3:2.5, what is the enthalpy of hydration of chloride ion?

(A) –140 kJmol^{-1} (B) –350 kJmol^{-1} (C) –351.81 kJmol^{-1} (D) –420 kJ/mol

37 The enthalpy of solution of anhydrous $CuSO_4$ is – 16 kcal and that of $CuSO_4.5H_2O$ is 3 kcal. Calculate the enthalpy of hydration of $CuSO_4$.

38 Calculate the electron gain enthalpy of fluorine atom using the following data . (All the values are in kJ mol^{-1} at 25° C). $\Delta H_{diss}\ (F_2) = 160$, $\Delta_f H\ (NaF(s)) = -571$, I.E. [Na(g)] = 494, ΔH_{sub} [Na(s)] = 101 , Lattice enthalpy of NaF(s) = 894.

39 The Born–Haber cycle for formation of rubidium chloride (RbCl) is given below (the enthalpies are in k Cal mol^{-1})



Find the value of X.

40 By using the following data, calculate the enthalpy change of hydration of (i) the chloride ion ; (ii) the iodide ion.

enthalpy change of solution of NaCl(s) = – 2 kJ/mol.
enthalpy change of solution of NaI(s) = + 2 kJ/mol.
enthalpy change of hydration of $Na^+(g)$ = – 390 kJ/mol.
lattice enthalpy of NaCl = – 772 kJ/mol.
lattice enthalpy of NaI = – 699 kJ/mol.

7.12 ENTHALPY CHANGES DURING PHASE TRANSFORMATIONS :

(i) Enthalpy of Fusion, $\Delta_{fus.}H$: It is the enthalpy change that accompanies melting of one mole of a solid substance at constant temperature (melting point of solid) and pressure.

For example,

$H_2O(s) \longrightarrow H_2O(l)$; $\Delta_{fus}H = +6.00$ kJ mol^{-1}

(ii) Enthalpy of Vaporisation, $\Delta_{vap}H$:

It is the enthalpy change to vapourise one mole of a liquid substance at constant temperature (boiling point of liquid) and pressure for example :

$H_2O(l) \longrightarrow H_2O(g)$; $\Delta_{vap}H = +40.79$ kJ mol^{-1}

(iii) Enthalpy of Sublimation, $\Delta_{sub}H$:

It is the amount of enthalpy change to sublime one mole of a solid substance at constant temperature (sublimation temperature of solid) and pressure. For example

$CO_2(s) \longrightarrow CO_2(g)$; $\Delta_{sub}H = +25.2$ kJ mol^{-1}

8. LAWS OF THERMOCHEMISTRY

(i) Lavoisier and Laplace law :

Heat absorbed or evolved in a process is equal to the heat evolved or absorbed when the process is reversed.

$H_2(g) \longrightarrow 2H(g)$ $\Delta H = +104$ kcal, $2H(g) \longrightarrow H_2(g)$ $\Delta H = -104$ kcal

It follows from this law that thermochemical equation may be reversed.

(ii) Hess's law of constant heat summation :

Heat change of a process is the same whether the process takes place in one step or several steps. It follows from this law that the thermochemical equation may be treated like alzebric equations. Hess's law is helpful in calculating those heat changes which cannot be determined experimentally. It has been experimentally verified and is also a consequence of the law of conservation of energy.

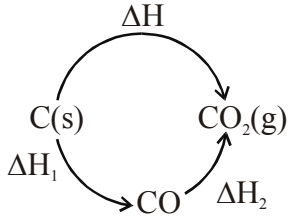
For example : Carbon can be converted into CO_2 is 1 step

$C(s) + O_2(g) \longrightarrow CO_2(g)$, $\Delta H = -94$ kcal

Or in two steps

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g),\ \Delta H_1 = -26.4 \text{ kcal}$$

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g),\ \Delta H_2 = -67.6 \text{ kcal}$$



According to Hess's law : $\Delta H = \Delta H_1 + \Delta H_2 = -26.4 - 67.6 = -94$ kcal.

Ex.9. *Calculate the heat of reaction for the hydrogenation of acetylene to ethylene at constant volume at 25°C from the following data.*

(i) Enthalpy of formation of water = –285.8 kJ mol^{-1}

(ii) Enthalpy of combustion of acetylene = –1299.6 kJ mol^{-1}

(iii) Enthalpy of combustion of ethylene = –1410.8 kJ mol^{-1}

Sol. : *(i)* $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$, $\Delta H = -285.8$ kJ mol^{-1}

(ii) $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(\ell)$, $\Delta H = -1299.6$ kJ mol^{-1}

(iii) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(\ell)$, $\Delta H = -1410.8$ kJ mol^{-1}

Equation (ii) + equation (i) – equation (iii), we get

$C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g)$

$\Delta H = -1299.6 - 285.8 + 1410.8 = -174.6$ kJ mol^{-1}

$\Delta E = -174.6 - (-1)(8.314 \times 10^{-3})(298) = -172.12$ kJ mol^{-1}

Ex.10. *Calculate $\Delta H°$ for the reaction*

$$FeO(s) + 2H^+(aq) \longrightarrow H_2O(\ell) + Fe^{2+}(aq.)$$

Given that $2Fe(s) + \frac{3}{2}O_2(g) \longrightarrow Fe_2O_3(s)$, $\Delta H° = -822.2$ kJ mol^{-1}

$2FeO(s) + \frac{1}{2}O_2(g) \longrightarrow Fe_2O_3(s)$, $\Delta H° = -284.2$ kJ mol^{-1}

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$, $\Delta H° = -286.0$ kJ mol^{-1}

$Fe(s) + 2H^+(aq.) \longrightarrow Fe^{2+}(aq.) + H_2(g)$, $\Delta H° = -284.1$ kJ mol^{-1}

Sol. Eq.(iii) + Eq.(iv) $-\frac{1}{2}\times$ Eq. (i) $+\frac{1}{2}\times$ Eq.(ii).

$\Delta H°_{required} = (-286.0) + (-284.1) - \frac{1}{2}(-822.2) + \frac{1}{2}(-284.2) = -301.1$ kJ/mol.

Ex.11. *From the following data, determine $\Delta H_f^0(B_2H_6)$ at 298 K;*

(a) $B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$, $\Delta H = -1941$ kJ mol^{-1}

(b) $2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s)$, $\Delta H = -2368$ kJ mol^{-1}

(c) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$, $\Delta H = -241.8$ kJ mol^{-1}

Sol. **Sol.** $B_2H_6(g) \longrightarrow 2B(s) + 3H_2(g)$; $\Delta H = -36$

$2B(s) + \frac{3}{2}O_2 \longrightarrow B_2O_3(s)$; $\Delta H = -1273$

$3H_2O(l) \longrightarrow 3H_2O(g)$; $\Delta H = 3 \times 44$

$3H_2 + \frac{3}{2}O_2(g) \longrightarrow 3H_2O(l)$; $\Delta H = -286 \times 3$

$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$; $\Delta H = -2035$ kJ/mol.

For eq.(a),

$(-1941) = [(-2368) + 3(-241.8)] - [\Delta_f H^0_{B_2H_6(g)} + 3\times 0]$

$\therefore [\Delta_f H^0_{B_2H_6(g)} = -1152.4$ kJ/mol.

