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Thermochemistry

The chapter deals with thermal as well as chemical changes during the course of reaction.

The thermochemical equation : 1. A thermochemical equation represents the thermal changes as well as chemical changes taking place during the course of reaction, *e.g.*,

$$C + O_2 \longrightarrow CO_2; \qquad \Delta H = -94.3 \text{ kcal}$$

2. A thermochemical equation is treated as an algebraic equation for all practical purposes, *e.g.*, it may be added, subtracted, multiplied or divided as the case may be.

3. A thermochemical equation should always be written in mole and never in g.

Exothermic and Endothermic reactions

For a given chemical change

$$A + B \longrightarrow C + D$$

Change in internal energy during reaction (ΔU)
= Internal energy of products – Internal energy of reactants

i.e., $\Delta U = \Sigma U_P - \Sigma U_R$

if $\Delta U = +\text{ve}$; the reaction is endothermic

if $\Delta U = -\text{ve}$; the reaction is exothermic

The exothermic and endothermic nature are expressed as

Exothermic : $C + O_2 \longrightarrow CO_2; \quad \Delta U = -94.3 \text{ kcal}$

or $C + O_2 \longrightarrow CO_2 + 94.3 \text{ kcal}$

Endothermic : $C + 2S \longrightarrow CS_2; \quad \Delta U = +22 \text{ kcal}$

or $C + 2S \longrightarrow CS_2 - 22 \text{ kcal}$

Heat of reaction : It is defined as,

—the amount of heat absorbed or released (*i.e.*, the change in internal energy or the change in heat enthalpy)

during the complete course of reaction as represented by balanced chemical equation *e.g.*,

$$C + O_2 \longrightarrow CO_2; \qquad \Delta H = -94.3 \text{ kcal}$$

i.e., 12 g C reacts with 32 g O_2 to give 44 g CO_2 along with 94.3 kcal of heat evolution,

$$C + 2S \longrightarrow CS_2; \qquad \Delta H = +22 \text{ kcal}$$

i.e., 12 g C reacts with 64 g S to give 76 g CS_2 along with 22.0 kcal of heat absorption.

Factor's influencing heat of reaction

1. Condition of constant *P* or *V* :

Heat changes at constant volume are expressed in ΔU.

Heat changes at constant pressure are expressed in ΔH.

Also, for a change $\quad \Delta H = \Delta U + P\Delta V \qquad$ ...(1)

where, P is the pressure and ΔV is change in volume.

Also, ΔH and ΔU are related together as

$$\Delta H = \Delta U + \Delta n \cdot RT \qquad \text{...(2)}$$

Δn = Mole of products – Mole of reactants

R = Molar gas constant

T = Temperature in kelvin.

Note : While using Eq. (2) for numericals one should keep in mind that for Δn

(1) Count only gaseous phase molecules.

(2) If $\Delta n = 0$; $\Delta H = \Delta U$.

(3) Δn may be +ve, –ve, integer or fraction.

(4) Put R in the same units in which ΔH and ΔU are given.

(5) Normally reactions are carried out at constant pressure and therefore, heat changes are to be taken as ΔH unless stated otherwise.

2. Physical nature of reactants and products :

For reactants : If C_{Diamond} and $C_{\text{Amorphous}}$ are allotropic forms of C.

$$C_{\text{Diamond}} + O_2(g) \longrightarrow CO_2(g); \qquad \Delta H = -94.3 \text{ kcal}$$

$$C_{\text{Amorphous}} + O_2(g) \longrightarrow CO_2(g); \qquad \Delta H = -97.6 \text{ kcal}$$

For products :

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \qquad \Delta H = -68.3 \text{ kcal}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g); \qquad \Delta H = -57.0 \text{ kcal}$$

3. Temperature : The variation of ΔH or ΔU with temperature is expressed in terms of Kirchhoff's equation.

$$\Delta H_2 - \Delta H_1 = \Delta C_p \, (T_2 - T_1)$$

$$\Delta U_2 - \Delta U_1 = \Delta C_v \, (T_2 - T_1)$$

where ΔH_2 and ΔU_2 are heats of reaction at temperature T_2

ΔH_1 and ΔU_1 are heats of reaction at temperature T_1

$\Delta C_p = C_p$ of products $- C_p$ of reactants

$\Delta C_v = C_v$ of products $- C_v$ of reactants

C_p and C_v are molar specific heats at constant P and V respectively.

Other terms used for heats of reactions :

Heat of formation : It is defined as the change in heat enthalpy or change in internal energy when **one mole** of a substance is formed from its **initial components,** *e.g.,*

CO_2 has C and O-atoms therefore, heat of formation of CO_2 is

$$C(s) + O_2(g) \longrightarrow CO_2(g); \qquad \Delta H(f) = -94.3 \text{ kcal}$$

H_2SO_4 has H, S and O-atoms therefore, heat of formation of H_2SO_4 is

$$H_2(g) + S(s) + 2O_2(g) \longrightarrow H_2SO_4(l); \qquad \Delta H(f) = q$$

and not $\quad H_2O + SO_3 \longrightarrow H_2SO_4; \qquad \Delta H = q$

Heat of combustion : It is defined as the change in heat enthalpy or change in internal energy when **one mole** of a substance is **completely oxidized** in air (O_2), *e.g.,*

$$C(s) + O_2(g) \longrightarrow CO_2(g); \qquad \Delta H = -94.3 \text{ kcal} \quad ...(1)$$

Heat of combustion of C is given by Eq. (1) and not by $C + \frac{1}{2}O_2 \rightarrow CO$, since C is not completely oxidized in this case.

Also, $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g); \Delta H = -115$ kcal but heat of combustion of H_2 is $-115/2$, *i.e.,* since 1 mole H_2 be taken

Also, $Mg + \frac{1}{2}O_2 \longrightarrow MgO; \ \Delta H =$ Heat of combustion

$$3Mg + N_2 \longrightarrow Mg_3N_2;$$

$\Delta H =$ Not heat of combustion since oxidation is not by O_2.

Note : (1) Heats of combustions are always exothermic except oxidation of N as :

$$N_2 + \frac{1}{2}O_2 \longrightarrow N_2O; \qquad \Delta H = + \text{ ve}$$

$$N_2 + O_2 \longrightarrow 2NO; \qquad \Delta H = + \text{ ve}$$

$$N_2 + 2O_2 \longrightarrow 2NO_2; \qquad \Delta H = + \text{ ve}$$

(2) In $F_2 + \frac{1}{2}O_2 \rightarrow F_2O$; $\Delta H = +$ ve; here O_2 is oxidized and not F_2, which is reduced.

Heat of solution : It is defined as the change in heat enthalpy or change in internal energy when **one mole** of the solute is dissolved in **excess of solvent** so that further dilution does not bring any heat change.

Further on dissolution of an electrolyte in water;

(1) Heat of ionisation (ΔH_i) is required to separate ions from each other, *i.e.,* $\Delta H_i = +$ ve.

(2) Heat of hydration is given out during hydration of ions, *i.e.,* $\Delta H_h = -$ ve.

Therefore, $\quad \Delta H_s = \Delta H_i + \Delta H_h$

$\Delta H_i > \Delta H_h \qquad$ then $\Delta H_s = +$ ve

if $\quad \Delta H_i < \Delta H_h \qquad$ then $\Delta H_s = -$ ve

Note : Remember in thermochemical equations

(1) $n \times aq. = aq.$, $\qquad$ where n is any no.

(2) $aq. = nH_2O \quad$ or $\quad aq. = -nH_2O$

Heat of neutralization : It is defined as the change in heat enthalpy or change in internal energy when **1 g equivalent of an acid** reacts completely with **1 g equivalent of base** in dilute solution. Dilute solution refers for complete ionisation of acids and bases in it, *i.e.,*

$$HCl(aq.) + NaOH(aq.) \longrightarrow NaCl(aq.) + H_2O; \qquad \Delta H = -13.7 \text{ kcal}$$

In dilute solutions

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O; \qquad \Delta H = -13.7 \text{ kcal}$$

or $\quad H^+ + OH^- \longrightarrow H_2O; \qquad \Delta H = -13.7$ kcal

i.e., heat of neutralization is also defined as heat of formation of water from H^+ and OH^- ions.

In case of weak acids or weak bases the observed value is little lower because a part of it is used in dissociating weak acid or weak base which is not at all completely ionised at dilute solution conditions. These are, however, completely ionised at infinite dilution, *e.g.,*

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O; \qquad \Delta H = -13.2 \text{ kcal}$$

$$CH_3COO^- + H^+; \ \Delta H = q; \ Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + H_2O; \Delta H = -13.2 \text{ kcal}$$

$$\therefore \quad H^+ + OH^- \longrightarrow H_2O; \qquad \Delta H = -13.2 - q$$

$$\therefore \quad -13.2 - q = -13.7$$

$$\therefore \quad q = 0.5 \text{ kcal}$$

where q is heat of dissociation of weak acid.

Bond energy : The change in heat enthalpy when a bond is broken into (or produced from), isolated gaseous atoms.

$$O{-}H \longrightarrow O(g) + H(g); \qquad \Delta H = +X$$

$$O(g) + H(g) \longrightarrow O{-}H; \qquad \Delta H = -X$$

Thus, bond energy is +ve when bond is broken up and bond energy is –ve when bond is formed.

Note : (1) Bond energy values are normally given +ve sign for breaking up of bond unless given otherwise.

(2) Bond energy data is normally expressed per mole.

(3) For like atoms bonds

H_2 or $\quad H{-}H \longrightarrow 2H(g); \qquad \Delta H = BE$

and $\quad \frac{1}{2}H_2 \longrightarrow H(g); \qquad \Delta H_f = \frac{BE}{2}$

ΔH_f is heat of formation of H-atom $= \frac{BE}{2}$

(4) For solving bond energy numericals say

$$H_2 + Cl_2 \longrightarrow 2HCl$$

$\Delta H =$ BE data of formation of bond + BE data of dissociation of bond

$$= -2\,BE_{[H-Cl]} + BE_{[H-H]} + BE_{[Cl-Cl]}$$

Since, bond formation is always exothermic.

(5) In some cases bond energy represents for average bond energy, *e.g.*,

$$CH_4 \longrightarrow C(g) + 4H(g);\ \text{Heat of dissociation} = \Delta H$$

Average bond energy of C—H

$$= \frac{\text{Heat of dissociation of } CH_4}{\text{No. of bonds broken}} = \frac{\Delta H}{4}$$

Standard heat of formation and heat enthalpy :

(1) Standard heat enthalpy H° of a substance is its heat enthalpy at 25°C and 1 atm P.

(2) Consider formation of a substance say CO_2 from its components at 25°C and 1 atm P.

$$C(s) + O_2(g) \longrightarrow CO_2(g):\quad \Delta H_f^\circ = -94.3\ \text{kcal}$$

$$\Delta H_f^\circ = H_{CO_2}^\circ - [H_C^\circ(s) + H_{O_2}^\circ(g)]$$

$$\Delta H_f^\circ = H_{CO_2}^\circ$$

Since, H° values for pure elements has been assumed to be zero

$$\therefore \quad H_C^\circ(s) = 0;\ H_{O_2}^\circ(g) = 0$$

i.e., standard heat of formation of a substance = standard heat enthalpy of that substance

Laws of thermochemistry :

(1) Lavoisier and Laplace law : The heat enthalpy change or internal energy change in a chemical reaction is equal but opposite to that of heat change, when reaction is reversed, *e.g.*,

$$\begin{array}{lll} & C + O_2 \longrightarrow CO_2; & \Delta H = -94.3\ \text{kcal} \\ \text{or} & CO_2 \longrightarrow C + O_2; & \Delta H = +94.3\ \text{kcal} \end{array}$$

(2) Hess's law of constant heat summation : Whether a reaction is made by one method or by other, in one step or in several steps, the total change in heat enthalpy or internal energy remains constant throughout the complete course of reaction, *e.g.*,

$$\begin{array}{l|ll} \textbf{I Method} & \textbf{II Method} & \\ A \longrightarrow \text{Products}, \Delta H = Q_1 & A \longrightarrow B & \Delta H = q_1 \\ & B \longrightarrow C & = q_2 \\ & C \longrightarrow \text{Products} & = q_3 \\ \hline & A \longrightarrow P; & \\ & \Delta H = q_1 + q_2 + q_3 = Q_2 & \end{array}$$

Therefore, according to Hess's law,

$$Q_1 = Q_2$$

The law has been verified theoretically, however, experimental verification is not possible.

• NUMERICAL PROBLEMS •

1. Heat of reaction for,

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(v)$$

at constant pressure is – 651 kcal at 17°C. Calculate the heat of reaction at constant volume at 17°C.

2. The reaction,

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

is carried out in a bomb calorimeter and the heat liberated during the course of reaction was found to be –742.7 kJ mol^{-1} at 25°C. Calculate the heat of reaction at constant pressure at 25°C.

3. The heat liberated on complete combustion of 7.8 g benzene is 327 kJ. This heat has been measured at constant volume and at 27°C. Calculate heat of combustion of benzene at constant pressure at 27°C. ($R = 8.3\ J\ mol^{-1}\ K^{-1}$) **(Roorkee 1996)**

4. Two mole of CO and one mole of O_2 are taken in a container of volume 1 litre to form 2 mole of CO_2 according to eq.

$$2\,CO + O_2 \longrightarrow 2\,CO_2; \qquad \Delta H = -560\ kJ$$

The pressure in the vessel changes from initial pressure of 70 atm to 40 atm. Find out the magnitude of absolute value of ΔU at 500 K. The gases deviates appreciably from ideal nature. (1 L-atm = 0.1 kJ) **(IIT 2006)**

5. Determine the value of ΔH and ΔU for the reversible isothermal evaporation of 90.0 g of water at 100°C. Assume that water vapours behaves as an ideal gas and heat of evaporation of water is 540 cal g^{-1}.
($R = 2\ cal\ mol^{-1}\ K^{-1}$) **(Roorkee 1998)**

6. When 1 mole of ice melts at 0°C and at constant pressure of 1 atm, 1440 cal of heat are absorbed by the system. The molar volume of ice and water are 0.0196 and 0.0180 litre respectively. Calculate ΔH and ΔU.

7. Standard heat of formation of HgO(*s*) at 298 K and at constant pressure is –90.8 kJ mol^{-1}. If excess of HgO(*s*) absorbs 41.84 kJ of heat at constant volume, calculate the amount of Hg that can be obtained at constant volume and 298 K. (At. wt. of Hg = 200).

8. When 1 mole of ice at 0°C and 4.6 mm of Hg is converted to water vapours at a constant temperature and pressure. Find ΔH and ΔU, if the latent heat of fusion of ice is 80 cal/g and latent heat of vaporisation of liquid water at 0°C is 536 cal/g. The volume of ice in comparison to volume of vapours may be neglected.

9. Calculate the heat of transition for carbon from the following :

$$C_{Diamond} + O_2 \longrightarrow CO_2(g); \qquad \Delta H = -94.3\ kcal$$
$$C_{Amorphous} + O_2 \longrightarrow CO_2(g); \qquad \Delta H = -97.6\ kcal$$

Also calculate the heat required to change 1g of $C_{Diamond}$ to $C_{Amorphous}$.

10. Calculate the enthalpy of vaporisation for water from the following :

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g); \qquad \Delta H = -57.0\ kcal$$
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \qquad \Delta H = -68.3\ kcal$$

Also calculate the heat required to change 1g $H_2O(l)$ to $H_2O(g)$.

11. The specific heats of iodine vapour and solid are 0.031 and 0.055 cal/g respectively. If heats of sublimation of iodine is 24 cal/g at 200°C, what is its value at 250°C?

12. The heat of reaction for $N_2 + 3H_2 \longrightarrow 2NH_3$ at 27°C is –91.94 kJ. What will be its value at 50°C? The molar heat capacities at constant *P* and 27°C for N_2, H_2 and NH_3 are 28.45, 28.32 and 37.07 joule respectively.

13. Calculate the standard internal energy change for the reaction $OF_2(g) + H_2O(g) \longrightarrow O_2(g) + 2HF(g)$ at 298 K. Given standard enthalpies of formation in kJ mol^{-1} are
$OF_2(g) = +20$; $H_2O(g) = -250$ and $HF(g) = -270$.