ANSWER KEY

EXERCISE-I

1. Ans.(D) 2. Ans.(A) 3. Ans. (D) 4. Ans.(B)
5. Ans.(B) 6. Ans. –741.5 kJ/mole
7. Ans. –3.502 kJ

EXERCISE-II

8. Ans. 602.49 kJ 9. (i) - 885 kJ/mol (ii) - 889.99 kJ/mol
10. W = 0, ΔU = –31.723 J

EXERCISE-III

11. Ans.(D) 12. Ans.(D) 13. Ans.(B) 14. Ans. (B)
15. Ans. (D) 16 Ans.(C) 17 Ans.(D) 18 Ans.(D)
19 Ans.(D) 20 129 kJ 21 –1560.1 kJ mol^{-1}

EXERISE-IV

21 Ans.(C) 22. Ans.(+ 20.6 kcal/mol.)
23. Ans. (400 kJ/mole) 24. Ans. – 119 kJ/mol
25. Ans.(B) 26. Ans.(C) 27 Ans.(C)
28 213 kJ / mol 29 Ans.(B) 30 Ans.(D)
31 Ans 132.5 kJ/mol 32 –207.5 kJ mol^{-1}

EXERCISE-V

33. Ans.(6) 34 Ans.(B)

EXERCISE-VI

35. Ans.(A) 36 Ans.(B) 37 – 19 kcal / mole
38 –352 kJ mol^{-1} 39 - 90.75 kcal mol^{-1}
40. for Cl^- - 384 kJ mol^{-1}, for I^- - 307 kJ mol^{-1}

MISCELLANEOUS PREVIOUS YEARS QUESTION

Q.1 Which of the following is not an endothermic reaction?

(A) Combustion of methane **[JEE 1999]**

(B) Decomposition of water

(C) Dehydrogenation of ethene to acetylene

(D) Conversion of graphite to diamond

Q.1 Ans.(A)

Sol. Combustion reaction is always an exothermic reaction

Q.2 Estimate the average S–F bond enthalpy in SF_6. The ΔH_f° values of SF_6 (g), S(g), and F (g) are – 1100 , 275 and 80 kJ/mol respectively. **[JEE 99, 5]**

Q.2 309.16 kJ/mol

Sol. $SF_6(g) \rightarrow S(g) + 6F(g)$

$$\Delta H^0_{rxn} = \Delta H^0_f[5(g)] + 6\Delta H^0_F[F(g)] - \Delta H_F[SF_6(g)]$$

$$\Delta H^0_{rxn} = 275 + (6 \times 80) + 1100$$

$$\Delta H^0_{rxn} = 1855$$

$$(S - F) = \frac{\Delta H^0_{rxn}}{6} = \frac{1855}{6} = 309.166 \text{ kJ/mol.}$$

Q.3 Diborane is a potential rocket fuel which undergoes combustion according to the reaction,

$$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$$

From the following data, calculate the enthalpy change for the combustion of diborane :**[JEE 2000]**

$2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s)$; $\Delta H = -1273$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta H = -286$ kJ

$H_2O(l) \longrightarrow H_2O(g)$; $\Delta H = 44$ kJ

$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g)$; $\Delta H = 36$ kJ

Q.3 –2035kJ mol^{-1}

Sol. $B_2H_6(g) \longrightarrow 2B(s) + 3H_2(g)$; $\Delta H = -36$ kJ

$2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s)$; $\Delta H = -1273$ kJ

$3H_2(g) + \frac{3}{2}O_2(g) \longrightarrow 3H_2(l)$; ΔH –8.58 kJ

$3H_2O(l) \longrightarrow 3H_2O_2(g)$; ΔH 132 kJ

$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$; $\Delta H = -2035$

Q.4 ΔH_f° for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are – 393.5, –110.5 and –241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction

$$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g) \text{ is}$$

(A) 524.1 (B) 41.2 (C) –262.5 (D) – 41.2 **[JEE 2000]**

Q.4 Ans.(B)

Sol. $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$

$$\Delta H^0_{rxn} = (\Delta H^0_f[CO(g)] + \Delta H^0_f[H_2O(g)]) - (\Delta H^0_f[CO_2(g)] + \Delta H^0_f[H_2O(g)])$$

$$\Delta H^0_{rxn} = (-110.5 - 241.8) - (-393.5 + 0)$$

$$= + 41.2 \text{ kJ/mol}$$

Q.5 Which of the following reactions defines ΔH_f° ?

(A) $C_{(diamond)} + O_2(g) \longrightarrow CO_2(g)$ (B) $1/2\ H_2(g) + 1/2\ F_2(g) \longrightarrow HF(g)$

(C) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3$ (D) $CO(g) + 1/2O_2(g) \longrightarrow CO_2(g)$ **[JEE 2003]**

Q.5 Ans.(B)

Sol. In the formation reaction, 1 mole proudcts should be formed from its elements and elements must be in their most abundance state this condition is fulfilled by options (B)

Q.6 In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1}, the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is

[JEE 2009]

Q.6 Ans.(9)

Sol. $q = (2.5)\ (0.45) = 1.125$

$$\Delta U_{combination} = (1.125)\left(\frac{28}{3.5}\right) = -9 kJ/mol$$

EXERCISE (S-I)

Relationship between ΔH & ΔU

Q.1 The enthalpy change for the reaction of 50 ml of ethylene with 50.0 ml of H_2 at 1.5 bar pressure is $\Delta H = -0.31$ KJ. What is the ΔU ? **TC0001**

Q.2 Ethyl chloride (C_2H_5Cl), is prepared by reaction of ethylene with hydrogen chloride:

$C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g)$ $\Delta H = -72.3$ kJ

What is the value of ΔE (in kJ), if 98 g of ethylene and 109.5 g of HCl are allowed to react at 300 K. **TC0002**

Q.3 Determine the amount of heat (in kcal) given off at constant volume when 0.5 mol of N_2 & 1.5 mol of H_2 reacted according to equation at 300 K.

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; $\Delta_r H_{300} = -380$ kcal/mol

(Given : R = 2 cal / mol-K) **TC0003**

Q.4 Ethyl chloride (C_2H_5Cl), is prepared by reaction of ethylene with hydrogen chloride :

$C_2H_4(g) + HCl(g) \longrightarrow C_2H_5Cl(g)$ $\Delta H = -72.3$ kJ/mol

What is the value of ΔU (in kJ), if 70 g of ethylene and 73 g of HCl are allowed to react at 300 K. **TC0004**

Q.5 Determine ΔH for the following reaction at 500K and constant pressure :

$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$

use the following data :

Substance	**C_p(J/mol K)**	**$\Delta_f H$(300K) (kJ/mol)**
CO (g)	29	–110
H_2O (g)	33	–241
CO_2 (g)	37	–393
H_2 (g)	29	0

TC0005

Enthalpy of formation and combustion

Q.6 When 2 moles of $C_2H_6(g)$ are completely burnt, 3120 kJ of heat is liberated . Calculate the enthalpy of formation, of $C_2H_6(g)$. Given $\Delta_f H$ for $CO_2(g)$ & $H_2O(l)$ are – 395 & – 286 kJ respectively. **TC0006**

Q.7 From the following data at 25°C, Calculate the standard enthalpy of formation of FeO(s) and of $Fe_2O_3(s)$.