14. The molar heats of combustion of $C_2H_2(g)$, $C_{(Graphite)}$ and $H_2(g)$ are 310.62, 94.05 and 68.32 kcal respectively. Calculate heat of formation of C_2H_2.

15. From the standard enthalpies of combustion given below in (kJ mol^{-1}) and standard enthalpy of acetylene, find the standard enthalpy change when acetylene is hydrogenated to ethane.
($C = -394$, $H_2 = -286$, $C_2H_6 = -1560$, $C_2H_2 = +227$)

16. The molar heat of formation of $NH_4NO_3(s)$ is –367.54 kJ and those of $N_2O(g)$, $H_2O(l)$ are 81.46 and –285.8 kJ respectively at 25°C and 1 atmosphere pressure. Calculate ΔH and ΔU of the reaction $NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(l)$.

17. At 300 K, the standard enthalpies of formation of $C_6H_5COOH(s)$, $CO_2(g)$ and $H_2O(l)$ are – 408, – 393 and –286 kJ mol^{-1} respectively. Calculate the heat of combustion of benzoic acid at (i) constant pressure and (ii) constant volume. ($R = 8.31\ J\ mol^{-1}\ K^{-1}$) **(Roorkee 1995)**

18. Given below are some standard heats of reaction;
(a) Heat of formation of water = – 68.3 kcal
(b) Heat of combustion of acetylene = – 310.6 kcal
(c) Heat of combustion of ethylene = – 337.2 kcal
Calculate the heat of reaction for the hydrogenation of acetylene at constant volume at 25°C.

19. When 2 mole of $C_2H_6(g)$ are completely burnt, 3129 kJ of heat is liberated. Calculate the heat of formation of $C_2H_6(g)$. ΔH_f for $CO_2(g)$ and $H_2O(l)$ are – 395 and –286 kJ mol^{-1} respectively.

20. The standard heats of formation for $CCl_4(g)$, $H_2O(g)$, $CO_2(g)$ and $HCl(g)$ are – 25.5, – 57.8, – 94.1 and –22.1 kcal respectively. Calculate $\Delta H_{(298)}$ for the reaction,

$$CCl_4(g) + 2H_2O(g) \longrightarrow CO_2(g) + 4HCl(g)$$

21. The standard enthalpy of combustion at 25°C of H_2, C_6H_{10} and cyclohexane (C_6H_{12}) are –241, –3800 and –3920 kJ mol^{-1} respectively. Calculate heat of hydrogenation of cyclohexene (C_6H_{10}).

22. Calculate standard heat of formation of CS_2. Given that standard heat of combustion of C, S and CS_2 are –393.3, –293.72 and –1108.76 kJ mol^{-1}.

23. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of $CO_2(g)$, $H_2O(l)$ and propene(g) are –393.5, –285.8 and 20.42 kJ mol^{-1} respectively. The enthalpy of isomerisation of cyclopropane to propene is –33.0 kJ mol^{-1}. **(IIT 1998)**

24. Determine enthalpy change for,

$$C_3H_8(g) + H_2(g) \longrightarrow C_2H_6(g) + CH_4(g)$$

at 25°C using heat of combustion values under standard conditions.

Compounds	$H_2(g)$	$CH_4(g)$	$C_2H_6(g)$	$C_{(Graphite)}$
ΔH° in kJ/mol	–285.8	–890.0	–1560.0	–393.5

The standard heat of formation of $C_3H_8(g)$ is –103.8 kJ mol^{-1}. **(IIT 1992)**

25. Standard heat of formation of CH_4, CO_2 and $H_2O(g)$ are –76.2, –394.8 and –241.6 kJ mol^{-1} respectively. Calculate the amount of heat evolved by burning 1 m^3 of CH_4 measured under normal conditions. **(Roorkee 1990)**

26. 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 :

$$2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s); \quad \Delta H = -1273\text{ kJ} \quad ...(1)$$

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

$$H_2O(l) \longrightarrow H_2O(g); \quad \Delta H = 44\text{ kJ} \quad ...(3)$$

$$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g); \quad \Delta H = 36\text{ kJ} \quad ...(4)$$

(IIT 2000)

27. Calculate heat of formation of KOH(*s*) using the following equations.

$$K(s) + H_2O(l) + aq. \longrightarrow KOH(aq.) + \frac{1}{2}H_2(g); \quad \Delta H = -48.0\text{ kcal} \quad ...(1)$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \; \Delta H = -68.4\text{ kcal} \quad ...(2)$$

$$KOH(s) + aq. \longrightarrow KOH(aq.); \Delta H = -14.0\text{ kcal} \quad ...(3)$$

28. Calculate ΔH_f° for chloride ion from the following data :

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g); \quad \Delta H_f^\circ = -92.4\text{ kJ}$$

$$HCl(g) + nH_2O \longrightarrow H^+(aq.) + Cl^-(aq.); \quad \Delta H^\circ = -74.8\text{ kJ}$$

$\Delta H_f^\circ H^+(aq.) = 0.0$ kJ **(Roorkee 1992)**

29. Benzene burns in O_2 according to the equation :

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

If standard heat enthalpy of $C_6H_6(l)$, $H_2O(g)$ and $CO_2(g)$ are 11.7, – 68.3 and – 94.0 kcal respectively, calculate the amount of heat liberated by burning 1 kg benzene.

30. The heat evolved on combustion of 1 g starch $(C_6H_{10}O_5)_n$ into CO_2 and $H_2O(l)$ is 17.49 kJ g^{-1}. Compute the enthalpy of formation of 1g starch. Given ΔH_f of $H_2O(l) = -285.85$ kJ mol^{-1}, ΔH_f of $CO_2 = -293.7$ kJ mol^{-1}.

31. The heat of combustion of ethane gas is 368 kcal/mol. Assuming that 60% of the heat is useful, how many m^3 of ethane measured at STP must be burnt to supply enough heat to convert 50 kg of water at 10°C to steam at 100°C? Specific heat of water is 1 cal/g. Heat of vaporisation of H_2O is 540 cal/g.

32. ΔH for combustion of ethane and ethyne are –341.1 and –310.0 kcal respectively. Which is better gas welder and why?

33. The combustion of 5.0 g of coke raised the temperature of 1.0 kg of water from 10 to 47°C. Calculate the fuel value of coke. Specific heat of H_2O is 1 cal/g.

34. A cooking gas cylinder is assumed to contain 11.2 kg isobutane having heat of combustion –2658 kJ mol^{-1}. If a family needs 15×10^3 kJ energy per day for cooking, how long a cylinder can last. Also if 30% heat is lost due to incomplete combustion, then how long would it take to last.

35. An athlete is given 100 g glucose of energy equivalent to 1560 kJ. He utilize 50% of this gained energy in an event. In order to avoid storage of energy in body, calculate the mass of water he would need to perspire. Enthalpy of H_2O for evaporation is 44 kJ mol^{-1}.

36. The enthalpy change involved in the oxidation of glucose is –2880 kJ mol^{-1}. Twenty five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk after eating 120 g of glucose? **(IIT May 1997)**

37. An athlete takes 20 breaths per minute at room temperature. The air inhaled in each breath is 200 mL which contains 20% oxygen by volume, while exhaled air contains 10% oxygen by volume. Assuming that all the oxygen consumed if used for converting glucose into CO_2 and $H_2O(l)$, how much glucose will be burnt in the body in one hour and what is the heat produced? (Room temperature = 27°C and enthalpy of combustion of glucose is -2822.5 kJ mol^{-1} at 0°C)

38. Calculate the ΔH for $NO_2(g) \longrightarrow NO(g) + O(g)$ if heat of formation of O-atoms is 249 kJ/mol and

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g); \quad \Delta H = -200 \text{ kJ}$$
$$3O_2(g) \longrightarrow 2O_3(g); \quad \Delta H = 285.4 \text{ kJ}$$

39. Calculate the heat of dissociation of N_2O_4 into NO_2 from the data :

$$N_2 + O_2 \longrightarrow 2NO; \quad \Delta H = +43.10 \text{ kcal} \ \ldots(1)$$
$$N_2 + 2O_2 \longrightarrow N_2O_4; \quad \Delta H = -1.870 \text{ kcal} \ \ldots(2)$$
$$2NO_2 \longrightarrow 2NO + O_2; \quad \Delta H = +26.10 \text{ kcal} \ \ldots(3)$$

40. 3.67 litre of ethylene and methane gaseous mixture on complete combustion at 25°C produces 6.11 litre of CO_2. Find out the amount of heat evolved on burning one litre of gaseous mixture. The heats of combustion of C_2H_4 and CH_4 are -1423 and -891 kJ mol^{-1} at 25°C. **(IIT 1991)**

41. An intimate mixture of Fe_2O_3 and Al is used in solid fuel rocket. Calculate the fuel value per g and per mL of mixture.

$$\Delta H_{Al_2O_3} = 399.0 \text{ kcal}, \quad \Delta H_{Fe_2O_3} = 199.0 \text{ kcal}$$

density of Fe_2O_3 and Al are 5.2 g/mL and 2.7 g/mL respectively.

42. The heat of solution of anhydrous $CuSO_4$ is -15.9 kcal and that of $CuSO_4 \cdot 5H_2O$ is 2.8 kcal. Calculate the heat of hydration of $CuSO_4$.

43. Calculate the integral heat of solution for

$$H_2SO_4 + 3H_2O \longrightarrow H_2SO_4 \cdot 3H_2O$$

and $H_2SO_4 \cdot 3H_2O + 5H_2O \longrightarrow H_2SO_4 \cdot 8H_2O$

Given that integral heat of solution for H_2SO_4 is given by : $\dfrac{75.6 \times n}{n + 1.8}$ kJ where n is number of water molecules associated with H_2SO_4.

44. The dissolution of 1 mole of NaOH (s) in 100 mole of $H_2O(l)$ give rise to evolution of heat as -42.34 kJ. However if 1 mole of NaOH(s) is dissolved in 1000 mole of $H_2O(l)$ the heat given out is 42.76 kJ. What would be enthalpy change when 900 mole of $H_2O(l)$ are added to a solution containing 1 mole of NaOH(s) in 100 mole of H_2O?

45. Calculate heat of dissociation for acetic acid from the following data :

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O; \quad \Delta H = -13.2 \text{ kcal}$$
$$H^+ + OH^- \longrightarrow H_2O; \quad \Delta H = -13.7 \text{ kcal}$$

Also, calculate heat of dissociation for NH_4OH if,

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O; \quad \Delta H = -12.27 \text{ kcal}$$

46. Calculate the heat of neutralization from the following data. 200 mL of 1 M HCl is mixed with 400 mL of 0.5 M NaOH. The temperature rise in calorimeter was found to be 4.4°C. Water equivalent of calorimeter is 12 g and specific heat is 1 cal/mL – degree for solution.

47. Calculate ΔH° for $2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3$ given that standard heat enthalpy of Fe_2O_3 and Al_2O_3 are -196.5 and -399.1 kcal.

48. Calculate the enthalpy change when 6.80 g of NH_3 is passed over heated CuO. The standard heat enthalpies of $NH_3(g)$, CuO(s) and $H_2O(l)$ are -46.0, -155.0 and -285.0 kJ mol^{-1} respectively and the change is

$$NH_3 + \frac{3}{2}CuO \longrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2O(l) + \frac{3}{2}Cu(s).$$

49. Calculate the enthalpy change when infinitely dilute solutions of $CaCl_2$ and Na_2CO_3 are mixed. ΔH_f° for $Ca^{2+}(aq.)$, $CO_3^{2-}(aq.)$ and $CaCO_3(s)$ are -129.80, -161.65 and -288.50 kcal mol^{-1} respectively.

50. The bond dissociation energy of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. Calculate the enthalpy of formation for HCl gas.

51. Calculate the C—C bond energy from the following data :

(a) $C(s) \longrightarrow C(g); \quad \Delta H = 170.9$ kcal

(b) $\frac{1}{2}H_2 \longrightarrow H(g); \quad \Delta H = 52.1$ kcal

(c) Heat of formation of ethane = -20.3 kcal

(d) C—H bond energy = 99.0 kcal

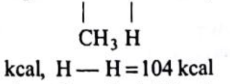
52. Heat of combustion of n-propane and n-butane are $-a$ kcal and $-b$ kcal per mole respectively. Calculate approximate value of heat of combustion of n-decane.

53. The enthalpy change for the following reaction at 25°C are given below :

$$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \longrightarrow OH(g); \quad \Delta H = -10.06 \text{ kcal} \ \ldots(1)$$
$$H_2(g) \longrightarrow 2H(g); \ \Delta H = 104.18 \text{ kcal} \ \ldots(2)$$
$$O_2(g) \longrightarrow 2O(g); \ \Delta H = 118.32 \text{ kcal} \ \ldots(3)$$

Calculate OH bond energy in hydroxyl radical.

54. Using bond energy data, calculate heat of formation of isoprene.

5 C(s) + $4H_2(g) \longrightarrow$ 

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

Given, C — H = 98.8 kcal, H — H = 104 kcal
C — C = 83 kcal, C = C = 147 kcal
and C(s) $\longrightarrow$ C(g) = 171 kcal

55. The dissociation energy of CH_4 is 360 kcal/mol and of ethane is 620 kcal/mol. Calculate C—C bond energy.

56. The heat of combustion of acetylene is 312 kcal. If heat of formation of CO_2 and H_2O are 94.38 and 68.38 kcal respectively, calculate C≡C bond energy. Given that heat of atomisation of C and H are 150.0 and 51.5 kcal respectively and C—H bond energy is 93.64 kcal.

57. Calculate enthalpy change of the following reaction :

$$H_2C=CH_2(g)+H_2(g)\longrightarrow H_3C-CH_3(g)$$

The bond energy of C—H, C—C, C=C, and H—H are 414, 347, 615 and 435 kJ mol^{-1} respectively.

(Roorkee 1985)

58. Heat of atomisation of NH_3 and N_2H_4 are x kcal mol^{-1} and y kcal mol^{-1} respectively. Calculate average bond energy of N—N bond.

59. Using the data (all values in kcal mol^{-1} at 25°C) given below, calculate bond energy of C—C and C—H bonds.

$$C(s)\longrightarrow C(g); \qquad \Delta H=172$$
$$H_2\longrightarrow 2H; \qquad \Delta H=104$$
$$H_2+\frac{1}{2}O_2\longrightarrow H_2O(l); \qquad \Delta H=-68.0$$
$$C(s)+O_2\longrightarrow CO_2; \qquad \Delta H=-94.0$$

Heat of combustion of $C_2H_6=-372.0$

Heat of combustion of $C_3H_8=-530.0$ **(IIT 1990)**

60. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25°C are –156 and +49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexane (l) at 25°C is –119 kJ mol^{-1}. Use these data to estimate the magnitude of the resonance energy of benzene. **(IIT 1996)**

61. Calculate the resonance energy of N_2O from the following data : ΔH_f° of N_2O is 82 kJ mol^{-1}.

N≡N	946 kJ mol^{-1}
N=N	418 kJ mol^{-1}
O=O	498 kJ mol^{-1}
N=O	607 kJ mol^{-1}

(Roorkee 1991)

62. Compute the heat of formation of liquid methyl alcohol in kilojoule per mol, using the following data. Heat of vaporisation of liquid methyl alcohol = 38 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states : H, 218 kJ/mol; C, 715 kJ/mol; O, 249 kJ/mol.

Average bond energies : C—H, 415 kJ/mol; C—O, 356 kJ/mol; O—H, 463 kJ/mol. **(IIT July 1997)**

63. Estimate ΔH for $2C_4H_{10}\longrightarrow C_8H_{18}+H_2$. Given bond energy of C—C, C—H are 347.3 and 414.2 kJ mol^{-1}. The heat of formation of H-atom is 217.55 kJ mol^{-1}.

64. Calculate the resonance energy of C_6H_6 using Kekule formula for C_6H_6 from the following data.

(1) ΔH_f° for $C_6H_6=-358.5$ kJ mol^{-1}

(2) Heat of atomisation of C = 716.8 kJ mol^{-1}

(3) Bond energy of C—H, C—C, C=C and H—H are 490, 340, 620 and 436.9 kJ mol^{-1} respectively.