Reaction	**$\Delta_r H^o$ (kJ/mole)**
(1) $Fe_2O_3(s) + 3C(graphite) \rightarrow 2Fe(s) + 3CO(g)$	492
(2) $FeO(s) + C(graphite) \rightarrow Fe(s) + CO(g)$	155
(3) $C(graphite) + O_2(g) \rightarrow CO_2(g)$	–393
(4) $CO(g) + 1/2\ O_2(g) \rightarrow CO_2(g)$	–282

TC0007

Q.8 At 300 K, the standard enthalpies of formation of $C_6H_5COOH(s)$, $CO_2(g)$ & $H_2O(l)$ are $-408, -393$ & -286 kJ mol^{-1} respectively . Calculate the heat of combustion of benzoic acid at : (i) constant pressure (ii) constant volume. **TC0008**

Q.9 A cylinder of gas is assumed to contains 11.6 kg of butane. If a normal family needs 26,500 kJ of energy per day for cooking, how long will the cylinder last if the enthalpy of combustion, $\Delta H = -2650$ kJ/mole for butane. **TC0009**

Q.10 0.821 *l* sample of a mixture of $CH_4(g)$ & $O_2(g)$ measured at 27° C & 760 torr was allowed to react at constant pressure in a calorimeter which together with its contents had a heat capacity of 1200 Cal/K. The complete combustion of methane to CO_2 & H_2O caused a temperature rise, in the calorimeter, of 0.25 K. What was the mole percent of CH_4 in the original mixture?

$\Delta H^\circ_{comb}(CH_4) = -200$ kcal mol^{-1} . **TC0010**

Bond Enthalpy

Q.11 Compute the enthalpy of formation of liquid methyl alcohol in kJ mol^{-1}, using the following data. Enthalpy of vaporisation of liquid $CH_3OH = 38$ kJ/ mol.

Enthalpy of formation of gaseous atoms from the elements in their standard states are

$H \rightarrow 218$ kJ / mol ; $C \rightarrow 715$ kJ / mol ; $O \rightarrow 249$ kJ / mol.

Bond Enthalpies

$C - H \rightarrow 415$ kJ / mol ; $C - O \rightarrow 356$ kJ / mol ; $O - H \rightarrow 463$ kJ / mol **TC0011**

Q.12 Find the enthalpy of S–S bond from the following data.

(i) $C_2H_5 - S - C_2H_5$ (g) $\Delta_f H^\circ = -150$ kJ/mol

(ii) $C_2H_5 - S - S - C_2H_5$ (g) $\Delta_f H^\circ = -200$ kJ/mol

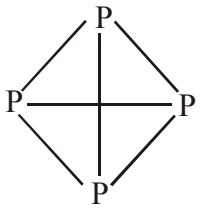
(iii) S (g) $\Delta_f H^\circ = 225$ kJ/mol **TC0012**

Q.13 The polymerisation of ethylene to linear polyethylene is represented by the reaction

$n\,CH_2 = CH_2(g) \rightarrow (-CH_2 - CH_2)_n(g)$

where n has a large integral value. Given that the average enthalpies of bond dissociation for C=C & C–C at 298 K are +590 & +331 kJ mol^{-1} respectively. Calculate the enthalpy of polymerisation per mole of ethylene at 298 K. **TC0013**

Q.14 White phosphorus is a tetra-atomic solid P_4 (s) at room temperature.



Find average (P –P) bond enthalpy in kJ/mol.

Given : $\Delta H_{sublimation}$ of P_4 (s) = 59 kJ/mol

$\Delta H_{atomisation}$ of P_4 (s) = 1265 kJ/mol **TC0014**

Q.15 Calculate enthalpy of combustion of propane [C_3H_8 (g)] in **kJ/mol** at 298 K.

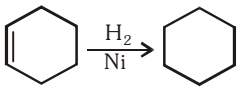
Given : B.E. (O = O) = 498 kJ/mole ; B.E. (C = O) = 804 kJ/mole

B.E. (C–H) = 410 kJ/mole ; B.E. (O–H) = 464 kJ/mole

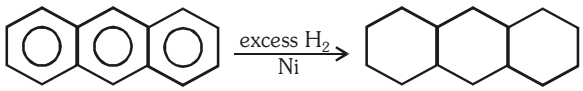
B.E. (C–C) = 345 kJ/mole ; Resonance energy of CO_2 (g) = – 143 kJ/mole

$\Delta H_{vaporization}$ (H_2O, *l*) = 41 kJ/mole **TC0015**

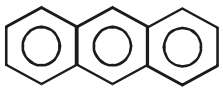
Q.16 Use the following data to answer the questions below :



; $\Delta H = -28.6$ Kcal mol^{-1} ;



; $\Delta H = -116.2$ Kcal mol^{-1}

Calculate the resonance energy of anthracene,  **TC0016**

Q.17 Calculate the magnitude of resonance enthalpy of $CO_2(g)$ from following data

$\Delta H^{\circ}_{combustion}[C_{(graphite)}] = -390$ kJ/mol

$\Delta H^{\circ}_{atomisation}[C_{(graphite)}] = 715$ kJ/mol

$\Delta H^{\circ}_{B.E.}[O=O] = 500$ kJ/mol

$\Delta H^{\circ}_{B.E.}[C=O] = 800$ kJ/mol **TC0017**

Other types of Enthalpy of reaction

Q.18 $H^+ + OH^- \longrightarrow H_2O$; $\Delta H^{\circ} = -57$ kJ/mol

$\Delta H^{0}_{ionisation}[HCN] = 45$ kJ/mol

If 200 ml , 1/10 M $Ba(OH)_2$ solution is mixed with 500 ml , 1/10M HCN, then evolved heat will be. **TC0018**

Q.19 The enthalpies of neutralization of NaOH & NH_4OH by HCl are – 13680 Cal/Eq and – 12270 Cal/Eq. respectively . What would be the enthalpy change if one gram equivalent of NaOH is added to one gram equivalent of NH_4Cl in solution ? Assume that NH_4OH and NaCl are quantitatively obtained. **TC0019**

Q.20 Two solutions initially at 25°C were mixed in an adiabatic constant pressure calorimeter. One contains 400 ml of 0.2 M weak monoprotic acid solution. The other contain 100 ml of 0.80 M NaOH. After mixing temperature increased to 26.2 °C. How much heat is evolved in the neutralization of 1 mole of acid? Assume density of solution 1.0 g/cm^3, and specific heat of solution 4.2 J/g-K. Neglect heat capacity of the calorimeter. **TC0020**

Q.21 If the enthalpy of formation of HCl (g) and Cl^- (aq) are –90 kJ/mole and – 170 kJ/mol, find the enthalpy of solution of hydrogen chloride gas. **TC0021**

Q.22 From the following data of ΔH of the following reactions

$C(s) + 1/2O_2(g) \longrightarrow CO(g)$; $\Delta H = -110$ kJ

and $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$; $\Delta H = 130$ kJ

Calculate the mole ratio of steam and oxygen on being passed over coke at 1273 K, keeping the reaction temperature constant. **TC0022**

Miscellaneous

Q.23 Lime is made commercially by decomposition of limestone, $CaCO_3$. What is the change in internal energy when 1.00 mole of solid $CaCO_3$(V = 34 ml) absorbs 180 kJ of heat and decomposes at certain temperature against a pressure of 1.0 bar to give solid CaO.(Volume = 16 ml) and $CO_2(g)$ (V = 20 L). **TC0023**

Q.24. One mole of solid Zn is placed in excess of dilute H_2SO_4 at 27°C in a cylinder fitted with a piston. Find the value of ΔU, q and w for the process if the area of piston is 500 cm^2 and it moves out by 50 cm against a pressure of 1 atm during the reaction. The heat given to surrounding is 36.5 kJ.

$Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$ **TC0024**

Q.25 For the gaseous reaction:

$3A + 2B \longrightarrow 4C$; $\Delta H = -300$ Cal/mol

If 5 moles of A are mixed with 4 moles of B at 300K, the magnitude of work involved in reaction is. **TC0025**

EXERCISE (S-II)

Q.1 The enthalpy of formation of $C_2H_5OH(l)$ is – 66 k Cal/mol . The enthalpy of combustion of $CH_3–O–CH_3$ is – 348 k Cal/mol . Given that the enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are – 94 k Cal/mol & – 68 kcal/mol respectively, calculate ΔH for the isomerisation of ethanol to methoxymethane. All data are at 25° C. **TC0026**

Q.2 Calculate the mass of mercury which can be liberated from HgO at 27° C by the treatment of excess HgO with 9 kJ of heat at (a) constant pressure , (b) constant volume
Given : ΔH_f° (HgO, s) = – 90 kJ mol^{-1} & Molar mass of (Hg) = 200 g mol^{-1} . **TC0027**

Q.3 A stoichiometric mixture of ferric oxide & Al is used as solid rocket fuel . Calculate the fuel value per gm & fuel value per CC of the mix . Enthalpy of formation & densities are :
ΔH_f° (Al_2O_3) = – 399 k Cal/mole ; ΔH_f° (Fe_2O_3) = – 199 kcal / mole,
density of Fe_2O_3 = 5.2 g/cc ; density of Al = 2.7 g/cc. **TC0028**

Q.4 Calculate the enthalpy change for the reaction : $XeF_4 \longrightarrow Xe^+ + F^- + F_2 + F$.
The average Xe–F bond enthalpy is 34 kcal/mol, first I.E. of Xe is 279 kcal/mol, electron affinity of F is 85 kcal/mol & bond dissociation enthalpy of F_2 is 38 kcal/mol. **TC0029**

Q.5 Calculate the enthalpy change when infinitely dilute solution of $CaCl_2$ and Na_2CO_3 are mixed $\Delta_f H°$ for Ca^{2+}(aq), CO_3^{2-} (aq) and $CaCO_3$ (s) are – 129, – 161, – 288 kcal mol^{-1} respectively. **TC0030**

Q.6 The enthalpy of formation of ethane(g), ethylene(g) and benzene(g) from the gaseous atoms are –2840, –2275 and –5530 kJmol^{-1} respectively. Calculate the magnitude of resonance energy of benzene. The bond enthalpy of C–H bond is given as equal to + 410 kJ/mol. **TC0031**

Q.7 Calculate the enthalpy of combustion of methyl alcohol (l) at 298 K from the following data

Bond	C – H	C – O	O – H	O = O	C = O
Bond Enthalpy(kJ mol^{-1})	414	351.5	464.5	494	711

Resonance energy of CO_2 = – 143 kJ mol^{-1}
Latent heat of vaporisation of methyl alcohol = 35.5 kJ mol^{-1}.
Latent heat of vaporisation of water = 40.6 kJ mol^{-1}. **TC0032**

Q.8 The bond enthalpies of C–C, C=C & C≡C bonds are 348, 610 & 835 kJ/mol respectively at 298K & 1 bar. What is of the enthalpy change of polymerisation at 298K & 1 bar per mole of 2-butyne?

$nCH_3–C \equiv C–CH_3(g) \rightarrow (–CH_2–CH=CH–CH_2–)_n$ (g)

['n' is a large integral value] **TC0033**

EXERCISE (O-I)

Relationship of ΔH & ΔU

Q.1 For a reaction, $2X(s) + 2Y(s) \rightarrow 2C(\ell) + D(g)$
The q_p at 27°C is – 28 Kcal mol^{-1}, the q_V is ---------- Kcal mol^{-1}
(A) – 27.4 (B) + 27.4 (C) – 28.6 (D) 28.6 **TC0034**

Q.2 Consider the reaction at 300 K
$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ $\Delta H = -185 kJ/mol$
Calculate ΔU if 3 mole of H_2 completely react with 3 mole of Cl_2 to form HCl.
(A) 0 (B) –185 kJ (C) 555 kJ (D) – 555 kJ **TC0035**

Enthalpy of formation and combustion

Q.3 Study the following thermochemical equations :
$A \rightarrow B$; $\Delta H = +100$ kcal
$B \rightarrow C$; $\Delta H = -80$ kcal
The correct order of enthalpies of formation of A, B and C is -
(A) A < B < C (B) A < C < B (C) C < A < B (D) B < C < A **TC0036**

Q.4 $N_2(g) + 2O_2(g) \rightarrow 2NO_2$ $\Delta H = +x$ kJ
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta H = +y$ kJ
The enthalpy of formation of NO is
(A) (2x – 2y) kJ/mol (B) (x – y) kJ/mol (C) $\frac{1}{2}(y-x)$ kJ/mol (D) $\frac{1}{2}(x-y)$ kJ/mol **TC0037**

Q.5 $2NO_2(g) \rightarrow N_2O_4(g)$; $\Delta U^\circ_f [N_2O_4(g)] = 2$kcal/ mole and $\Delta U^\circ_{reaction} = -16$ kcal /mol then calculate $\Delta H^\circ_{formation}$ of NO_2 at 727ºC
(A) 9 kcal /mol (B) 4.5 kcal /mol (C) 8 kcal /mol (D) 10 kcal /mol **TC0038**

Q.6 Find $\Delta_r U°$ for the reaction $4HCl(g) + O_2(g) \rightarrow 2Cl_2(g) + 2H_2O(g)$ at 300 K. Assume all gases are ideal.
Given: $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ $\Delta_r H^\circ_{300} = -184.5$ kJ/mole
$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$ $\Delta_r H^\circ_{300} = -483$ kJ/mole (Use R = 8.3 J/mole)
(A) 111.5 kJ/mole (B) –109.01 kJ/mole (C) –111.5 kJ/mole (D) –114 kJ/mole **TC0039**

Q.7 What amount of heat energy (kJ) is released in the combustion of 12.0 g of C_3H_4 at 1atm constant pressure.
$C_3H_4(g) + 4O_2(g) \rightarrow 3CO_2(g) + 2H_2O(l)$; $\Delta H^\circ = -1939$ kJ
(A) 696.3 (B) 1939 (C) 6463.3 (D) 581.7 **TC0040**

Q.8 $NH_3(g) + 3Cl_2(g) \rightarrow NCl_3(g) + 3HCl(g)$; ΔH_1
$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; ΔH_2
$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$; ΔH_3
The enthalpy of formation of $NCl_3(g)$ in the terms of ΔH_1, ΔH_2 and ΔH_3 is
(A) $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$ (B) $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$
(C) $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$ (D) $\Delta H_f = \Delta H_1 + \Delta H_2 - \Delta H_3$ **TC0041**

Bond enthalpy

Q.9 The bond dissociation energy of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. The enthalpy of formation for HCl gas will be :-

(A) –44.0 kcal/mol (B) –22.0 kcal/mol (C) 22.0 kcal/mol (D) 44.0 kcal/mol **TC0042**

Q.10 The reaction $CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$ has $\Delta H = -25$ kcal.

Bond	Bond Enthalpy kCal
$\varepsilon_{C—Cl}$	84
$\varepsilon_{H—Cl}$	103
$\varepsilon_{C—H}$	x
$\varepsilon_{Cl—Cl}$	y
x : y = 9 : 5	

From the given data, what is the bond enthalpy of Cl—Cl bond

(A) 70 kcal/mol (B) 80 kcal/mol (C) 67.75 kcal/mol (D) 57.86 kcal/mol **TC0043**

Q.11 If x_1, x_2 and x_3 are enthalpies of H–H, O=O and O–H bonds respectively, and x_4 is the enthalpy of vaporisation of water, estimate the standard enthalpy of combustion of hydrogen

(A) $x_1+\frac{x_2}{2}-2x_3+x_4$ (B) $x_1+\frac{x_2}{2}-2x_3-x_4$ (C) $x_1+\frac{x_2}{2}-x_3+x_4$ (D) $2x_3-x_1-\frac{x_2}{2}-x_4$ **TC0044**

Q.12 If bond enthalpy of C–C and C = C are 348 kJ /mole and 615 kJ/mole respectively then calculate enthalpy change (in kJ/mole) which occurs during the isomerisation of cyclopropane (g) into propene(g)

(A) –267 (B) 81 (C) –81 (D) 267 **TC0045**

Q.13 If enthalpy change for hydrogenation of ethylene is –132 kJ/mole and enthalpy of formation 1,3-butadiene (g) and butane (g) are 115 kJ and –140 kJ/mole respectively then calculate resonance energy of 1,3-budadiene (in kJ).