65. Assume that for a domestic hot water supply 150 kg of water per day must be heated from 10°C to 65°C and gaseous fuel propane C_3H_8 is used for this purpose. What mole and volume of propane in litre at STP would have to be used for heating domestic water? ΔH for combustion of propane is –2050 kJ and specific heat of water is 4.184×10^{-3} kJ/g.

66. The temperature of a bomb calorimeter was found to rise by 1.617 K when a current of 3.20 ampere was passed for 3 seconds from a 12.0 V source. 100 g sample of a liquid (molar mass = 40) is now placed in this calorimeter and a passage of 0.5 ampere current for 3 minutes from a 1.50 V source gave a temperature rise of 0.8°C. What is molar heat capacity of liquid?

67. A slice of banana mass 2.502 g was burnt in a bomb calorimeter producing a temperature rise of 3.05°C. The combustion of 0.316 g of benzoic acid in the same calorimeter produced a temperature rise of 3.24°C. The heat of combustion of benzoic acid at constant volume is –3227 kJ mol^{-1}. If average banana mass is 125 g, how many calories can be obtained from one average banana?

68. The commercial production of water gas utilizes the reaction under standard conditions : $C+H_2O(g)\rightarrow H_2+CO$. The heat required for this endothermic reaction may be supplied by adding a limited amount of air and burning some carbon to CO_2. How many g of carbon must be burnt to CO_2 to provide enough heat for the water gas conversion of 100 g carbon? Neglect all heat losses to the environment. Also ΔH_f° of CO, $H_2O(g)$ and CO_2 are –110.53, –241.81 and –393.51 kJ/mol respectively.

69. The specific heat at constant volume for a gas 0.075 cal/g and at constant pressure is 0.125 cal/g. Calculate :

(i) the molar mass of gas

(ii) atomicity of gas

(iii) No. of atoms of gas in its 1 mole.

70. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner, which has been adjusted for methane as fuel (with X litre/hour of CH_4 and $6X$ litre/hour of O_2), is to be readjusted for butane C_4H_{10}. In order to get same calorific output, what should be the rate of supply of butane and oxygen? Assume that losses due to incomplete combustion, etc., are the same for both fuels and that gases behave ideally. Heats of combustion $CH_4=809$ kJ mol^{-1}; $C_4H_{10}=2878$ kJ mol^{-1}. **(IIT 1993)**

71. From the following data of ΔH, of the following reactions,

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

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g); \qquad \Delta H = 132\ kJ$$

Calculate the mole composition of the mixture of steam and oxygen on being passed over coke at 1273 K, keeping temperature constant.

72. A person inhales 640 g of O_2 per day. If all the O_2 is used for converting sugar into CO_2 and H_2O, how much sucrose ($C_{12}H_{22}O_{11}$) is consumed in the body in one day and what is the heat evolved? $\Delta H_{\text{Combustion of sucrose}} = -5645\ kJ\ mol^{-1}$.

73. When 12.0 g of carbon reacted with oxygen to form CO and CO_2 at 25°C and constant pressure, 75.0 kcal of heat was liberated and no carbon remained. Calculate the mass of oxygen needed for it and the mole of CO and CO_2 formed. Given, $\Delta H_f\ CO_2 = -94.05$ and $\Delta H_f\ CO = -26.41\ kcal\ mol^{-1}$.

74. 1.0 g magnesium atoms in vapour phase absorbs 50.0 kJ of energy to convert all Mg into Mg ions. The energy absorbed is needed for the following changes :

$$Mg(g) \longrightarrow Mg^+(g) + e; \qquad \Delta H = 740\ kJ\ mol^{-1}$$

$$Mg^+(g) \longrightarrow Mg^{2+}(g) + e; \qquad \Delta H = 1450\ kJ\ mol^{-1}$$

Find ou. the % of Mg^+ and Mg^{2+} in final mixture.

75. Estimate the average S—F bond energy in SF_6. The standard heat of formation values of $SF_6(g)$, $S(g)$ and $F(g)$ are : -1100, 275 and 80 $kJ\ mol^{-1}$ respectively.

(IIT 1999)

76. Consider the following reactions :

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

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

If 1 mole of $HAuBr_4$ was mixed with 4 mole of HCl, 0.44 kcal heat was absorbed, what fraction of $HAuBr_4$ was converted into $HAuCl_4$? Also report the percentage conversion.

77. The enthalpies of neutralisation of a strong acid HA and weak acid HB by NaOH are -13.68 kcal/eq. and -2.9 kcal / eq., respectively. If one equivalent of HA and one equivalent of HB are mixed with one equivalent of NaOH, the enthalpy change was found to be -6.9 kcal / eq., calculate the distribution of NaOH to neutralise HA and HB.

78. The standard enthalpy of formation of FeO and Fe_2O_3 is $-65\ kcal\ mol^{-1}$ and $-197\ kcal\ mol^{-1}$ respectively. If a mixture containing FeO and Fe_2O_3 in 2 : 1 mole ratio on oxidation is changed into 1 : 2 mole ratio, how much of thermal energy will be released per mole of the initial mixture?

79. Ethanol undergoes decomposition to form two sets of products.

$$\begin{tikzcd}
 & C_2H_4(g) + H_2O(g); \Delta H^\circ = -45.54\ kJ \\
C_2H_5OH(g) \arrow[ur, "1"] \arrow[dr, "2"'] & \\
 & CH_3CHO(g) + H_2(g); \Delta H^\circ = -68.91\ kJ
\end{tikzcd}$$

If the products molar ratio of C_2H_4 to CH_3CHO formed are in the ratio of 8 : 1 in a set of product gas, determine the energy involved in the decomposition of 1 mole of ethanol.

80. Calculate the enthalpy change for the reaction :

$$XeF_4 \longrightarrow Xe^+ + F^- + F_2 + F; \qquad \Delta H$$

The average Xe—F bond energy is 34 kcal/mol. IE_1 of Xe is 279 kcal/mol and electron affinity of F is 85 kcal / mol and bond dissociation energy of F_2 is 38 kcal / mol.

81. In a constant volume calorimeter, 3.5 g of a gas with molar mass 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 is $kJ\ mol^{-1}$ is.

(IIT 2009)

SOLUTIONS (Numerical Problems)

1. We know, $\Delta H = \Delta U + \Delta nRT$

Given, $\Delta H = -651 \times 10^3$ cal; $R = 2$ calorie

$T = 290\,\text{K}$; $\Delta n = 6+6-6 = 6$

$\therefore\ -651 \times 10^3 = \Delta U + 6 \times 2 \times 290$

$\therefore\ \Delta U = -654480\,\text{cal}$

$\therefore\ \Delta U = \mathbf{-654.48\ kcal}$

NOTE : For $C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(v)$

Δn = No. of products molecules – No. of reactants molecules (only in gaseous phase)

$= 6+6-6 = 6$

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

$\therefore\ \Delta n = 2 - \frac{3}{2} = \frac{1}{2}$

Given, $\Delta U = -742.7\,\text{kJ}$; $T = 298\text{K}$; $R = 8.314 \times 10^{-3}$ kJ

$\because\ \Delta H = \Delta U + \Delta nRT$

$= -742.7 + \frac{1}{2} \times 8.314 \times 10^{-3} \times 298$

$= \mathbf{-741.46\ kJ}$

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

$\therefore\ \Delta n = 6 - \frac{15}{2} = -\frac{3}{2}$

Also, ΔU per mol $= -\frac{327 \times 78}{7.8} = \mathbf{-3270\ kJ}$

Now, $\Delta H = \Delta U + \Delta nRT \doteqdot -3270 + \left(-\frac{3}{2}\right) \times 8.3 \times 300 \times 10^{-3}$

$\Delta H = \mathbf{-3273.735\ kJ}$

4. $\Delta H = \Delta U + \Delta(PV)$

$= \Delta U + P_2V_2 - P_1V_1$ ...(1)

We cannot use here $\Delta H = \Delta U + \Delta nRT$ since, gases deviate from ideal gas behaviour. Thus,

$\Delta(PV) = P_2V_2 - P_1V_1 = 40 \times 1 - 70 \times 1$

$= -30$ litre-atm $= -3.0$ kJ

$\therefore$ By Eq. (1) $-560 = \Delta U - 3.0$ $\therefore\ \Delta U = \mathbf{-557\ kJ}$

5. Water $\rightleftharpoons$ Vapour

Mole before evaporation $90/18 = 5$ 0

The evaporation of 5 moles of water takes place reversibly and isothermally into vapours.

Thus, heat given at constant pressure

ΔH = heat of evaporation × amount evaporated

$\Delta H = 540 \times 90$

$\Delta H = \mathbf{48600\ cal}$

Also, $\Delta H = \Delta U + \Delta nRT$

$\Delta U = 48600 - \Delta nRT$

$= 48600 - 5 \times 1 \times 2 \times 373 = 48600 - 3730$

$\Delta U = \mathbf{44870\ cal}$

6. Ice $\longrightarrow$ Water ; $\Delta H = 1440$ cal/mol

(Since, at constant pressure heat is given)

$\because\ \Delta H = \Delta U + P\Delta V$

and $P\Delta V = 76 \times 13.6 \times 981 \times (18 - 19.6)$ erg

(where, P in dyne cm^{-2} ; V in mL)

$= -1.62 \times 10^6\ \text{erg} = -\frac{1.62 \times 10^6}{4.18 \times 10^7} = -0.039\,\text{cal}$

$\because\ P\Delta V$ is negligible amount.

$\therefore\ \boldsymbol{\Delta H \simeq \Delta U}$

7. Given, $Hg(l) + \frac{1}{2}O_2(g) \longrightarrow HgO(s)$; $\Delta H^\circ = -90.8$ kJ

$\therefore\ HgO(s) \longrightarrow Hg(l) + \frac{1}{2}O_2(g)$; $\Delta H^\circ = +90.8$ kJ

$\Delta H^\circ = \Delta U^\circ + \Delta nRT$

$90.8 \times 10^3 = \Delta U^\circ - \frac{1}{2} \times 8.314 \times 298$ $\left(\because \Delta n = -\frac{1}{2}\right)$

$\therefore\ \Delta U^\circ = \mathbf{89.56\ kJ\ mol^{-1}}$

ΔU° is heat of formation of $Hg(l)$ from $HgO(s)$.

Now 41.84 kJ heat is absorbed by HgO, thus mole of Hg formed

$= \frac{41.84}{89.56} = 0.4672$

$\therefore\ w_{Hg} = 0.4672 \times 200 = \mathbf{93.44}$ **g**

8. Ice $\longrightarrow$ Vapour

$\Delta H = \Delta H_f + \Delta H_v = 80 \times 18 + 536 \times 18$

$= \mathbf{11088\ cal / mol}$

Now, $\Delta H = \Delta U + P\Delta V$

ΔV = Volume of vapours – Volume of ice = Volume of vapours at 4.6 mm and 0°C ($\because V_{ice}$ = negligible)

Now, $PV = nRT$ for gas

$\therefore$ PV or $P\Delta V = nRT = 1 \times 8.314 \times 273$ Nm or J

$= \frac{8.314 \times 273}{4.18}$ cal $= 543$ cal

$\Delta U = \Delta H - P\Delta V = 11088 - 543.0 = \mathbf{10545\ cal}$

9. Given,

$C_D + O_2 \longrightarrow CO_2(g)$; $\Delta H = -94.3$ kcal ...(1)

$C_A + O_2 \longrightarrow CO_2(g)$; $\Delta H = -97.6$ kcal ...(2)

$-\quad -\qquad -\qquad +$

Subtracting Eq. (2) from Eq. (1);

$C_D - C_A \longrightarrow 0$; $\Delta H = +3.3$

or $C_D \longrightarrow C_A$; $\Delta H = \mathbf{+3.3\ kcal}$

i.e., heat of transition for $C_D \longrightarrow C_A$ = **+3.3 kcal**

Also, 12 g C_D changes to C_A with heat change = + 3.3 kcal

$\therefore$ 1 g C_D changes to C_A with heat change $= +\frac{3.3}{12}$ kcal

= **0.275 kcal**

10. Given,

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(g)\,;\ \Delta H=-57.0\,\text{kcal} \quad ...(1)$$

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(l)\,;\ \Delta H=-68.3\,\text{kcal} \quad ...(2)$$

$$\underline{-\qquad -\qquad\qquad -\qquad\qquad +\qquad\qquad\qquad}$$

Subtracting Eq. (2) from Eq. (1);

$$H_2O(l)\longrightarrow H_2O(g)\,;\quad \Delta H=-11.3\,\text{kcal}$$

∴ Enthalpy of vaporisation for $H_2O=$ **+ 11.3 kcal**

Also, 18 g H_2O requires enthalpy of vaporisation

$$=+11.3\,\text{kcal}$$

∴ 1 g H_2O requires enthalpy of vaporisation $=\dfrac{11.3}{18}$ kcal

$$= \mathbf{0.628\ kcal}$$

11. Given, $\quad I_2(s)\longrightarrow I_2(v);\qquad \Delta H=24\,\text{cal/g at }200°\text{C}$

$$\Delta C_{p(\text{cal/g})}=C_p\text{ of product}-C_p\text{ of reactant}$$
$$=0.031-0.055$$
$$=-0.024\,\text{cal/g}$$

Now, $\quad \Delta H_2-\Delta H_1=\Delta C_p\,(T_2-T_1)$

$$\Delta H_2-24=-0.024\times(523-473)$$

∴ $\quad \Delta H_2=24-1.2=$ **22.8 cal / g**

12. Given,

$$N_2+3H_2\longrightarrow 2NH_3;\ \Delta H=-91.94\,\text{kJ at }300\,\text{K}$$

$$\Delta C_{p(\text{j/mol})}=2\times C_p\text{ of }NH_3-C_p\text{ of }N_2-3\times C_p\text{ of }H_2$$
$$=2\times37.07-28.45-3\times28.32$$
$$=-39.27\,\text{joule}$$

∴ $\quad \Delta H_2-\Delta H_1=\Delta C_p\,(T_2-T_1)$

$$\Delta H_2+91940=-39.27\times(323-300)$$
$$\Delta H_2=-92843.2\,\text{joule}=\mathbf{-92.843\ kJ}$$

13. $\quad OF_2(g)+H_2O(g)\longrightarrow O_2(g)+2HF(g)$

Given,

$$\frac{1}{2}O_2(g)+F_2(g)\longrightarrow OF_2(g);\quad \Delta H°=+20\,\text{kJ} \ ...(1)$$

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(g);\ \Delta H°=-250\,\text{kJ} \ ...(2)$$

$$\frac{1}{2}H_2(g)+\frac{1}{2}F_2\longrightarrow HF(g);\quad \Delta H°=-270\,\text{kJ} \ ...(3)$$

Adding Eqs. (1) and (2);

$$H_2(g)+F_2(g)+O_2(g)\longrightarrow OF_2(g)+H_2O(g);$$
$$\Delta H°=-230\,\text{kJ} \ ...(4)$$

Multiply Eq. (3) by 2 and subtract from Eq. (4),

$$O_2(g)+2HF(g)\longrightarrow OF_2(g)+H_2O(g);\ \Delta H°=+310\,\text{kJ}$$

or $\quad OF_2(g)+H_2O(g)\longrightarrow O_2(g)+2HF(g);$

$$\Delta H°=-310\,\text{kJ}$$

Now, $\quad \Delta H°=\Delta U°+\Delta n\,RT$

$$\Delta n=3-2=1, R=8.314\,\text{J},\ T=298\,\text{K}$$

∴ $\quad -310000=\Delta U°+1\times8.314\times298$

∴ $\quad \Delta U°=-312477.5\,\text{joule}=$ **−312.48 kJ**

14. We have to calculate

$$2C_{\text{Graphite}}+H_2(g)\longrightarrow C_2H_2(g);\qquad \Delta H=?$$

Given, $\quad C_2H_2(g)+\frac{5}{2}O_2(g)\longrightarrow 2CO_2(g)+H_2O(g);$

$$\Delta H=-310.62\,\text{kcal} \ ...(1)$$

$$C_{\text{Graphite}}+O_2(g)\longrightarrow CO_2(g);$$
$$\Delta H=-94.05\,\text{kcal} \ ...(2)$$

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(g);$$
$$\Delta H=-68.32\,\text{kcal} \ ...(3)$$

Multiply Eq. (2) by 2 and add in Eq. (3)

$$2C_{\text{Graphite}}+\frac{5}{2}O_2(g)+H_2(g)\longrightarrow 2CO_2(g)+H_2O(g);$$
$$\Delta H=-256.42\,\text{kcal} \ ...(4)$$

Subtract Eq. (1) from Eq. (4)

$$2C_{\text{Graphite}}+H_2(g)\longrightarrow C_2H_2(g);$$
$$\Delta H=\mathbf{+54.2\ kcal}$$

15. To find,

$$C_2H_2+2H_2\longrightarrow C_2H_6;\qquad \Delta H=?$$

Given, $\quad C_2+O_2\longrightarrow CO_2;\quad \Delta H=-394\,\text{kJ} \ ...(1)$

$$H_2+\frac{1}{2}O_2\longrightarrow H_2O;\quad \Delta H=-286\,\text{kJ} \ ...(2)$$

$$C_2H_6+\frac{7}{2}O_2\longrightarrow 2CO_2+3H_2O;$$
$$\Delta H=-1560\,\text{kJ} \ ...(3)$$

and $\quad 2C+H_2\longrightarrow C_2H_2;\quad \Delta H=+227\,\text{kJ} \ ...(4)$

Multiplying Eq. (1) by 2, Eq. (2) by 3, and then add them

$$2C+\frac{7}{2}O_2+3H_2\longrightarrow 2CO_2+3H_2O;$$
$$\Delta H=-1646\,\text{kJ} \ ...(5)$$

Subtract Eq. (3) from Eq. (5)

$$2C+3H_2\longrightarrow C_2H_6\,;\quad \Delta H=-86\,\text{kJ} \ ...(6)$$

Subtract Eq. (4) from Eq. (6)

$$C_2H_2+2H_2\longrightarrow C_2H_6\,;\qquad \Delta H=-313\,\text{kJ}$$

i.e., Heat of hydrogenation of $C_2H_2=$ **−313 kJ**

16. We have to find ΔH for

$$NH_4NO_3(s)\longrightarrow N_2O(g)+2H_2O(l);\qquad \Delta H=?$$

$$\Delta H_{\text{Reaction}}=\Delta H_{\text{Products}}-\Delta H_{\text{Reactants}}$$
$$=\Delta H_{N_2O}+\Delta H_{H_2O}\times2-\Delta H_{NH_4NO_3}$$

Given, $\quad \Delta H_{N_2O}=+81.46\,\text{kJ}$

$$\Delta H_{H_2O}=-285.8\,\text{kJ}$$
$$\Delta H_{NH_4NO_3}=-367.54\,\text{kJ}$$

∴ $\quad \Delta H_{\text{Reaction}}=+81.46+2(-285.8)-(-367.54)$

$$\Delta H=\mathbf{-122.6\ kJ}$$

Further $\quad \Delta H=\Delta U+\Delta nRT\ (\Delta n=1-0, R=8.314\,\text{J}, T=298\,\text{K})$

∴ $\quad -122.6\times10^3=\Delta U+1\times8.314\times298$

∴ $\quad \Delta U=-125077\,\text{joule}$

$$=\mathbf{-125.077\ kJ}$$

17. Given,

$$7C(s)+3H_2(g)+O_2(g)\longrightarrow C_6H_5COOH(s)$$
$$\Delta H°=-408\,\text{kJ} \ ...(1)$$

$$C(s)+O_2(g)\longrightarrow CO_2(g);$$
$$\Delta H°=-393\,\text{kJ} \ ...(2)$$

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(l);\Delta H°=-286\,\text{kJ} \ ...(3)$$

$$C_6H_5COOH(s)+\frac{15}{2}O_2(g)\longrightarrow 7CO_2(g)+3H_2O(l);$$

$$\Delta H = ?\ ...(4)$$

By Eq. $(2)\times 7+(3)\times 3-(1)$

$$C_6H_5COOH(s)+\frac{15}{2}O_2(g)\longrightarrow 7CO_2(g)+3H_2O(l);$$

$$\Delta H^\circ=[-393\times 7-286\times 3+408]$$

$\therefore$ $\quad \Delta H^\circ = \mathbf{-3201\ kJ}$

Also, $\quad \Delta H^\circ=\Delta H+\Delta nRT$

$\therefore$ $\quad -3201=\Delta U^\circ+(-0.5)\times 8.314\times 10^{-3}\times 300$

$(\because \Delta n = 0.5 \text{ and } R = 8.314\times 10^{-3}\text{ kJ})$

$\therefore$ $\quad \Delta U^\circ = -3201+1.2471 = \mathbf{-3199.7529}$

18. Standard heats of reaction means ΔH at 1 atm and 25°C.

Given,

$$H_2+\frac{1}{2}O_2\longrightarrow H_2O;\ \Delta H=-68.3\text{ kcal}\ ...(1)$$

$$C_2H_2+\frac{5}{2}O_2\longrightarrow 2CO_2+H_2O;$$

$$\Delta H=-310.6\text{ kcal}\ ...(2)$$

$$C_2H_4+3O_2\longrightarrow 2CO_2+2H_2O;$$

$$\Delta H=-337.2\text{ kcal}\ ...(3)$$

$$C_2H_2+H_2\longrightarrow C_2H_4;\qquad \Delta H=?$$

Add Eqs. (1) and (2) and subtract Eq. (3)

$$C_2H_2+H_2\longrightarrow C_2H_4;\qquad \Delta H=-41.7\text{ kcal}$$

Now, $\quad \Delta H=\Delta U+\Delta nRT$

$\Delta n = 1-2=-1,\quad R = 2\text{ cal},\quad T = 298\text{ K}$

$-41.7\times 10^3=\Delta U+(-1)\times 2\times 298$

$\Delta U=-41104\text{ cal}$

$\therefore$ $\quad \Delta U = \mathbf{-41.104\ kcal}$

19. We have to find

$$2C(s)+3H_2(g)\longrightarrow C_2H_6(g);\qquad \Delta H=?\ ...(1)$$

Given, $C(s)+O_2(g)\longrightarrow CO_2(g);\quad \Delta H=-395\text{ kJ}\ ...(2)$

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(l);\quad \Delta H=-286\text{ kJ}\ ...(3)$$

$$C_2H_6(g)+\frac{7}{2}O_2(g)\longrightarrow 2CO_2(g)+3H_2O(l);$$

$$\Delta H=-\frac{3129}{2}\text{ kJ}\ ...(4)$$

$$=-1564.5\text{ kJ}$$

Multiplying Eq. (2) by 2 and Eq. (3) by 3, then adding

$$2C(s)+3H_2(g)+\frac{7}{2}O_2(g)\longrightarrow 2CO_2(g)+3H_2O(l);$$

$$\Delta H=-1648\text{ kJ}\ ...(5)$$

Subtracting Eq. (4) from Eq. (5)

$$2C(s)+3H_2(g)\longrightarrow C_2H_6(g);\qquad \Delta H=-83.5\text{ kJ}$$

$\therefore$ $\quad \Delta H_f$ of $C_2H_6 = \mathbf{-83.5\ kJ}$

20. At 298 K, ΔH values are ΔH°, *i.e.*, standard heat of formation. For

$$CCl_4(g)+2H_2O(g)\longrightarrow CO_2(g)+4HCl(g);\quad \Delta H^\circ=?$$

$$\Delta H^\circ_{\text{Reaction}}=\Delta H^\circ_{\text{Products}}-\Delta H^\circ_{\text{Reactants}}$$

$$=\Delta H^\circ_{CO_2}+4\times\Delta H^\circ_{HCl}-\Delta H^\circ_{CCl_4}-2\times\Delta H^\circ_{H_2O}$$

$$=-94.1+4\times(-22.1)-(-25.5)-2\times(-57.8)$$

$$\Delta H^\circ_{\text{Reaction}}=\mathbf{-41.4\ kcal}$$

21. We have to find ΔH for

$$C_6H_{10}+H_2\longrightarrow C_6H_{12};\qquad \Delta H=?$$

Given, $H_2+\frac{1}{2}O_2\longrightarrow H_2O;\qquad \Delta H=-241\text{ kJ}\ ...(1)$

$$C_6H_{10}+\frac{17}{2}O_2\longrightarrow 6CO_2+5H_2O;$$

$$\Delta H=-3800\text{ kJ}\ ...(2)$$

$$C_6H_{12}+9O_2\longrightarrow 6CO_2+6H_2O;$$

$$\Delta H=-3920\text{ kJ}\ ...(3)$$

Adding Eqs. (1) and (2) and then subtracting Eq. (3) as above

$$C_6H_{10}+H_2\longrightarrow C_6H_{12};\qquad \Delta H=-121\text{ kJ}$$

$\therefore$ Heat of hydrogenation of $C_6H_{10} = \mathbf{-121\ kJ}$

22. We have to find ΔH for

$$C+2S\longrightarrow CS_2;\qquad \Delta H=?$$

Given, $C+O_2\longrightarrow CO_2;\qquad \Delta H=-393.3\text{ kJ}\ ...(1)$

$$S+O_2\longrightarrow SO_2;\qquad \Delta H=-293.72\text{ kJ}\ ...(2)$$

$$CS_2+3O_2\longrightarrow CO_2+2SO_2;\ \Delta H=-1108.76\text{ kJ}\ ...(3)$$

Multiply Eq. (2) by 2 and add in Eq. (1)

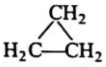
$$C+2S+3O_2\longrightarrow CO_2+2SO_2;\ \Delta H=-980.74\text{ kJ}\ ...(4)$$

Subtract Eq. (3) from Eq. (4)

$$C+2S\longrightarrow CS_2;\qquad \Delta H=+128.02\text{ kJ}$$

ΔH_f of $CS_2 = \mathbf{+128.02\ kJ}$

23. Given,



$\longrightarrow CH_3CH{=}CH_2;\ \Delta H=-33.0\text{ kJ}\ ...(1)$

$$C+O_2\longrightarrow CO_2(g);\qquad \Delta H=-393.5\text{ kJ}\ ...(2)$$

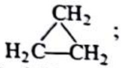
$$H_2+\frac{1}{2}O_2\longrightarrow H_2O(l);\qquad \Delta H=-285.8\text{ kJ}\ ...(3)$$

$$3C+3H_2\longrightarrow CH_3\cdot CH{=}CH_2(g);$$

$$\Delta H=20.42\text{ kJ}\ ...(4)$$

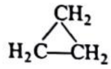
(4)−(1) yields

$3C+3H_2\longrightarrow$



$;\quad \Delta H=53.42\text{ kJ}\ ...(5)$

$[3\times(2)+3\times(3)]-(5)$ yields



$+\frac{9}{2}O_2\longrightarrow 3CO_2+3H_2O;$

$$\Delta H=\mathbf{-2091.32\ kJ}$$

24. Given,

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(g);\quad \Delta H=-285.8\text{ kJ}\ ...(1)$$

$$CH_4(g)+2O_2(g)\longrightarrow CO_2(g)+2H_2O(g);$$

$$\Delta H=-890\text{ kJ}\ ...(2)$$

$$C_2H_6(g)+\frac{7}{2}O_2(g)\longrightarrow 2CO_2(g)+3H_2O(g);$$

$$\Delta H=-1560.0\text{ kJ}\ ...(3)$$

$$3C(s)+4H_2(g) \longrightarrow C_3H_8(g); \quad \Delta H=-103.8 \text{ kJ} \ldots(4)$$
$$C(s)+O_2(g) \longrightarrow CO_2(g); \quad \Delta H=-393.5 \text{ kJ} \ldots(5)$$

Add Eqs. (2) and (3)

$$CH_4(g)+C_2H_6(g)+\frac{11}{2}O_2(g) \longrightarrow 3CO_2(g)+5H_2O(g);$$
$$\Delta H=-2450 \text{ kJ} \ldots(6)$$

Add Eqs. (4) and (6)

$$CH_4(g)+C_2H_6(g)+3C(s)+4H_2(g)+\frac{11}{2}O_2(g) \longrightarrow$$
$$3CO_2(g)+5H_2O(g)+C_3H_8(g); \Delta H=-2553.8 \text{ kJ} \ldots(7)$$

Multiply Eq. (1) by 5 and Eq. (5) by 3, then add them

$$5H_2(g)+3C(s)+\frac{11}{2}O_2(g) \longrightarrow 5H_2O(g)+3CO_2(g);$$
$$\Delta H=-2609.5 \text{ kJ} \ldots(8)$$

Subtract Eq. (8) from Eq. (7) and on rearranging

$$CH_4(g)+C_2H_6(g)+3C(s)+4H_2(g)+\frac{11}{2}O_2(g) \longrightarrow$$
$$3CO_2(g)+5H_2O(g)+C_3H_8(g); \quad \Delta H=-2553.8 \text{ kJ}$$
$$5H_2(g)+3C(s)+\frac{11}{2}O_2(g) \longrightarrow 5H_2O(g)+3CO_2(g);$$
$$\Delta H=-2609.5 \text{ kJ}$$
$$- \quad - \quad - \quad - \quad - \quad +$$
$$H_2(g)+C_3H_8(g) \longrightarrow CH_4(g)+C_2H_6(g);$$
$$\Delta H=\mathbf{-55.7 \text{ kJ}}$$

25. Given,

$$C+2H_2 \longrightarrow CH_4; \quad \Delta H=-76.2 \text{ kJ} \ldots(1)$$
$$C+O_2 \longrightarrow CO_2; \quad \Delta H=-394.8 \text{ kJ} \ldots(2)$$
$$H_2+\frac{1}{2}O_2 \longrightarrow H_2O(g); \quad \Delta H=-241.6 \text{ kJ} \ldots(3)$$

Multiply Eq. (3) by 2 and add in Eq. (2)

$$C+2H_2+2O_2 \longrightarrow CO_2+2H_2O(g); \Delta H=-878 \text{ kJ} \ldots(4)$$

Subtract Eq. (1) from Eq. (4)

$$CH_4+2O_2 \longrightarrow CO_2+2H_2O(g); \quad \Delta H=-801.8 \text{ kJ}$$

∵ 22.4 litre CH_4 on burning gives energy = 801.8 kJ

or 22.4×10^{-3} m^3 CH_4 on burning gives energy = 801.8 kJ

∴ 1 m^3 CH_4 on burning gives energy

$$=\frac{801.8}{22.4\times10^{-3}}=35.795\times10^3 \text{ kJ}$$

∴ Heat evolved by burning 1 m^3 CH_4 = **35.795×10^3 kJ**

26. To get $B_2H_6(g)+3O_2(g) \longrightarrow B_2O_3(s)+3H_2O(g)$

By Eqs. (1) + 3 × (2) + 3 × (3)

$$2B(s)+3H_2(g)+3O_2(g) \longrightarrow B_2O_3(s)+3H_2O(g);$$
$$\Delta H=-1999 \ldots(A)$$

By Eq. (A) − (4)

$$B_2H_6(g)+3O_2(g) \longrightarrow B_2O_3(s)+3H_2O(g);$$
$$\Delta H=\mathbf{-2035 \text{ kJ}}$$

27. We have to evaluate ΔH for

$$K(s)+\frac{1}{2}O_2(g)+\frac{1}{2}H_2(g) \longrightarrow KOH(s); \quad \Delta H=?$$

Adding Eqs. (1) and (2),

$$K(s)+\frac{1}{2}H_2(g)+\frac{1}{2}O_2(g)+aq. \longrightarrow KOH(aq.);$$
$$\Delta H=-116.4 \text{ kcal} \ldots(4)$$

Subtracting Eq. (3) from Eq. (4)

$$K(s)+\frac{1}{2}H_2(g)+\frac{1}{2}O_2(g) \longrightarrow KOH(s);$$
$$\Delta H=\mathbf{-102.4 \text{ kcal}}$$

28. Given,

$$\frac{1}{2}H_2(g)+aq. \longrightarrow H^+(aq.)+e;$$
$$\Delta H^\circ=0 \ldots(1)$$
$$\frac{1}{2}H_2(g)+\frac{1}{2}Cl_2(g) \longrightarrow HCl(g);$$
$$\Delta H^\circ=-92.4 \text{ kJ} \ldots(2)$$
$$HCl(g)+nH_2O(l) \longrightarrow H^+(aq.)+Cl^-(aq.);$$
$$\Delta H^\circ=-74.8 \text{ kJ} \ldots(3)$$