(A) 9 (B) 18 (C) 4 (D) 10 **TC0046**

Q.14 Given the correct order of initials **T** (true) or **F** (false) for following statements.

(i) For the reaction $CaCO_3$ (Calcite) $\rightarrow$ $CaCO_3$ (aragonite) ; $\Delta H = -1127.75$ kJ/mol, then Calcite form is more stable at standard conditions.

(ii) For the reaction,

(a) $C(diamond) + 2H_2(g) \rightarrow CH_4(g)$; ΔH_1

(b) $C(g) + 4H(g) \rightarrow CH_4(g)$; ΔH_2

then more heat is evolved in reaction (b)

(iii) $\Delta_f H°\ (I_2,g) = \Delta_{sub}H\ [I_2, s]$ at 25°C

(iv) For the exothermic reaction $2Ag(s) + 1/2\ O_2(g) \rightarrow 2Ag_2O(s)$ at 298 K. $\Delta H < \Delta U$

(A) FTTT (B) TTFT (C) TFTF (D) TTTT **TC0047**

Q.15 $\Delta_r H$ of which of the following reactions is zero ?

(A) $H_2(g) \rightarrow 2H^+(g) + 2e^-$ (B) $2H(g) + aq \rightarrow 2H^+(aq) + 2e^-$

(C) $2H(g) \rightarrow 2H^+(g) + 2e^-$ (D) $H_2(g) + aq \rightarrow 2H^+(aq) + 2e^-$ **TC0048**

Q.16 ΔH_f^0 of water is – 285.8 kJ mol^{-1}. If enthalpy of neutralisation of monoacid strong base and mono basic strong acid is –57.3 kJ mol^{-1}, ΔH_f^0 of OH^- ion will be

(A) – 228.5 kJ mol^{-1} (B) 228.5 kJ mol^{-1} (C) 114.25 kJ mol^{-1} (D) –114.25 kJ mol^{-1} **TC0049**

Q.17 Ethanol can undergoes decomposition to form two sets of products

$$C_2H_5OH\,(g) \longrightarrow \begin{cases} \xrightarrow{1} C_2H_4(g) + H_2O\,(g) \quad ; \quad \Delta H^\circ = 45 \text{ kJ} \\ \xrightarrow{2} CH_3CHO(g) + H_2\,(g) \; ; \quad \Delta H^\circ = 63 \text{ kJ} \end{cases}$$

if the molar ratio of C_2H_4 to CH_3CHO is 8 : 1 in a set of product gases, then the enthalpy involved in the decomposition of 1 mole of ethanol is

(A) 423 kJ (B) 47 kJ (C) 61 kJ (D) 549 kJ **TC0050**

Q.18 The enthalpy changes of the following reactions at 27°C are

$$Na(s) + \frac{1}{2}Cl_2\,(g) \longrightarrow NaCl\,(s) \qquad \Delta_rH = -411 \text{ kJ/mol}$$

$$H_2(g) + S\,(s) + 2O_2\,(g) \longrightarrow H_2SO_4\,(l) \qquad \Delta_rH = -811 \text{ kJ/mol}$$

$$2Na(s) + S(s) + 2O_2\,(g) \longrightarrow Na_2SO_4\,(s) \qquad \Delta_rH = -1382 \text{ kJ/mol}$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl\,(g) \qquad \Delta_rH = -92 \text{ kJ/mol;}$$

from these data, the heat change of reaction at constant volume (in kJ/mol) at 27°C for the process $2NaCl\,(s) + H_2SO_4\,(l) \longrightarrow Na_2SO_4\,(s) + 2HCl\,(g)$ is (R = 8.3 J/K-mol)

(A) 67 (B) 62.02 (C) 71.98 (D) 64.51 **TC0051**

Q.19 Reactions involving gold have been of particular interest to a chemist . Consider the following reactions,

$Au(OH)_3 + 4\,HCl \longrightarrow HAuCl_4 + 3\,H_2O$, $\Delta H = -28$ kcal

$Au(OH)_3 + 4\,HBr \longrightarrow HAuBr_4 + 3\,H_2O$, $\Delta H = -36.8$ kcal

In an experiment there was an absorption of 0.44 kcal when one mole of $HAuBr_4$ was mixed with 4 moles of HCl . What is the percentage conversion of $HAuBr_4$ into $HAuCl_4$?

(A) 0.5 % (B) 0.6 % (C) 5 % (D) 50 % **TC0052**

EXERCISE (O-II)

Single Correct :

Q.1 What is the ratio of the enthalpy yield on combustion of hydrogen atoms to steam to the yield on combustion of an equal mass of hydrogen molecules to steam?

Given: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$; $\Delta H = -242$ kJ

B.E. (H – H) = 436 kJ

(A) 0.80 : 1 (B) 1 : 0.80 (C) 1.80 : 1 (D) 2.80 : 1 **TC0053**

Q.2 For the allotropic change represented by the equation C (graphite) $\longrightarrow$ C (diamond), $\Delta H = 1.9$ kJ. If 6 g of diamond and 6 g of graphite are separately burnt to yield CO_2, the heat liberated in first case is

(A) less than in the second case by 1.9 kJ (B) more than in the second case by 11.4 kJ

(C) more than in the second case by 0.95 kJ (D) less than in the second case by 11.4 kJ **TC0054**

Q.3 (i) Cis–2 – butene $\rightarrow$ trans – 2 – butene, ΔH_1

(ii) Cis – 2– butene $\rightarrow$ 1 – butene, ΔH_2

(iii) Enthalpy of combustion of 1–butene, $\Delta H = -649.8$ kcal/mol

(iv) $9\Delta H_1 + 5\,\Delta H_2 = 0$

(v) Enthalpy of combustion of trans 2 – butene, $\Delta H = -647.0$ kcal/mol.

The value of ΔH_1 & ΔH_2 in Kcal/mole are

(A) –1.0 , 1.8 (B) 1.8, -1.0 (C) –5, 9 (D) –2, 3.6 **TC0055**

Q.4 Hydrazine, a component of rocket fuel, undergoes combustion to yield N_2 and H_2O.

$N_2H_4\,(l) + O_2\,(g) \longrightarrow N_2\,(g) + 2H_2O\,(l)$

What is the enthalpy change of combustion of N_2H_4 (kJ/mole)

Given Reaction	**ΔH/kJ**
$2NH_3\,(g) + 3N_2O\,(g) \longrightarrow 4N_2\,(g) + 3H_2O\,(l)$	– 1011 kJ
$N_2O\,(g) + 3H_2\,(g) \longrightarrow N_2H_4\,(l) + H_2O\,(l)$	– 317 kJ
$4NH_3\,(g) + O_2\,(g) \longrightarrow 2N_2H_4\,(l) + 2H_2O\,(l)$	– 286 kJ
$H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l)$	– 285 kJ

(A) – 620.5 (B) – 622.75 (C) 1167.5 (D) + 622.75 **TC0056**

Q.5 The enthalpy change for the reaction,

$CH_3CHO\,(g) \rightarrow CH_4(g) + CO(g)$ at 300 K is – 17.0 kJ/mol

Calculate the temperature at which $\Delta_r H$ for the reaction will be zero.