Add Eqs. (2) and (3)

$$\frac{1}{2}H_2(g)+\frac{1}{2}Cl_2(g)+nH_2O \longrightarrow H^+(aq.)+Cl^-(aq.);$$
$$\Delta H=-1672 \text{ kJ} \ldots(4)$$

Subtract Eq. (1) from (4)

$$\therefore \quad e+\frac{1}{2}Cl_2(g)+aq. \longrightarrow Cl^-(aq.);$$
$$\Delta H=-1672 \text{ kJ}$$

Heat of formation for $Cl^-(aq.)$ = **−167.2 kJ**

29. Standard heat enthalpy of a compound (H°)

= Standard heat of formation of that compound (ΔH°)

$$\therefore \quad 6C+3H_2 \longrightarrow C_6H_6(l); \quad \Delta H^\circ=11.7 \text{ kcal} \ldots(1)$$
$$H_2+\frac{1}{2}O_2 \longrightarrow H_2O(g); \Delta H^\circ=-68.3 \text{ kcal} \ldots(2)$$
$$C+O_2 \longrightarrow CO_2(g); \quad \Delta H^\circ=-94.0 \text{ kcal} \ldots(3)$$

Multiplying Eq. (2) by 3 and Eq. (3) by 6, and then add

$$6C+3H_2+\frac{15}{2}O_2 \longrightarrow 6CO_2+3H_2O;$$
$$\Delta H^\circ=-768.9 \text{ kcal} \ldots(4)$$

Subtracting Eq. (1) from Eq. (4)

$$C_6H_6+\frac{15}{2}O_2 \longrightarrow 6CO_2+3H_2O; \Delta H^\circ=-780.6 \text{ kcal}$$

∴ 78 g C_6H_6 gives heat = 780.6 kcal

∴ 1000 g C_6H_6 gives heat $=\frac{780.6\times1000}{78}=10007.7$ kcal

Thus, heat produced by burning 1 kg C_6H_6 = **10007.7 kcal**

30. Given, $H_2+\frac{1}{2}O_2 \longrightarrow H_2O(l); \quad \Delta H=-285.85 \text{ kJ} \ldots(1)$

$$C+O_2 \longrightarrow CO_2(g); \quad \Delta H=-293.7 \text{ kJ} \ldots(2)$$

∵ 1 g starch on combustion gives 17.49 kJ energy

∴ 162n g starch on combustion gives = 17.49 × 162n kJ energy = 2833.38n kJ

Molar mass of starch $(C_6H_{10}O_5)_n$ = 162n

Therefore,

$$(C_6H_{10}O_5)_n+6n\,O_2 \longrightarrow 6n\,CO_2+5n\,H_2O;$$
$$\Delta H=-2833.38\,n \text{ kJ} \ldots(3)$$

Multiply Eq. (2) by 6n and Eq. (1) by 5n, then add

$$5n\,H_2+\frac{5n}{2}O_2+6n\,C+6n\,O_2 \longrightarrow 5nH_2O+6nCO_2;$$
$$\Delta H=-3191.45\,n \text{ kJ} \ldots(4)$$

Subtract Eq. (3) from Eq. (4)

$$6n\text{C} + 5n\text{H}_2 + \frac{5n}{2}\text{O}_2 \longrightarrow (\text{C}_6\text{H}_{10}\text{O}_5)_n\,;\ \Delta H = -358.07\,n\text{ kJ}$$

∴ Heat of formation for $162n$ g starch $= -358.07\,n$ kJ

∴ Heat of formation for 1 g starch $= -\dfrac{358.07}{162n} = \mathbf{-2.21\ kJ}$

31. ΔH needed for change $= \Delta H_{\text{Heating}} + \Delta H_{\text{Vaporisation}}$

$$= 50\times10^3\times1\times90 + 540\times50\times10^3$$
$$= 31500\times10^3\text{ cal}$$

ΔH actually needed $= \dfrac{31500\times10^3\times100}{60}$

(since only 60% of heat is used to do so)

Now 368×10^3 cal heat is given on combustion by 22.4 litre C_2H_6

∴ $\dfrac{31500\times10^3\times100}{60}$ heat is given by

$$= \frac{22.4\times31500\times10^3\times100}{60\times368\times10^3}$$
$$= 3.196\times10^3\text{ litre} = \mathbf{3.196\ m^3}$$

32. A better gas welder is one which posses high **calorific value, *i.e.*, heat produced by 1 g of fuel.**

$\Delta H_{\text{Combustion}}$ for $\text{C}_2\text{H}_6 = -341.1$ kcal

∴ Calorific value $= \dfrac{-341.1}{30}$ kcal/g $= \mathbf{-11.37\ kcal/g}$

$\Delta H_{\text{Combustion}}$ for $\text{C}_2\text{H}_2 = -310.0$ kcal

∴ Calorific value $= \dfrac{-310.0}{26}$ kcal/g $= \mathbf{-11.92\ kcal/g}$

∴ **$\mathbf{C_2H_2}$ is better gas welder.**

33. ΔH supplied $= 10^3\times1\times37 = 37\times10^3$ cal

Thus, fuel value $= \dfrac{37\times10^3}{5} = \mathbf{7400\ cal/g}$

34. I. $\text{C}_4\text{H}_{10}(g) + \dfrac{13}{2}\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 5\text{H}_2\text{O}(l)\,;$

$\Delta H = -2658$ kJ

Heat obtained by burning 11.2 kg isobutane

$$= \frac{11.2\times10^3}{58}\times2658$$
$$= 5.13\times10^5\text{ kJ}$$

∴ Day for which cylinder can serve $= \dfrac{5.13\times10^5}{15\times10^3} = \mathbf{34}$

II. If 30% heat is lost due to incomplete combustion, then

Heat obtained $= \dfrac{5.13\times10^5\times70}{100} = 3.59\times10^5$

Day for which cylinder can serve $= \dfrac{3.59\times10^5}{15\times10^3} = \mathbf{24}$

35. Energy supplied to athlete by consuming 100 g glucose $= 1560$ kJ

Energy utilized in event $= \dfrac{50}{100}\times1560 = 780$ kJ

Energy left as excess in body $= 1560 - 780 = 780$ kJ

∵ 44 kJ energy used to evaporate $= 18\text{ g H}_2\text{O}$

∴ 780 kJ energy used to evaporate $= \dfrac{18\times780}{44}\text{ g H}_2\text{O}$

$= \mathbf{319.09\ g}$

Thus, athlete should perspire 319.09 g of H_2O in order to avoid any storage of energy in body.

36. Energy available for muscular work $= \dfrac{2880\times25}{100}$

$= 720$ kJ/ mol

∴ Energy available for muscular work for 120 g glucose

$= \dfrac{720\times120}{180} = 480$ kJ

∵ 100 kJ is used in 1 km distance.

∴ 480 kJ is used in **4.8 km** distance.

37. Inhaled O_2 in one breath $= \dfrac{200\times20}{100}$ mL

Exhaled O_2 in one breath $= \dfrac{200\times10}{100}$ mL

∴ Used O_2 in one breath $= \dfrac{200\times20}{100} - \dfrac{200\times10}{100} = 20$ mL

Now 20 breaths are taken in one minute

∴ Breaths taken in 1 hour $= 20\times60 = 1200$ breaths

∴ Volume of O_2 used in 1 hour $= 20\times1200$

$= 24000$ mL at 27°C

$= \dfrac{24000}{300}\times273$ mL at 0°C

$= 21840$ mL $= 21.84$ litre

For glucose $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \longrightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}\,;$

$\Delta H = -2822.5$ kJ

∵ 6×22.4 litre O_2 is used for 180 g glucose

∴ 21.84 litre O_2 is used for $= \dfrac{180\times21.84}{6\times22.4} = \mathbf{29.25\ g}$

Also, 6×22.4 litre O_2 with glucose gives $= 2822.5$ kJ

∴ 21.84 litre O_2 with glucose gives $= \dfrac{2822.5\times21.84}{6\times22.4}$

$= \mathbf{458.66\ kJ}$

38. Given,

$$\tfrac{1}{2}\text{O}_2 \longrightarrow \text{O}\,; \qquad \Delta H = 249\text{ kJ} \quad ...(1)$$
$$\text{NO}_2 + \text{O}_2 \longrightarrow \text{NO} + \text{O}_3\,; \quad \Delta H = +200\text{ kJ} \quad ...(2)$$
$$\text{O}_3 \longrightarrow \tfrac{3}{2}\text{O}_2\,; \quad \Delta H = -\frac{285.4}{2}\text{ kJ} \quad ...(3)$$

Adding Eqs. (1), (2) and (3)

$$\text{NO}_2 \longrightarrow \text{NO} + \text{O}\,; \qquad \mathbf{\Delta H = 306.3\ kJ}$$

39. We have to find ΔH for

$$\text{N}_2\text{O}_4 \longrightarrow 2\text{NO}_2\,; \qquad \Delta H = ?$$

Add Eqs. (2) and (3)

$$\text{N}_2 + 2\text{O}_2 \longrightarrow \text{N}_2\text{O}_4\,; \qquad \Delta H = -1.87\text{ kcal}$$
$$2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2\,; \quad \Delta H = +26.10\text{ kcal}$$

∴ $\text{N}_2 + 2\text{O}_2 + 2\text{NO}_2 \longrightarrow \text{N}_2\text{O}_4 + 2\text{NO} + \text{O}_2\,;$

$\Delta H = +24.23$ kcal

or $\text{N}_2 + \text{O}_2 + 2\text{NO}_2 \longrightarrow \text{N}_2\text{O}_4 + 2\text{NO}\,;$

$\Delta H = 24.23$ kcal ...(4)

Subtract Eq. (1) from Eq. (4)

$$2NO_2 \longrightarrow N_2O_4\ ; \qquad \Delta H = -18.87\ \text{kcal}$$

or $$N_2O_4 \longrightarrow 2NO_2\ ; \qquad \Delta H = +18.87\ \text{kcal}$$

i.e., Heat of dissociation of N_2O_4 = **+18.87 kcal**

40. Let volume of C_2H_4 and CH_4 be a and b litre respectively at 25°C.

$$a + b = 3.67\ \text{litre} \qquad ...(1)$$

Also, $$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$
$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

∴ Volume of CO_2 produced by a litre $C_2H_4 = 2a$
and volume of CO_2 produced by b litre $CH_4 = b$

∴ $$2a + b = 6.11\ \text{litre} \qquad ...(2)$$

By Eqs. (1) and (2)

$$a = 2.44\ \text{litre}$$
$$b = 1.23\ \text{litre}$$

∴ Volume of C_2H_4 in 1 litre mixture at 25°C

$$= \frac{2.44}{3.67} \times 1 = 0.6648\ \text{litre}$$

and volume of CH_4 in 1 litre mixture at 25°C

$$= \frac{1.23}{3.67} \times 1 = 0.3352\ \text{litre}$$

Now, volume of 1 mole C_2H_4 at 0°C = 22.4 litre

∴ Volume of 1 mole C_2H_4 at 25°C

$$= \frac{22.4 \times 298}{273} = 24.45\ \text{litre}$$

Similarly, volume of 1 mole CH_4 at 25°C

$$= \frac{22.4 \times 298}{273} = 24.45\ \text{litre}$$

∵ 24.45 litre C_2H_4 produces = + 1423 kJ at 25°C

∴ 0.6648 litre C_2H_4 produces $= \frac{+1423 \times 0.6648}{24.45}$

$$= +38.69\ \text{kJ}$$

Similarly, 24.45 litre CH_4 produces = + 891 kJ at 25°C

∴ 0.3352 litre CH_4 produces $= \frac{+891 \times 0.3352}{24.45}$

$$= +12.22\ \text{kJ}$$

Total heat produced = 38.69 + 12.22 = **50.91 kJ**

41. $$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe; \qquad \Delta H = ?$$

Given, $$2Al + \frac{3}{2}O_2 \longrightarrow Al_2O_3\ ;\ \Delta H = -399.0\ \text{kcal} \ ...(1)$$

$$2Fe + \frac{3}{2}O_2 \longrightarrow Fe_2O_3\ ;\ \Delta H = -199.0\ \text{kcal} \ ...(2)$$

Subtracting Eq. (2) from Eq. (1)

$$\underset{\text{Fuel mixture}}{2Al + Fe_2O_3} \longrightarrow 2Fe + Al_2O_3\ ;\ \Delta H = -200\ \text{kcal}$$

Molar mass of fuel mixture
$= 2 \times 27 + 2 \times 56 + 48 = 214$ g

∵ 214 g mixture produces = 200 kcal heat

∴ 1 g mixture produces $= \frac{200}{214} =$ **0.9346 kcal/g**

Also, volume of fusion mixture = vol. of Al + vol. of Fe_2O_3

$$= \frac{54}{2.7} + \frac{160}{5.2} = 20 + 30.76 = 50.76\ \text{mL}$$

∵ 50.76 mL mixture produces = 200 kcal

∴ 1 mL mixture produces $= \frac{200}{50.76} =$ **3.94 kcal/mL**

42. Given,

$$CuSO_4 + aq. \longrightarrow CuSO_4 \cdot 5H_2O(aq.);$$
$$\Delta H = -15.9\ \text{kcal} \ ...(1)$$

$$CuSO_4 \cdot 5H_2O + aq. \longrightarrow CuSO_4 \cdot 5H_2O(aq.);$$
$$\Delta H = +2.8\ \text{kcal} \ ...(2)$$

Subtracting Eq. (2) from Eq. (1)

$$CuSO_4 + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O;$$
$$\Delta H = -15.9 - 2.8 = -18.7\ \text{kcal}$$

∴ Heat of hydration of $CuSO_4$ = **−18.7 kcal**

43. $$H_2SO_4 + 3H_2O \longrightarrow H_2SO_4 \cdot 3H_2O$$

$$\Delta H_1 = \frac{75.6 \times 3}{3 + 1.8} = \mathbf{47.25\ kJ}$$

$$H_2SO_4 + 8H_2O \longrightarrow H_2SO_4 \cdot 8H_2O$$

$$\Delta H_2 = \frac{75.6 \times 8}{8 + 1.8} = \mathbf{61.72\ kJ}$$

$$H_2SO_4 \cdot 3H_2O + 5H_2O \longrightarrow H_2SO_4 \cdot 8H_2O$$

∵ $$\Delta H_3 = \Delta H_2 - \Delta H_1 = 61.72 - 47.25 = \mathbf{14.47\ kJ}$$

44. ΔH_1 for 1 mole NaOH in 100 mole $H_2O(l) = -42.34$ kJ

ΔH_2 for 1 mole NaOH in 1000 mole $H_2O(l) = -42.76$ kJ

Thus, if 900 mole of H_2O are added to a solution containing 1 mole NaOH in 100 mole $H_2O(l)$, then

$$\Delta H = \Delta H_2 - \Delta H_1$$
$$= -42.76 + 42.34 = \mathbf{-0.42\ kJ}$$

45. For acetic acid :

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O;$$
$$\Delta H = -13.2\ \text{kcal}$$

or $CH_3COOH + Na^+ + OH^-$

$$\longrightarrow CH_3COO^- + Na^+ + H_2O;$$
$$\Delta H = -13.2\ \text{kcal} \ ...(1)$$

Since, NaOH and CH_3COONa are strong electrolytes and thus, completely ionise. Also, CH_3COOH is weak electrolyte and thus,

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

or $$CH_3COOH \longrightarrow CH_3COO^- + H^+\ ; \qquad \Delta H = q \ ...(2)$$

Add Eqs. (1) and (2)

$CH_3COO^- + H^+ ; \Delta H = q ;$

$$Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + H_2O; \qquad \Delta H = -13.2$$

or $$H^+ + OH^- \longrightarrow H_2O; \qquad \Delta H = -13.2 - q$$

Given, $$H^+ + OH^- \longrightarrow H_2O; \qquad \Delta H = -13.7$$

∴ $$-13.7 = -13.2 - q$$

∴ $$q = \mathbf{0.5\ kcal}$$

where, q is heat of dissociation of acetic acid.