[Given : $C_{p,m}\,(CH_4,g) = 38$ J/K mol ; $C_{p,m}\,(CO, g) = 31$ J/K mol & $C_{p,m}\,(CH_3CHO,g) = 52$ J/K mol]

(A) 1300°C (B) 1027°C (C) 700°C (D) 754°C **TC0057**

More than one may correct

Q.6 Select the correct option -

(A) $\Delta H_f(H(g))$ is equal to $\Delta H_{atomisation}$ of $H_2(g)$

(B) $\Delta H_{BE}(H–H)$ is equal to ΔH_f of $H(g)$

(C) $\Delta H_{BE}(H–H)$ is equal to $\Delta H_{atomisation}$ of $H_2(g)$

(D) $\Delta H_{combustion}[H_2(g)]$ is equal to $\Delta H_f[H_2O(\ell)]$ at 300K **TC0058**

Q.7 Which of the following statement is (are) correct ?

(A) for any reaction $\Delta_r H^o = \sum \Delta_f H^0_{product} - \sum \Delta_f H^0_{reactant}$

(B) ΔH_f° of $CO_2(g)$ is same as the $\Delta H°_{comb.}$ of carbon graphite

(C) All exothermic gaseous reactions , $\sum (B.E.)_{reactants} > \sum (B.E.)_{products}$

(D) for a reaction $N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$, the heat at constant pressure and the heat at constant volume at a given temperature are same **TC0059**

Q.8 Which of the following do(es) not represent ΔH^0 formation of the product.

(A) $H_2(g) + I_2(s) \longrightarrow 2HI(g)$ (B) $\frac{2}{3}O_3(g) \longrightarrow O_2(g)$

(C) $NH_4^+(g) + Cl^-(g) \longrightarrow NH_4Cl(s)$ (D) $P_4(\text{black}) + 5O_2(g) \longrightarrow P_4O_{10}(s)$

(E) Reaction representing $\Delta H_{combustion}$ of C (graphite). **TC0060**

Q.9 From the following data at 25°C

Reaction	**$\Delta_r H°$ kJ/mol**
$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \longrightarrow OH(g)$	42
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$	–242
$H_2(g) \longrightarrow 2H(g)$	436
$O_2(g) \longrightarrow 2O(g)$	495

Which of the following statement(s) is/are correct:

(A) $\Delta_r H°$ for the reaction $H_2O(g) \longrightarrow 2H(g) + O(g)$ is 925.5 kJ/mol

(B) $\Delta_r H°$ for the reaction $OH(g) \longrightarrow H(g) + O(g)$ is 502 kJ/mol

(C) Enthalpy of formation of H(g) is –218 kJ/mol

(D) Enthalpy of formation of OH(g) is 42 kJ/mol **TC0061**

Match the column :

Q.10

Column–I		**Column–II**	
(A)	$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$	(P)	$\Delta H^0_{formation}$
(B)	$C(\text{graphite}) \rightarrow C(\text{gas})$	(Q)	$\Delta H^0_{combustion}$
(C)	$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(\ell)$	(R)	$\Delta H^0_{atomization}$
(D)	$CH_4(g) \rightarrow C(g) + 4H(g)$	(S)	$\Delta H^0_{neutralization}$

TC0062

Match list :

Q.11 Match the enthalpy change (ΔH) mentioned in list-II for 16 gm O_2 with the various reaction in list-I.

List-I		**List-II (ΔH in kJ)**
(P)	$2C_2H_2 + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l)$, ΔH– 2601 kJ	(A) –285.8
(Q)	$H_2(g) + 1/2O_2(g) \longrightarrow H_2O(g)$, ΔH= – 285.8 kJ	(B) –196.75
(R)	$3FeO(s) + 1/2O_2(g) \longrightarrow Fe_3O_4(s)$, ΔH = –302.4 kJ	(C) –260.1
(S)	$C_{graphite} + O_2(g) \longrightarrow CO_2(g)$, ΔH = –393.5 kJ	(D) –302.4

Code :

	P	**Q**	**R**	**S**
(A)	4	1	3	2
(B)	3	1	4	2
(C)	3	4	1	2
(D)	2	3	1	4

TC0063

Passage (Q. 12 to Q.13)

Bond dissociation enthalpy of the first H–S bond in hydrogen sulphide is 376 kJ/mole. The enthalpies of formation of $H_2S(g)$ and S(g) are –20.0 and 277.0 kJ/mole respectively. The enthalpy of formation of gaseous hydrogen atom is 218 kJ/mole. Using above information, answer following questions :

Q.12 The enthalpy of formation of free radical HS is

(A) 138 kJ/mole (B) –138 kJ/mole (C) –10 kJ/mole (D) 357 kJ/mole **TC0064**

Q.13 The bond dissociation enthalpy of the free radical HS is

(A) 138 kJ/mole (B) 276 kJ/mole (C) 357 kJ/mole (D) 376 kJ/mole **TC0064**

Paragraph for Q.14 to Q.15

Amount of heat evolved during complete combustion of liquid benzene can be calculated from the following data.

(i) 18 gm of graphite on complete combustion evolve 591 kJ heat

(ii) $\Delta H_f^{\circ}(H_2O, \ell) = -286$ kJ/mol

(iii) The heat of formation of liquid benzene is 50 kJ /mole

Q.14 Heat of formation of $CO_2(g)$ from following data is-

(A) –286 kJ/mole (B) –590 kJ/mole (C) –394 kJ/mole (D) –3268 kJ/mole **TC0065**

Q.15 Find heat evolved from combustion of 78 gm benzene

(A) 3272 kJ (B) 6345 kJ (C) 4536 kJ (D) 5364 kJ **TC0065**

Table Type Question :

Column-I	**Column-II**	**Column-III**
(Reactions)	**(Characteristics)**	**(Characteristics)**
(I) $C(s) + O_2(g) \rightarrow CO_2(g)$	(i) ΔH = +ve	(P) $\Delta H > \Delta E$
(II) $SO_3(g) \rightarrow SO_2(g) + \frac{1}{2}O_2(g)$	(ii) Δn_g = +ve	(Q) $\lvert \Delta H \rvert > \lvert \Delta E \rvert$
(III) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$	(iii) Δn_g = –ve	(R) $\Delta H < \Delta E$
(IV) $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$	(iv) ΔH = –ve	(S) $\lvert \Delta H \rvert < \lvert \Delta E \rvert$

Q.16 Which of the following is only correct match ?
(A) I , i , P (B) II , ii , Q (C) III , iii , S (D) IV , iv , R **TC0066**

Q.17 Which of the following is only incorrect match ?
(A) II , i , P (B) III , iv , R (C) IV , iii , S (D) II , ii , Q **TC0066**

Q.18 Which of the following is only correct match ?
(A) I , ii , Q (B) II , iii , Q (C) III , iv , S (D) IV , ii , P **TC0066**

EXERCISE-J-MAIN

1. Consider the reaction : **[AIEEE-2011]**

$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g)$, $\Delta_rH = -111kJ$.

If $N_2O_5(s)$ is formed instead of $N_2O_5(g)$ in the above reaction, the Δ_rH value will be :-

(given, ΔH of sublimation for N_2O_5 is 54 kJ mol^{-1})

(1) –165 kJ (2) +54 kJ (3) +219 kJ (4) –219 kJ **TC0067**

2. The value of enthalpy change (ΔH) for the reaction

$C_2H_5OH_{(\ell)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(\ell)}$

at 27°C is –1366.5 kJ mol^{-1}. The value of internal energy change for the above reaction at this temperature will be :- **[AIEEE-2011]**

(A) –1371.5 kJ (B) –1369.0 kJ (C) –1364.0 kJ (D) –1361.5 kJ **TC0068**

3. The enthalpy of neutralisation of NH_4OH with HCl is –51.46 kJ mol^{-1} and the enthalpy of neutralisation of NaOH with HCl is –55.90 kJ mol^{-1}. The enthalpy of ionisation of NH_4OH is:

[JEE-MAINS (online) 2012]

(1) +107.36 kJ mol^{-1} (2) –4.44 kJ mol^{-1} (3) –107.36 kJ mol^{-1} (4) +4.44 kJ mol^{-1}

TC0069

4. Given **[JEE-MAINS (online) 2013]**

Reaction	**Energy Change (in kJ)**
$Li(s) \longrightarrow Li(g)$	161
$Li(g) \longrightarrow Li^+(g)$	520
$\frac{1}{2}F_2(g) \longrightarrow F(g)$	77
$F(g) + e^- \longrightarrow F^-(g)$	(Electron gain enthalpy)
$Li^+(g) + F^-(g) \longrightarrow LiF(s)$	–1047
$Li(s) + \frac{1}{2}F_2(g) \longrightarrow Li\,F(s)$	–617

Based on data provided, the value of electron gain enthalpy of fluorine would be :

(1) –300 kJ mol^{-1} (2) –328 kJ mol^{-1} (3) –350 kJ mol^{-1} (4) –228 kJ mol^{-1} **TC0070**

5. Given : **[JEE-MAINS (online) 2013]**

(1) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta H^\circ_{298K} = -285.9$ kJ mol^{-1}

(2) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$; $\Delta H^\circ_{298K} = -241.8$ kJ mol^{-1}

The molar enthalpy of vapourisation of water will be :-

(1) 241. 8 kJ mol^{-1} (2) 527.7 kJ mol^{-1} (3) 44.1 kJ mol^{-1} (4) 22.0 kJ mol^{-1} **TC0071**

6. The standard enthalpy of formation ($\Delta_fH^\circ_{298}$) for methane, CH_4 is– 74.9 kJ mol^{-1}. In order to calculate the average energy given out in the formation of a C–H bond from this it is necessary to know which one of the following? **[JEE-MAINS(online) 2014]**

(1) the dissociation energy of the hydrogen molecule, H_2.

(2) the dissociation energy of H_2 and enthalpy of sublimation of carbon (graphite).

(3) the first four ionisation energies of carbon and electron affinity of hydrogen.

(4) the first four ionisation energies of carbon. **TC0072**

7. For complete combustion of ethanol, $C_2H_5OH(\ell) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$, the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25°C. Assuming ideality the Enthalpy of combustion, Δ_cH, for the raction will be :- **[JEE-MAINS(offline)2014]**
($R = 8.314$ J mol^{-1})
(1) –1460.50 kJ mol^{-1} (2) – 1350.50 kJ mol^{-1} (3) – 1366.95 kJ mol^{-1} (4) – 1361.95 kJ mol^{-1} **TC0073**

8. The heats of combustion of carbon and carbon monoxide are – 395.5 and – 285.5 kJ mol^{-1}, respectively. The heat of formation (in kJ) of carbon monoxide per mole is :- **[JEE-MAINS(offline)2016]**
(1) – 110.5 (2) 110.5 (3) 676.5 (4) – 676.5 **TC0074**

9. The enthalpy change on freezing of 1 mol of water at 5°C to ice at –5°C is :
(Given $\Delta_{fus}H = 6$ kJ mol^{-1} at 0°C, $C_P(H_2O, l) = 75.3$ J mol^{-1} K^{-1}, $C_P(H_2O, s) = 36.8$ J mol^{-1} K^{-1})
[JEE-MAINS(online)2017]
(1) 6.56 kJ mol^{-1} (2) 5.81 kJ mol^{-1} (3) 6.00 kJ mol^{-1} (4) 5.44 kJ mol^{-1} **TC0075**

10. Given **[JEE-MAINS(offline)2017]**
$C_{(grahite)} + O_2(g) \rightarrow CO_2(g)$;
$\Delta_rH° = -393.5$ kJ mol^{-1}

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$;

$\Delta_rH° = -285.8$ kJ mol^{-1}
$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$;
$\Delta_rH° = +890.3$ kJ mol^{-1}
Based on the above thermochemical equations, the value of $\Delta_rH°$ at 298 K for the reaction
$C_{(grahite)} + 2H_2(g) \rightarrow CH_4(g)$ will be :-
(1) +74.8 kJ mol^{-1} (2) +144.0 kJ mol^{-1} (3) –74.8 kJ mol^{-1} (4) –144.0 kJ mol^{-1} **TC0076**

11. The combustion of benzene (l) gives $CO_2(g)$ and $H_2O(l)$. Given that heat of combustion of benzene at constant volume is –3263.9 kJ mol^{-1} at 25° C ; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be - **[JEE-MAINS(offline)2018]**
($R = 8.314$ JK^{-1} mol^{-1})
(1) –452.46 (2) 3260 (3) –3267.6 (4) 4152.6 **TC0077**

12. Given **[JEE-MAINS(online)2018]**
(i) $2Fe_2O_3(s) \rightarrow 4Fe(s) + 3O_2(g)$;
$\Delta_rG° = +1487.0$ kJ mol^{-1}
(ii) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$;
$\Delta_rG° = -514.4$ kJ mol^{-1}
Free energy change, $\Delta_rG°$ for the reaction
$2Fe_2O_3(s) + 6CO(g) \rightarrow 4Fe(s) + 6CO_2(g)$
will be :-
(1) –112.4 kJ mol^{-1} (2) –56.2 kJ mol^{-1} (3) 168.2 kJ mol^{-1} (4) 208.0 kJ mol^{-1} **TC0078**

13. Given : **[JEE-MAINS(online)2019]**

(i) $C(graphite) + O_2(g) \rightarrow CO_2(g)$;

$\Delta rH° = x \text{ kJ mol}^{-1}$

(ii) $C(graphite) + \frac{1}{2}O_2(g) \rightarrow CO(g)$;

$\Delta rH° = y \text{ kJ mol}^{-1}$

(iii) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$;

$\Delta rH° = z \text{ kJ mol}^{-1}$

Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct ?