For NH_4OH:

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O; \quad \Delta H = -12.27 \text{ kcal}$$

Since, HCl and NH_4Cl are strong electrolytes and completely ionise, therefore,

$$NH_4OH + H^+ + Cl^- \longrightarrow NH_4^+ + Cl^- + H_2O; \quad \Delta H = -12.27 \text{ kcal} \quad ...(3)$$

For NH_4OH,

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

or $\quad NH_4OH \longrightarrow NH_4^+ + OH^- ; \quad \Delta H = q \quad ...(4)$

By Eqs. (3) and (4)

$NH_4^+ + OH^-; \Delta H = q; H^+ + Cl^- \longrightarrow NH_4^+ + Cl^- + H_2O;$

$$\Delta H = -12.27$$

or $\quad H^+ + OH^- \longrightarrow H_2O; \quad \Delta H = -12.27 - q$

$\therefore \quad -12.27 - q = -13.7 \;\; \therefore \;\; q = \mathbf{1.43\ kcal}$

where, q is heat of dissociation of NH_4OH.

46. Given total solution = 200 + 400 = 600 mL

200 mL of 1 M HCl neutralize 400 mL of 0.5 M NaOH

$\because \quad$ Meq. $= N \times V$

$\therefore$ mM or Meq. of acid and base = 200 (For mono valent nature)

i.e., 200 Meq. of HCl react with 200 Meq. of NaOH to produce heat = ΔH

1000 Meq. of HCl + 1000 Meq. of NaOH will give heat $= 5 \times \Delta H$

i.e., heat of neutralization. Now,

ΔH, *i.e.*, heat produced during neutralization of 200 Meq. of acid and base = Heat taken up by calorimeter + solution

$$= m_1 s_1 \,\Delta T + m_2 s_2 \,\Delta T$$

$$= 12 \times 4.4 + 600 \times 1 \times 4.4 = 2692.8 \text{ cal}$$

$\therefore$ Heat of neutralization $= -5 \times 2692.8 \text{ cal} = \mathbf{-13.464\ kcal}$

47. $\Delta H^\circ_{\text{Reaction}} = \Delta H^\circ_{\text{Products}} - \Delta H^\circ_{\text{Reactants}}$

$$= 2 \times \Delta H^\circ_{Fe} + \Delta H^\circ_{Al_2O_3} - (2 \times \Delta H^\circ_{Al}) = \Delta H^\circ_{Fe_2O_3}$$

$$= 2 \times 0 + (-399.1) - (2 \times 0) - (-196.5)$$

$$\Delta H^\circ = \mathbf{-202.6\ kcal}$$

NOTE : ΔH° for free elements are zero.

48. Given,

$$NH_3 + \frac{3}{2}CuO \longrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2O(l) + \frac{3}{2}Cu\,(s)$$

ΔH for change $= \Sigma H_{\text{Products}} - \Sigma H_{\text{Reactants}}$

$\because \quad H^\circ_{\text{Element}} = 0 \quad$ and $\quad H^\circ_{\text{Compound}} = \Delta H^\circ_f$

$\therefore \quad \Delta H$ for change $= \frac{3}{2}H^\circ_{H_2O} - H^\circ_{NH_3} - \frac{3}{2}H^\circ_{CuO}$

$$= \frac{3}{2} \times (-285) - (-46) - \frac{3}{2}(-155) = -149 \text{ kJ}$$

$\because \quad$ 17 g NH_3 brings change in $\Delta H = 149$ kJ

$\therefore \quad$ 6.8 g NH_3 brings change in $\Delta H = \frac{149 \times 6.8}{17}$ kJ

$$= 59.6 \text{ kJ}$$

$\therefore \qquad \Delta H = \mathbf{-59.6\ kJ}$

49. On mixing $CaCl_2(aq.)$ and Na_2CO_3

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

Solutions are very dilute and thus, 100% dissociation occurs.

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

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

$\therefore \quad \Delta H = \Sigma H^\circ_{\text{Products}} - \Delta H^\circ_{\text{Reactants}}$ or

$$\Delta H = \Delta H^\circ_{f\,CaCO_3} - [\Delta H^\circ_{f\,Ca^{2+}} + \Delta H^\circ_{f\,CO_3^{2-}}]$$

$\because \quad H^\circ$ of a compound $= \Delta H^\circ_{\text{Formation}}$

$$= -288.5 - (-129.80 - 161.65)$$

$$= \mathbf{2.95\ kcal}$$

50. Given,

$$H_2(g) \longrightarrow 2H(g); \quad \Delta H = 104 \text{ kcal} \quad ...(1)$$
$$Cl_2(g) \longrightarrow 2Cl(g); \quad \Delta H = 58 \text{ kcal} \quad ...(2)$$
$$HCl(g) \longrightarrow H(g) + Cl(g); \quad \Delta H = 103 \text{ kcal} \quad ...(3)$$

Heat of formation for HCl

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g); \quad \Delta H = ?$$

Divide Eqs. (1) and (2) by 2 and then add

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow H(g) + Cl(g); \quad \Delta H = 81 \text{ kcal} \quad ...(4)$$

Subtracting Eq. (3) from Eq. (4)

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g); \quad \Delta H = \mathbf{-22.0\ kcal}$$

$\therefore$ Enthalpy of formation for HCl gas = **– 22.0 kcal**

51. $\quad 2C + 3H_2 \longrightarrow C_2H_6; \quad \Delta H = -20.3$ kcal

Also,

$$\Delta H = -[1e_{C-C} + 6e_{C-H}] + [2(C(s) \rightarrow C(g)) + 3e_{H-H}]$$

$\therefore \quad -20.3 = -[e_{C-C} + 6 \times 99] + [2 \times 170.9 + 3 \times (2 \times 52.1)]$

or $\quad e_{C-C} = -594 + 341.8 + 312.6 + 20.3$

C—C bond energy = **80.7 kcal**

52. $\quad \Delta_C H_{C_3H_8} = 2 \times \Delta_C H_{CH_3 \text{ unit}} + 1 \times \Delta_C H_{CH_2 \text{ unit}} = -a$

$$\Delta_C H_{C_4H_{10}} = 2 \times \Delta_C H_{CH_3 \text{ unit}} + 2 \times \Delta_C H_{CH_2 \text{ unit}} = -b$$

$\therefore \quad \Delta_C H_{CH_2} = a - b$ kcal

Also, $\Delta_C H_{CH_3} = \frac{b - 2a}{2}$ kcal

Now,

$$\Delta_C H_{C_{10}H_{22}} = \Delta_C H_{CH_3(CH_2)_8 \cdot CH_3}$$
$$= 2 \times \Delta_C H_{CH_3 \text{ unit}} + 8 \times \Delta_C H_{CH_2 \text{ unit}}$$
$$= 2 \times \frac{(b - 2a)}{2} + [8 \times (a - b)]$$
$$= \mathbf{6a - 7b\ kcal/mol}$$

53. We have to find

$$O-H(g) = O(g) + H(g); \quad \Delta H = ?$$

Divide Eq. (2) by 2 and Eq. (3) by 2, then add

$$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H(g) + O(g);$$

$$\Delta H = 111.25 \text{ kcal} \quad ...(4)$$

Subtract Eq. (1) from Eq. (4)

$\therefore \quad OH(g) \longrightarrow H(g) + O(g); \; \Delta H = 121.31 \text{ kcal}$

$\therefore$ Bond energy of OH radical is **121.31 kcal**

54. $\Delta H_{\text{Reaction}}$ = Bond energy data used for formation of bond + Bond energy data used for dissociation of bond

$$\Delta H_{\text{Reaction}} = -[2(C—C) + 2(C=C) + 8(C—H) + [5C_{S\to g} + 4(H—H)]$$
$$= -[2 \times 83 + 2 \times 147 + 8 \times 98.8] + [5 \times 171 + 4 \times 104]$$
$$= \mathbf{+20.6\ kcal}$$

55. Given, $\quad CH_4 \longrightarrow C + 4H; \qquad \Delta H = 360 \text{kcal}$

$\therefore$ Bond energy of 4(C—H) bond = 360 kcal

$\therefore$ Bond energy of C—H bond $= \frac{360}{4} = 90$ kcal

In $\quad C_2H_6 \longrightarrow 2C + 6H$

Bond energy of $\quad C_2H_6 = 1(C—C) + 6(C—H)$

$$620 = 1(C—C) + 6 \times 90$$

$\therefore \quad C—C = 620 - 540 = 80 \text{kcal}$

$\therefore$ Bond energy of C—C = **80 kcal**

56. Given,

$$C_2H_2 + \frac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O; \Delta H = -312 \text{ kcal} \quad ...(1)$$

($\because$ Heat of combustion are exothermic)

$$C + O_2 \longrightarrow CO_2; \qquad \Delta H = -94.38 \text{ kcal} \quad ...(2)$$
$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O; \qquad \Delta H = -68.38 \text{ kcal} \quad ...(3)$$

Multiply Eq. (2) by 2 and add in Eq. (3)

$$2C + H_2 + \frac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O; \qquad \Delta H = -257.14 \text{ kcal} \quad ...(4)$$

Subtracting Eq. (1) from Eq. (4)

$$2C + H_2 \longrightarrow C_2H_2; \qquad \Delta H = +54.86 \text{ kcal} \quad ...(5)$$

Also, ΔH for

$$2C + H_2 \longrightarrow C_2H_2$$

ΔH = Bond energy data of formation of bond + Bond energy data of dissociation of bond

$$\Delta H = -[1(C\equiv C) + 2(C—H) + [2(C_{s\to g}) + 1(H—H)]$$

Also given, $\quad C_{s\to g} = 150 \text{kcal}$

$$\frac{1}{2}H_2(g) \longrightarrow H(g) = 51.5 \text{kcal}$$

$\therefore \quad e_{H—H} = 51.5 \times 2 \text{ kcal} = 103.0 \text{ kcal}$

$\quad e_{C—H} = 93.64 \text{ kcal}$

$\therefore \quad 54.86 = -[1(C\equiv C) + 2 \times 93.64] + [2 \times 150 + 1 \times 103.0]$

$\therefore \quad e_{C\equiv C} = \mathbf{160.86\ kcal}$

57. $\Delta H_{\text{Reaction}}$ = Bond energy data for formation of bond + Bond energy data for the dissociation of bond

$$= -[1(C—C) + 6(C—H)] + [1(C=C) + 4(C—H) + 1(H—H)]$$
$$= -1(C—C) - 2(C—H) + 1(C=C) + 1(H—H)$$
$$= -347 - 2 \times 414 + 615 + 435 = -125 \text{kJ}$$

$\therefore$ Enthalpy change for the reaction = **−125 kJ**

58. $\quad NH_3 \longrightarrow N(g) + 3H(g); \quad \Delta H_1 = x \text{ kcal mol}^{-1}$

$\quad N_2H_4 \longrightarrow 2N(g) + 4H(g); \quad \Delta H_2 = y \text{ kcal mol}^{-1}$

$$\Delta H_1 = 3 \times e_{N—H} = x \quad ...(1)$$
$$\Delta H_2 = 4 \times e_{N—H} + e_{N—N} = y \quad ...(2)$$

From Eqs. (1) and (2)

$\therefore \quad y = 4 \cdot \frac{x}{3} + e_{N—N}$

$\therefore \quad e_{N—N} = y - \frac{4x}{3} = \mathbf{\frac{3y - 4x}{3}\ kcal\ mol^{-1}}$

59. For C_2H_6: $\quad 2C + 3H_2 \longrightarrow C_2H_6; \qquad \Delta H_1$

For C_3H_8: $\quad 3C + 4H_2 \longrightarrow C_3H_8; \qquad \Delta H_2$

$$\therefore \quad \Delta H_1 = -[1(C—C) + 6(C—H)] + [2(C_{s\to g}) + 3(H—H)] \quad ...(1)$$

$$\text{and} \quad \Delta H_2 = -[2(C—C) + 8(C—H)] + [3(C_{s\to g}) + 4(H—H)] \quad ...(2)$$

Let C—C bond energy be a kcal

and C—H bond energy be b kcal

$$\therefore \quad \Delta H_1 = -[a + 6b] + [2 \times 172 + 3 \times 104] \quad ...(3)$$
$$\text{and} \quad \Delta H_2 = -[2a + 8b] + [3 \times 172 + 4 \times 104] \quad ...(4)$$

Also from $\quad C + O_2 \longrightarrow CO_2; \qquad \Delta H = -94.0 \text{ kcal} \quad ...(5)$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O; \qquad \Delta H = -68.0 \text{ kcal} \quad ...(6)$$
$$C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O; \qquad \Delta H = -372 \text{ kcal} \quad ...(7)$$
$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O; \qquad \Delta H = -530 \text{ kcal} \quad ...(8)$$

Multiply Eq. (5) by 2 and Eq. (6) by 3, then add

$$2C + 3H_2 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O; \qquad \Delta H = -392 \text{ kcal} \quad ...(9)$$

Subtracting Eq. (7) from Eq. (9)

$$2C + 3H_2 \longrightarrow C_2H_6; \qquad \Delta H = -20 \text{ kcal} \quad ...(10)$$

Similarly also from Eq. (5) multiplying by 3, Eq. (6) multiplying by 4 and adding both of them, then subtracting Eq. (8), we get

$$3C + 4H_2 \longrightarrow C_3H_8; \qquad \Delta H_2 = -24 \text{ kcal} \quad ...(11)$$

By Eqs. (3), (4), (10) and (11)

$$a + 6b = 676$$
$$2a + 8b = 956$$

$\therefore \quad a = 82$ kcal $\quad$ and $\quad b = 99$ kcal

$\therefore$ Bond energy of C—C bond = **82 kcal**

Bond energy of C—H bond = **99 kcal**

60. Given, $\quad C_6H_{10} + H_2 \longrightarrow C_6H_{12}; \qquad \Delta H = -119 \text{ kJ}$

(involves breaking up of one double bond and addition of one H_2 molecule)

$\therefore \quad C_6H_6 + 3H_2 \longrightarrow C_6H_{12}; \Delta H = 3 \times (-119) = -357 \text{kJ}$

(involves breaking up of three double bond and addition of three H_2 molecules)

Also given $\quad 6C + 6H_2 \longrightarrow C_6H_{12}(l); \quad \Delta H = -156$

we have $\quad C_6H_6 + 3H_2 \longrightarrow C_6H_{12}(l); \quad \Delta H = -357$

$$\begin{array}{cccc} - & - & - & + \\ \hline 6C + 3H_2 & \longrightarrow & C_6H_6; & \Delta H = +201 \text{kJ} \\ \hline \end{array}$$

Therefore, resonance energy $= \underset{\text{(Exp.)}}{49} - \underset{\text{(Theoretical)}}{201} = \mathbf{-152\ kJ}$

61. Given, for N_2O

$$N_2 + \frac{1}{2}O_2 \longrightarrow N_2O; \qquad \Delta H_{exp} = 82\,\text{kJ}$$

Also, from bond energy data, using N═N═O structure for N_2O

$$\Delta H_{f\,\text{cal.}} = -[1(\text{N═N}) + 1[(\text{N═O})] + [(\text{N≡N}) + \frac{1}{2}(\text{O═O})]$$

$$= -[418 + 607] + [946 + \frac{1}{2}(498)] = +170\,\text{kJ}$$

Now, resonance energy

$$= \text{Exp.}\,\Delta H_{f\,N_2O} - \text{Calculated}\,\Delta H_{f\,N_2O}$$

$$= 82 - 170 = \mathbf{-88\ kJ\ mol^{-1}}$$

62. $C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(l); \qquad \Delta H = ?$

ΔH = Bond energy data for formation + Bond energy data for dissociation + Energy released during liquefaction

$$= -[3\text{C—H} + 1\text{C—O} + 1\text{O—H}] + [C_{s\rightarrow g} + 2\text{H—H} + \frac{1}{2}\text{O—O}] - [CH_3OH(g) \longrightarrow CH_3OH(l)]$$

$$= -[3\times 415 + 356 + 463] + [715 + 2\times 436 + \frac{1}{2}\times 249] - 38$$

$$= \mathbf{-266\ kJ\ mol^{-1}}$$

63. For $\qquad 2C_4H_{10} \longrightarrow C_8H_{18} + H_2; \qquad \Delta H = ?$

Using bond energy data

ΔH = [Bond energy data for formation of bond + Bond energy data for dissociation of bond]

$$= -[7(\text{C—C}) + 18(\text{C—H}) + 1(\text{H—H})] + 2[3(\text{C—C}) + 10(\text{C—H})]$$

$$\Delta H = -(\text{C—C}) + 2(\text{C—H}) - 1(\text{H—H})$$

Given, $\qquad \frac{1}{2}H_2 \longrightarrow H; \qquad \Delta H = 217.55$

$\therefore \qquad H_2 \longrightarrow 2H; \qquad \Delta H = 2\times 217.55 = 435.1\,\text{kJ}$