(1) z = x + y (2) x = y – z (3) x = y + z (4) y = 2z – x **TC0079**

14. The difference between ΔH and ΔU (ΔH–ΔU), when the combustion of one mole of heptane (1) is carried out at a temperature T, is equal to: **[JEE-MAINS-(ONLINE)-2019]**

(1) 3RT (2) –3RT (3) –4RT (4) 4RT **TC0080**

15. Enthalpy of sublimation of iodine is 24 cal g^{-1} at 200°C. If specific heat of $I_2(s)$ and $I_2(vap)$ are 0.055 and 0.031 cal $g^{-1}K^{-1}$ respectively, then enthalpy of sublimation of iodine at 250°C in cal g^{-1} is :

[JEE-MAINS(online)2019]

(1) 2.85 (2) 11.4 (3) 5.7 (4) 22.8 **TC0081**

16. The standard heat of formation $\left(\Delta_f H^0_{298}\right)$ of ethane in (kJ/mol), if the heat of combustion of ethane, hydrogen and graphite are –1560, –393.5 and –286 kJ/mol, respectively is _____ **TC0082**

[JEE-MAINS(online)2020]

17. If enthalpy of atomisation for $Br_{2(1)}$ is x kJ/mol and bond enthalpy for Br_2 is y kJ/mol, the relation between them : **[JEE-MAINS(online)2020]**

(1) is x = y (2) is x < y (3) does not exist (4) is x > y **TC0083**

18. Lattice enthalpy and enthalpy of solution of NaCl are 788 kJ mol^{-1} and 4 kJ mol^{-1}, respectively. The hydration enthalpy of NaCl is : **[JEE-MAINS(online)2020]**

(1) –780 kJ mol^{-1} (2) –784 kJ mol^{-1} (3) 780 kJ mol^{-1} (4) 784 kJ mol^{-1} **TC0084**

19. The heat of combustion of ethanol into carbon dioxides and water is –327 kcal at constant pressure. The heat evolved (in cal) at constant volume and 27°C (if all gases behave ideally) is (R = 2 cal mol^{-1} K^{-1}) **[JEE-MAINS(online)2020]**

TC0085

20. The internal energy change (in J) when 90g of water undergoes complete evaporation at 100°C is ____.

(Given : ΔH_{vap} for water at 373 K = 41 kJ/mol, R = 8.314 JK^{-1} mol^{-1}) **[JEE-MAINS(online)2020]**

TC0086

EXERCISE (J-ADVANCE)

Q.1 Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a C ≡ C bond in C_2H_2. That energy is (take the bond energy of a C–H bond as 350 kJ mol^{-1}.) **[JEE 2012]**

$2\ C(s) + H_2(g) \longrightarrow C_2H_2(g)$ $\Delta H = 225\ kJ\ mol^{-1}$

$2\ C(s) \longrightarrow 2C(g)$ $\Delta H = 1410\ kJ\ mol^{-1}$

$H_2(g) \longrightarrow 2H(g)$ $\Delta H = 330\ kJ\ mol^{-1}$

(A) 1165 (B) 837 (C) 865 (D) 815 **TC0087**

Q.2. The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose(s) at 25°C are –400 kJ/mol, –300 kJ/mol & –1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25°C is - **[JEE 2013]**

(A) + 2900 kJ (B) – 2900 kJ (C) –16.11 kJ (D) + 16.11 kJ **TC0088**

Paragraph For Questions 3 and 4

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7 °C was measured for the beaker and its contents. **(Expt-1).** Because the enthalpy of neutralisation of a strong acid with a strong base is a constant (–57.0 kJmol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment **(Expt-2)**, 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0M NaOH (under identical conditions to **(Expt-1))** where a temperature rise of 5.6 °C was measured. (Consider heat capacity of all solutions as 4.2 $Jg^{-1}K^{-1}$ and density of all solutions as 1.0 g mL^{-1}) **[JEE 2015]**

Q.3 Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the **Expt-2** is

(A) 1.0 (B) 10.0 (C) 24.5 (D) 51.4 **TC0089**

Q.4 The pH of the solution after **Expt-2**

(A) 2.8 (B) 4.7 (C) 5.0 (D) 7.0 **TC0089**

Q.5 Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation. **[JEE 2019]**

(1) $\frac{3}{2}O_2(g) \rightarrow O_3(g)$ (2) $\frac{1}{8}S_8(s) + O_2(g) \rightarrow SO_2(g)$

(3) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ (4) $2C(g) + 3H_2(g) \rightarrow C_2H_6(g)$ **TC0090**

ANSWER KEY

EXERCISE (S-I)

Q.1 Ans. – 0.3025 kJ
Q.2 Ans. –209.41
Q.3 Ans. 189.4 kcal
Q.4 –139.6
Q.5 ΔH = – 41.2 kJ
Q.6 – 88 kJ/mol
Q.7 –266 kJ/mol and –825 kJ/mol
Q.8 (i) - 3201 kJ/mol (ii) - 3199.75 kJ/mol
Q.9 20 days
Q.10 4.5%
Q.11 - 266 kJ mol^{-1}
Q.12 275 kJ/mol
Q.13 - 72 kJ mol^{-1}
Q.14 Ans. 201
Q.15 Ans. (–2669)
Q.16 Ans. (–84 kcal / mol)
Q.17 Ans. (5 kJ/mol)
Q.18 Ans. (480 J)
Q.19 — 1410 Cal
Q.20 31.5 kJ/mole
Q.21 – 80 kJ/mole
Q.22 22 : 13
Q.23 Ans. 178 kJ
Q.24 Ans. ΔU = –39.03 kJ ; q = –36.5 kJ; w = –2.53 kJ
Q.25 1000 Cal

EXERCISE (S-II)

Q.1 22 kcal mol^{-1}
Q.2 (a) 20 g (b) 20.28 g
Q.3 0.935 kcal g^{-1}, 3.94 kcal cm^{-3}
Q.4 292 kcal/mol
Q.5 2 kcal
Q.6 25 kJ/mol
Q.7 – 669.7 kJ mol^{-1}
Q.8 Ans. –123 kJ/mol

ΔH = 835 – 610 = 348
= – 123

EXERCISE (O-I)

Q.1 Ans.(C)	**Q.2** Ans.(D)	**Q.3** Ans.(B)	**Q.4** Ans.(D)
Q.5 Ans. (C)	**Q.6** Ans.(C)	**Q.7** Ans.(D)	**Q.8** Ans.(B)
Q.9 Ans.(B)	**Q.10** Ans.(D)	**Q.11** Ans.(B)	**Q.12** Ans. (B)
Q.13 Ans. (A)	**Q.14** Ans. (A)	**Q.14** Ans. (D)	**Q.16** Ans.(A)
Q.17 Ans.(B)	**Q.18** Ans.(B)	**Q.19** Ans.(C)	

EXERCISE (O-II)

Q.1 Ans.(D)	**Q.2** Ans.(C)	**Q.3** Ans.(A)	**Q.4** Ans.(A)
Q.5 Ans.(B)	**Q.6** Ans.(C, D)	**Q.7** Ans.(A, B, D)	**Q.8** Ans.(A,B,C,D)
Q.9 Ans.(A,D)			

Q.10 Ans. (A) P, Q ; (B) P, R ; (C) S, D - (R) **Q.11 Ans.(B)**

Q.12 Ans. (A) **Q.13 Ans.(C)** **Q.14 Ans.(C)** **Q.15. Ans.(A)**

Q.16 Ans.(B) **Q.17 Ans.(C)** **Q.18 Ans.(D)**

EXERCISE-J-MAIN

Q.1. Ans.(4) **Q.2. Ans.(C)** **Q.3. Ans.(4)** **Q.4. Ans.(2)**

Q.5. Ans.(3) **Q.6. Ans.(2)** **Q.7. Ans.(3)** **Q.8. Ans.(1)**

Q.9. Ans.(1) **Q.10. Ans.(3)** **Q.11. Ans.(3)** **Q.12. Ans.(2)**

Q.13 Ans.(3) **Q.14. Ans.(3)** **Q.15 Ans.(4)** **Q.16. (–192.50)**

Q.17. Ans.(4) **Q.18 Ans.(2)** **Q.19 Ans.(–326400.00)**

Q.20 Ans.(189494.00)

EXERCISE (J-ADVANCE)

Q.1 Ans.(D) **Q.2 Ans.(C)** **Q.3 Ans. (A)** **Q.4 Ans. (B)**

Q.5 Ans.(1,2)