$\therefore \qquad BE(\text{H—H}) = 435.1\,\text{kJ};$

Also, $\qquad BE(\text{C—C}) = 347.3\,\text{kJ}; \qquad BE(\text{C—H}) = 414.1\,\text{kJ}$

$\therefore \qquad \Delta H = -347.3 + 2\times(414.2) - 1\times(435.1)$

$$\Delta H = \mathbf{46.0\ kJ\ mol^{-1}}$$

64. For C_6H_6 : $6C(s) + 3H_2(g) \longrightarrow C_6H_6;$

$$\Delta H_{exp.} = -358.5\,\text{kJ}$$

$\therefore\ \Delta H_{cal.}$ = [BE data for formation of bonds + BE data for dissociation of bonds]

$$= -[3(\text{C—C}) + 3(\text{C═C}) + 6(\text{C—H})] + [6C_{s\rightarrow g} + 3(\text{H—H})]$$

$$= -[3\times 340 + 3\times 620 + 6\times 490] + [6\times 716.8 + 3\times 436.9]$$

$$= \Delta H_f = -208.5\,\text{kJ mol}^{-1}$$

$\therefore$ Resonance energy = Exp. ΔH_f − Calculated ΔH_f

$$= -358.5 - (208.5) = \mathbf{-150.0\ kJ\ mol^{-1}}$$

65. Temp. rise for water $= 55°C$

Mass of water to be heated $= 150\times 10^3$ g

$\therefore$ Heat used for water

$$= m\cdot s\times\Delta T = 150\times 10^3\times 4.184\times 10^{-3}\times 55$$

$$= 34518\,\text{kJ}$$

For propane : $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O;$

$$\Delta H = 2050\,\text{kJ}$$

$\because$ 2050 kJ heat is provided by 1 mole C_3H_8

$\therefore$ 34518 kJ heat is produced by $= \frac{34518}{2050}$

$$= \mathbf{16.838\ mol\ C_3H_8}$$

$\therefore$ Volume of C_3H_8 at NTP $= 16.838\times 22.4$ litre

$$= \mathbf{3.77\times 10^2\ litre}$$

66. I Case : Energy produced during passage of current is used to raise the temperature of calorimeter.

$\therefore \qquad Q\cdot V = mS\Delta T$

$3.20\times 3\times 12.0 = mS\times 1.617$

$\therefore \qquad mS\,\text{calorimeter} = 71.24\,\text{JK}^{-1}$

II Case : $Q_1V_1 = [mS\ \text{calorimeter} + mS\ \text{liquid}]\times\Delta T$

$0.5\times 1.50\times 3\times 60 = [71.24 + 100\times S]\times 0.8$

$\therefore \qquad S = 0.975\,\text{J/g}$

$\therefore \qquad$ Molar heat $= 0.975\times 40 = \mathbf{39.04\ J}$

67. $q = ms\cdot\Delta T$ for combustion of benzoic acid

(**NOTE** : In bomb calorimeter reaction is made at constant volume.)

$$\frac{0.316\times 3227}{122} = ms\times 3.24$$

$\therefore$ Water equivalent of bomb calorimeter (*ms*)

$$= \frac{0.316\times 3227}{122\times 3.24} = 2.58\,\text{kJ/°C}$$

For banana slice;

$$q = ms\times\Delta T$$

$$q = 2.58\times 3.05 = 7.87\,\text{kJ per 2.502 g banana}$$

$\therefore$ Heat produced by 125 g banana $= \frac{7.87\times 125}{2.502} = 393.18\,\text{kJ}$

$$= \frac{393.18}{4.184}\,\text{kcal}$$

$$= \mathbf{93.97\ kcal}$$

68. $\qquad C + H_2O(g) \longrightarrow H_2 + CO; \qquad \Delta H° = ?$

($\because$ $H°$ for C and H_2 are zero)

$$\therefore \qquad \Delta H° = H°_{CO} - H°_{H_2O} = -110.53 - (-241.81)$$

$$= 131.28\,\text{kJ/mol}$$

Thus, $\Delta H°$ needed for 100 g carbon $= \frac{131.28\times 100}{12}$ kJ

Now 393.51 kJ energy is provided by 12 g C

$\therefore\ \frac{131.28\times 100}{12}$ kJ energy is provided by

$$= \frac{12\times 131.28\times 100}{12\times 393.51}$$

$$= \mathbf{33.36\ g\ carbon}$$

69. Given,

Specific heat at constt. $P, c_p = 0.125$ cal/g

Specific heat at constt. $V, c_v = 0.075$ cal/g

(i) We have $c_p - c_v = \frac{R}{M}$ $\therefore$ $0.125 - 0.075 = \frac{2}{M}$

$\therefore$ $M = \mathbf{40}$

(ii) For atomicity $\gamma = \frac{c_p}{c_v} = \frac{0.125}{0.075} = 1.66$

$\therefore$ **Gas is monoatomic.**

(iii) Being monoatomic nature 1 molecule of gas has 1 atom.

$\therefore$ No. of atoms of gas in 1 mole = $\mathbf{6.023 \times 10^{23}}$ **atoms**

70. Given,

$$\underset{X}{CH_4} + \underset{6X}{2O_2} \longrightarrow CO_2 + 2H_2O; \Delta H = -809 \text{ kJ mol}^{-1}$$

Initial volume/hr

(in litre)

Let the temperature be T and assume volume of 1 mole of a gas is V litre at this condition.

$\therefore$ V litre or 1 mole CH_4 gives energy on combustion

$= 809 \text{kJ}$

$\therefore$ X litre of CH_4 gives energy on combustion

$= \frac{809(X)}{V}$ kJ

$\because$ 2878 kJ energy is obtained by 1 mole or V litre C_4H_{10}

$\therefore$ $\frac{809(X)}{V}$ kJ energy is obtained by $= \frac{809(X) \times V}{V \times 2878}$ litre C_4H_{10}

$= 0.281(X)$ litre C_4H_{10}

Thus, butane supplied for same calorific output

$= \mathbf{0.281(X)}$ **litre**

$\because C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O; \Delta H = -2878$ kJ/mol

Vol. of O_2 required = 3× vol. of O_2 for combustion of C_4H_{10}

$= 3 \times \frac{13}{2} \times$ vol. of C_4H_{10}

$= 3 \times \frac{13}{2} \times 0.281\,(X) = \mathbf{5.48\,(X)}$ **litre** $\mathbf{O_2}$

71. The first reaction is exothermic and the second one is endothermic. If a mixture of steam and O_2 is passed over coke and temperature is kept constant, the conversion of each to CO should not show any heat change, *i.e.*, total heat evolved in I = total heat absorbed in II.

$$n_1 \times 2 \times 110 = n_2 \times 132$$

$$\therefore \quad \frac{n_1}{n_2} = \frac{132}{110 \times 2} = \frac{\mathbf{0.6}}{\mathbf{1}}$$

where, n_1 and n_2 are mole of O_2 and H_2O used during reaction.

72. $C_{12}H_{22}O_{11} + 12O_2 \longrightarrow 12CO_2 + 11H_2O; \Delta H = -5645$ kJ

Mole of O_2 used per day $= \frac{640}{32} = 20$

$\therefore$ Mole of sucrose used per day $= \frac{20}{12}$ mole

$= \frac{20}{12} \times 342 \text{ g} = \mathbf{570\ g}$

Also, $\Delta H = \frac{5645 \times 20}{12} = \mathbf{9408.33\ kJ}$

73. Given, $C + O_2 \longrightarrow CO_2;$ $\Delta H = -94.05$ kcal

$C + \frac{1}{2}O_2 \longrightarrow CO;$ $\Delta H = -26.41$ kcal

Let a mole of carbon reacts to form CO_2 and b mole of carbon reacts to form CO. Since, only 12 g carbon, *i.e.*, 1 mole is used up, thus,

$$a + b = \frac{12}{12} = 1 \qquad \text{...(1)}$$

Also, $a \times 94.05 + b \times 26.41 = 75$

$\therefore$ $a = 0.718,$ *i.e.*, mole of CO_2 formed

$b = 0.282,$ *i.e.*, mole of CO formed

Also, mole of O_2 used for this change $= 0.718 + \frac{0.282}{2}$

$= 0.859$

Thus, mass of O_2 used $= 0.859 \times 32 = \mathbf{27.49\ g}$

74. Total mole of Mg $= \frac{1}{24}$

Let a mole of Mg^+ and b mole of Mg^{2+} are present, then

$$a + b = \frac{1}{24} \qquad \text{...(1)}$$

Also, $50 = a \times 740 + b \times 2190$ ...(2)

$\therefore$ From Eqs. (1) and (2),

$a = 2.845 \times 10^{-2}$

$b = 1.322 \times 10^{-2}$

$\therefore$ % of Mg^+ = **68.28%**

% of Mg^{2+} = **31.72%**

75. Given, $S(s) + 3F_2(g) \longrightarrow SF_6;$ $\Delta H = -1100$ kJ ...(1)

$S(s) \longrightarrow S(g);$ $\Delta H = 275$ kJ ...(2)

$\frac{1}{2}F_2(g) \longrightarrow F(g);$ $\Delta H = 80$ kJ ...(3)

To get $SF_6(g) \longrightarrow S(g) + 6F(g)$, we can proceed as $(2) + 6 \times (3) - (1)$

$SF_6(g) \longrightarrow S(g) + 6F(g);$ $\Delta H = 1855$ kJ

Thus, average bond energy $= \frac{1855}{6} = \mathbf{309.17}$

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

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

$\therefore$ $HAuBr_4 + 4HCl \longrightarrow HAuCl_4 + 4HBr;$ $\Delta H = 8.8$ kcal

$\therefore$ Fraction of $HAuBr_4$ converted to $HAuCl_4 = \frac{0.44}{8.8} = 0.05$

$\therefore$ % of $HAuBr_4$ converted $= 0.05 \times 100 =$ **5%**

77. Let a eq. of NaOH be used by HA, and b eq. of NaOH be used by HB. Also, heat of dissociation of $HB = +13.68 - 2.9 = 10.78$ kcal/eq.

$\therefore$ $a \times (-13.68) + b \times (-2.9) + b \times (10.78) = -6.9$

$\therefore$ $-13.68a + 7.88b = -6.9$

or $-13.68a + 7.88(1 - a) = -6.9$ $(a + b = 1)$

$\therefore$ $-21.56a = -14.78$ $\therefore$ $a = \mathbf{0.685}$

78. $Fe + \frac{1}{2}O_2 \longrightarrow FeO;$ $\Delta H = -65 \text{ kcal mol}^{-1}$ ...(i)

$2Fe + \frac{3}{2}O_2 \longrightarrow Fe_2O_3;$ $\Delta H = -197 \text{ kcal mol}^{-1}$ ...(ii)

By Eq. (ii) $-2\times$(i)

Also,

$$2FeO+\frac{1}{2}O_2 \longrightarrow Fe_2O_3\,;\ \Delta H=-67\text{ kcal mol}^{-1} \quad \text{...(iii)}$$

Let a mole of FeO and b mole of Fe_2O_3 are present such that

$$a+b=1 \text{ and } \frac{a}{b}=2$$

$$\therefore \quad a=\frac{2}{3} \text{ and } b=\frac{1}{3}$$

$$2FeO+\frac{1}{2}O_2 \longrightarrow Fe_2O_3$$

Initial	a	b
After oxidation	$(a-2a')$	$b+a'$

Given, $\frac{a}{b}=2$ and $\frac{a-2a'}{b+a'}=\frac{1}{2}$

$$\therefore \quad \frac{a-2a'}{\frac{a}{2}+a'}=\frac{1}{2} \qquad \therefore \quad 2a-4a'=\frac{a}{2}+a'$$

$$\therefore \quad a'=\frac{3a}{10}=\frac{3\times 2}{10\times 3}=\frac{1}{5} \qquad \therefore \quad \text{FeO used}=\frac{2}{5}$$

$\because$ 2 mole FeO gives heat = 67 kcal

$\therefore$ $\frac{2}{5}$ mole FeO gives heat $=\frac{67\times 2}{2\times 5}=$ **13.4 kcal heat**

79. $C_2H_5OH(g) \longrightarrow C_2H_4(g)+H_2O(g)$;

$$\Delta H^\circ=-45.54\text{ kJ} \quad \text{...(i)}$$

$C_2H_5OH(g) \longrightarrow CH_3CHO(g)+H_2(g)$;

$$\Delta H^\circ=-68.91\text{ kJ} \quad \text{...(ii)}$$

Let a mole of ethanol be decomposed by Eq. (i) and b mole be decomposed by Eq. (ii)

$$\therefore \quad a+b=1 \quad \text{...(iii)}$$

Also, the ratio of C_2H_4 and CH_3CHO formed is a/b

$$\therefore \quad \frac{a}{b}=8 \quad \text{...(iv)}$$

By Eqs. (iii) and (iv)

$$\therefore \quad 8b+b=1$$

$$b=\frac{1}{9} \text{ and } a=\frac{8}{9}$$

$$\therefore \quad \Delta H^\circ_{\text{Total}}=-\left[45.54\times\frac{8}{9}+68.91\times\frac{1}{9}\right]=\mathbf{-48.13\text{ kJ}}$$

80. $\Delta H=+4\times e_{\text{Xe-F}}+IE_{1\,\text{Xe}}-EA_{1\,\text{F}}-e_{\text{F-F}}$

$$=4\times 34+279-85-38=\mathbf{+292\text{ kcal/mol}}$$

81. Heat released during combustion of 3.5 g gas

$$=(mS)\times\Delta T=2.5\times 0.45=1.125\text{ kJ}$$

$\therefore$ Heat released for combustion of 1 mole (or 28 g) gas

$$=\frac{28}{3.5}\times 1.125=\mathbf{9\text{ kJ mol}}$$

• SINGLE INTEGER ANSWER PROBLEMS •

1. The ΔH_f° of $BaSO_{4(s)}$, $Ba^{2+}_{(aq)}$ and $SO^{2-}_{4(aq.)}$ are –350.6, –128.3 and –216.3 kcal. The heat of reaction (in kcal) is minus :
$BaCl_{2(aq.)} + H_2SO_{4(aq.)} \longrightarrow BaSO_{4(s)} + 2HCl_{(aq.)}$ is ......

2. The heat evolved in kcal for the process at 25°C of dissolving 1.0 mole of KCl in excess of water as
$$KCl_{(s)} \longrightarrow K^+ + Cl^-$$
(Given : ΔH_f° of $K^+_{(aq)}, Cl^-_{(aq)}$ and $KCl_{(s)}$ are –60, –40 and –104 kcal/mole).

3. If ΔH_f° of $H_2S_{(g)}$ and $H_2S_{(aq.)}$ are –4.5 and –9.5 kcal. How much heat is required for the change ?
$$H_2S_{(aq.)} \longrightarrow H_2S_{(g)}$$

4. If heat of reaction for the given acid base reaction :
$$HA + NaOH \longrightarrow NaA + H_2O; \quad \Delta H = -4.7\,\text{kcal}$$
The heat of dissociation of HA is ......

5. For a gas the numerical value (in cal) of $\left[\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V\right]$ is equal to ......

6. The enthalpy changes of some processes are given below
$$\alpha\text{-}D\text{-glucose}_{(s)} + H_2O \longrightarrow \alpha\text{-}D\text{-glucose}_{(aq.)}; \quad \text{Heat of dissolution} = 10.84\,\text{kJ}$$
$$\beta\text{-}D\text{-glucose}_{(s)} + H_2O \longrightarrow \beta\text{-}D\text{-glucose}_{(aq.)}; \quad \text{Heat of dissolution} = 4.68\,\text{kJ}$$
$$\alpha\text{-}D\text{-glucose}_{(aq.)} \longrightarrow \beta\text{-}D\text{-glucose}_{(aq.)}; \quad \text{Heat of mutarotation} = -1.16\,\text{kJ}$$
The ΔH° for $\alpha\text{-}D\text{-glucose} \longrightarrow \beta\text{-}D\text{-glucose}$ is ......

7. 10 mL of dissolution of a strong acid (HA) on mixing with 10 mL of strong alkali (BOH) at the same temperature shows a temperature rise of 4°C. If 50 mL of same acid are mixed with 50 mL of same alkali; the temperature rise will be ...... °C. Assume all the heat produced is used up in increasing temperature of mixture only.

8. Standard molar heat enthalpy for converting carbon from graphite and diamond form into vapour state directly are 725 and 713 kJ respectively. The standard enthalpy change for polymorphism of 1 g carbon $C_{G \to D}$ is ......

9. If heat of formation of $CaCl_2$ and NaCl are 191 and 97.5 kcal, the heat of reaction for $CaCl_2 + 2Na \longrightarrow 2NaCl + Ca$ is ......

10. The difference of $\Delta H - \Delta U$ for the given reaction is nRT. The value of n is ......
$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_v$$

11. Heat of combustion of a fuel molar mass 86 is 688 kJ/mole. The calorific value of fuel is ......

12. The combustion of 5.0 g of coke raised the temperature of 1.0 g of water from 10°C to 55°C. If specific heat of water of 1 cal/g, the calorific value of coke is ......

13. The enthalpy change involved in the oxidation of glucose is –2880 kJ mol^{-1}. 25% of this energy is available for muscular work. If 80 kJ of muscular work is needed to walk one km, what is the maximum distance that a person will walk after eating 120g glucose.

14. Heat of solution of anhydrous $CuSO_4$ is –15.9 kcal and heat of hydration of anhydrous $CuSO_4$ is –18.9 kcal. The heat of solution of $CuSO_4 \cdot 5H_2O$ is ......

15. ΔH_f° of Fe_2O_3 and Al_2O_3 are –189 kJ mol^{-1} and –405 kJ mol^{-1} respectively. How much heat (in kJ) is given out during reaction of 1 g Al according to
$$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe\ ?$$

16. How much of the following have their standard heat of formation zero at 298K. $O_2\,(l)$, C_{graphite}, P_{Black}, $S_{\text{monoclinic}}$, $I_{2\,(\text{solid})}$

17. How much of the following possess heat of neutralization less than –13.7 kcal.
$HCl(aq.) + NaOH(aq.)$, $HF(aq.) + NaOH(aq.)$,
$CH_3COOH(aq.) + NH_4OH(aq.)$,
$CCl_3COOH(aq.) + KOH(aq.)$,
$C_6H_5COOH(aq.) + KOH(aq.)$

18. For $Au(OH)_3 + 4HCl \longrightarrow HAuCl_4 + 3H_2O$; $\Delta H = -28$ kcal
and $Au(OH)_3 + 4HBr \longrightarrow HAuBr_4 + 3H_2O$; $\Delta H = -36.8$ kcal
If 1 mole of $HAuBr_4$ was mixed with 4 mole of HCl, 0.44 kcal heat was absorbed. The percentage conversion of $HAuBr_4$ to $HAuCl_4$ is ......

ANSWERS

1. Six **2.** Four **3.** Five **4.** Nine **5.** Two **6.** Five **7.** Four **8.** One **9.** Four **10.** Six **11.** Eight **12.** Nine
13. Six **14.** Three **15.** Four **16.** Three **17.** Two **18.** Five

OBJECTIVE PROBLEMS (One Answer Correct)

1. The e_{P-H} and e_{P-P} are 76 and 51 kcal mol^{-1}. The difference in the heat of atomisation for PH_3 and P_2H_4 in kcal mol^{-1} is:
(a) 127 (b) 178
(c) 203 (d) 25

2. Which of the following on mixing will give rise to maximum heat of reaction ?
(a) 100 mL of 0.1 *M* HCl + 40 mL of 0.1 *M* NaOH
(b) 60 mL of 0.1 *M* HCl + 60 mL of 0.1 *M* NaOH
(c) 40 mL of 0.1 *M* HCl + 30 mL of 0.1 *M* NaOH
(d) 40 mL of 0.1 *M* HCl + 100 mL of 0.1 *M* NaOH

3. The amount of heat released during the reaction of 300 mL of 1 *M* HCl with 100 mL of 1 *M* NaOH is :
(a) 57.3 kJ (b) 5.73 kJ
(c) 573 kJ (d) 573×10^3 kJ

4. Equal volumes of 1 *M* HCl and 1 *M* H_2SO_4 are neutralised by dilute NaOH solution producing *X* and *Y* kcal of heat respectively, then $(Y - X)$ is :
(a) 1 *Y* (b) 0.5 *Y*
(c) 0.1 *Y* (d) 5 *Y*

5. A solution of 200 mL of 1 *M* KOH is added to 200 mL of 1 *M* HCl and the mixture after attaining reaction equilibrium shows a rise in temperature by ΔT_1. The experiment is repeated by using 50 mL of 1 *M* KOH and 50 mL 1 *M* HCl which at equilibrium shows a rise in temperature by ΔT_2. Thus :
(a) $\Delta T_1 = \Delta T_2$ (b) $\Delta T_1 = 4 \times \Delta T_2$
(c) $\Delta T_1 = 2 \times \Delta T_2$ (d) $\Delta T_1 > \Delta T_2$

6. Given :
$HCl_{(g)} + 40H_2O \longrightarrow HCl(40H_2O)$; $\Delta H = -73.0$ kJ
$HCl_{(g)} + 10H_2O \longrightarrow HCl(10H_2O)$; $\Delta H = -69.0$ kJ
then integral heat of dilution for two moles of $HCl(10H_2O)$ to $HCl(40H_2O)$ is :
(a) – 4.5 kJ (b) – 3.5 kJ
(c) – 8.0 kJ (d) – 2.0 kJ

7. Heat of neutralisation for weak acid HF is :
(a) 13.7 kcal (b) > 13.7 kcal
(c) < 13.7 kcal (d) either of these

8. Molar heat capacity of water in equilibrium water $\rightleftharpoons$ vapours at constant pressure is :
(a) zero (b) infinity
(c) $\frac{80}{18}$ cal/mol (d) $\frac{540}{18}$ cal/mol

9. Which of the following is not endothermic ?
(a) $C + 2S \longrightarrow CS_2$ (b) $F_2 + \frac{1}{2}O_2 \longrightarrow F_2O$
(c) $N_2 + \frac{1}{2}O_2 \longrightarrow N_2O$ (d) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$

10. Two moles of CO and 1 mole of O_2 were allowed to react completely to form CO_2 at 300 K. If the heat liberated during the course of reaction : $2CO + O_2 \longrightarrow 2CO_2$ at constant pressure is 560 kJ, the amount of heat liberated by carrying the reaction in 1 litre vessel will be:
(1 litre-atm = 0.1 kJ)
(a) + 58 kJ (b) + 535.37 kJ
(c) + 557.54 kJ (d) + 55.75 kJ

11. One mole of ice melts at 0°C and 1 atm absorbing 1440cal of heat. The molar volume of ice and water are 0.0196 and 0.0180 litre respectively. The ΔU for the change is :
(a) $\simeq$ 1440 cal (b) >> 1400 cal
(c) << 1440 cal (d) = 1440 cal

12. The combustion of 10.0 g coke raised the temperature of 1.0 kg water from 10°C to 50°C. If specific heat of H_2O is 1 cal/g then the fuel value of coke is :
(a) 1000 cal (b) 2000 cal
(c) 3000 cal (d) 4000 cal

13. Molar heat capacity of water in equilibrium with the ice at constant pressure is :
(a) zero (b) infinity (∞)
(c) 40.45 kJ K^{-1} mol^{-1} (d) 75.48 JK^{-1} mol^{-1}

14. Standard molar enthalpy of formation of CO_2 is equal to :
(a) zero
(b) the standard molar enthalpy of combustion
(c) the sum of standard molar enthalpies of formation of CO and O_2
(d) the standard molar enthalpy of combustion of carbon (graphite)

15. For the reaction, $2O_3 \rightarrow 3O_2$, $\Delta H, \Delta S$ and ΔG are respectively:
(a) +ve, +ve, +ve (b) –ve, +ve, –ve
(c) –ve, –ve, +ve (d) +ve, –ve, –ve

16. For the reaction, $2Br_{(g)} \rightarrow Br_{2(l)}$, ΔH and ΔS are :
(a) –ve, –ve (b) +ve, –ve
(c) –ve, +ve (d) +ve, +ve

17. A reaction $X \rightarrow Y$ involves three steps. If
$X \rightarrow A; \Delta H = -a$ kcal ...(i)
$B \rightarrow A; \Delta H = -b$ kcal ...(ii)
$B \rightarrow Y; \Delta H = -c$ kcal ...(iii)
then ΔH for $X \rightarrow Y$ is:
(a) $a + b + c$ (b) $b - a - c$
(c) $a + b - c$ (d) $c + b - a$

18. Which of the following reaction shows standard enthalpy of formation of $CH_3Cl_{(g)}$, if reactions are made at 1 atm and 25°C:
(a) $CH_{4(g)} + Cl_{2(g)} \longrightarrow CH_3Cl_{(g)} + HCl_{(g)}$

(b) $C_{(G)} + \frac{3}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \longrightarrow CH_3Cl_{(g)}$

(c) $C_{(D)} + \frac{3}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \longrightarrow CH_3Cl_{(g)}$

(d) $C_{(S)} + \frac{3}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \longrightarrow CH_3Cl_{(g)}$

19. If $\Delta_f H°$ of $C_2H_{4(g)}$ and $\Delta_f H°$ of $C_2H_{6(g)}$ are q_1 and q_2 kcal mol^{-1}, then heat of hydrogenation of $C_2H_{4(g)}$ is:

(a) $q_2 - q_1$ (b) $q_2 + q_1$
(c) $q_1 + 2q_2$ (d) $q_1 - q_2$

20. If heat of formation of $NH_{3(g)}$ is –46 kJ mol^{-1}, then ΔH for the reaction : $2NH_3 \rightleftharpoons N_2 + 3H_2$ is :

(a) +46 kJ (b) +92 kJ
(c) –92 kJ (d) None of these

21. e_{H-H} is 436.4 kJ, then heat of formation of H atom is:

(a) 872.8 kJ mol^{-1} (b) – 218.2 kJ mol^{-1}
(c) +218.2 kJ mol^{-1} (d) – 436.4 kJ mol^{-1}

22. The amount of heat released when 20 mL of 0.5 *M* NaOH is mixed with 100 mL of 0.1 *M* HCl is *x* kJ. The heat of neutralisation (in kJ) is:

(a) –100 *x* (b) – 50 *x*
(c) 100 *x* (d) 50 *x*

23. For the reactions:

$A \rightarrow B; \Delta H = +24$ kJ mol^{-1}

$B \rightarrow C; \Delta H = -18$ kJ mol^{-1}

The decreasing order of enthalpy of *A*, *B*, *C* is:

(a) $A > B > C$ (b) $B > C > A$
(c) $C > B > A$ (d) $C > A > B$

24. One g sample of NH_4NO_3 is decomposed

$(NH_4NO_{3(s)} \rightarrow N_2O_{(g)} + 2H_2O_{(g)})$

in bomb calorimeter. The temperature of calorimeter increases by 6.12 K. The heat capacity of system is 1.23 kJ|g|°. The molar heat of decomposition is:

(a) –7.5 kJ (b) +7.5 kJ
(c) –16.1 kJ (d) +16.1 kJ

25. The enthalpy change for the process $C_{(s)} \rightarrow C_{(g)}$ is called:

(a) heat of vaporisation
(b) heat of atomisation
(c) heat of allotropic change
(d) heat of sublimation

26. The difference between heats of reaction at constant pressure and constant volume for the reaction:

$2C_6H_{6(l)} + 15O_{2(g)} \rightarrow 12CO_{2\,g)} + 6H_2O_{(l)}$ at 25°C in kJ is:

(a) –7.43 (b) +3.72
(c) –3.72 (d) +7.43

27. The products of combustion of an aliphatic thiol at 298 K are:

(a) $CO_{2(g)}$, $H_2O_{(g)}$ and $SO_{2(g)}$
(b) $CO_{2(g)}$, $H_2O_{(l)}$ and $SO_{2(g)}$
(c) $CO_{2(l)}$, $H_2O_{(l)}$ and $SO_{2(g)}$
(d) $CO_{2(g)}$, $H_2O_{(l)}$ and $SO_{2(l)}$

28. For which change, $\Delta H \neq \Delta E$

(a) $H_2 + I_2 \rightarrow 2HI$
(b) $HCl + NaOH \rightarrow NaCl + H_2O$
(c) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$
(d) $N_2 + 3H_2 \rightarrow 2NH_3$

29. Under the same conditions how many mL of 1*M* KOH and 0.5 *M* H_2SO_4 solution respectively when mixed for a total volume of 100 mL produce the highest rise in temperature :

(a) 67 : 33 (b) 33 : 67
(c) 40 : 60 (d) 50 : 50

30. One mole of ideal gas is kept in a cubical vessel of length *a* cm at 330 K. The gas is then transferred completely to a large cubical vessel of length 2*a* cm at 330 K. The change in entropy in cal/° for the ideal gas assuming reversible process.

(a) 2.07 (b) 4.15
(c) 6.21 (d) 1.03

31. The standard enthalpy of combustion of propane gas at 27°C –2220 kJ mol^{-1} and standard enthalpy of vaporisation of C_3H_8 is 15 kJ mol^{-1} at 27°C. What is the standard internal energy change for combustion of liquid propane. Water is formed during combustion.

(a) – 2205 kJ (b) – 2200 kJ
(c) – 1100 kJ (d) – 6600 kJ

32. $\Delta G°$ for the reaction : $Br_2(g) \rightleftharpoons 2Br(g)$ at 2400 K is –72.8 kJ mol^{-1}. If $\Delta H°$ being independent of temperature and equal to 205 kJ mol^{-1}, what will be the value of K at 2600 K.

(a) 38.39 (b) 84.46
(c) 19.19 (d) 42.32

SOLUTIONS (One Answer Correct)

1. (a) $PH_3 \longrightarrow P + 3H; \Delta H_1 = e_{P-H} \times 3 = 76 \times 3 = 228$ kcal

$P_2H_4 \longrightarrow 2P + 4H; \Delta H_2 = e_{P-P} + 4\,e_{P-H}$

$= 51 + (76 \times 4) = 355$ kcal

$\Delta H_2 - \Delta H_1 = 355 - 228 = 127$ kcal mol^{-1}

2. (b) 6 Meq. of HCl will react with 6 Meq. of NaOH to give maximum heat of reaction.

3. (b) Meq. of NaOH $= 100 \times 1 = 100$

Meq. of HCl $= 300 \times 1 = 300$

∴ 100 Meq. of HCl will react with 100 Meq. of NaOH
1000 Meq. of each react to give 57.27 kJ
∴ 100 Meq. of each react to give 5.727 kJ

4. (b) 1 *M* HCl = 1 *N* HCl, *i.e.*, $1 \times V$ Meq. gives heat = *X* kcal

$1\,M\,H_2SO_4 = 2\,N\,H_2SO_4$, *i.e.*, $2\times V$ Meq. gives heat $= Y$ kcal

Thus, $Y = 2X$ or $X = 0.5\,Y$

$Y - X = Y - 0.5\,Y = 0.5\,Y$

5. (a) No doubt more heat will be liberated in I reaction which will be used to heat mixture (400 mL). In II heat liberated will be 1/4 of I which will be used to heat mixture (1/4 of I, *i.e.*, 100 mL).

6. (c) Integral heat of dilution is the change in enthalpy when a solution containing 1 mole of a solute is diluted from one concentration to other.

7. (b) Due to extensive hydration of F^- ion because of smallest size.

8. (b) $C_p = \left(\frac{\partial H}{\partial T}\right)_p$; At equilibrium T is constant, *i.e.*, molar heat capacity at equilibrium is infinity.

9. (d) Rest all are endothermic.

10. (c) $\Delta H = \Delta U + \Delta nRT$

$\Delta n = -1$

Now, $\Delta H = \Delta U - 1\times 0.0821\times 300 = \Delta U - 24.62$

$-560 = \Delta U - 2.463$ $(\because 1\,\text{litre-atm} = 1\,\text{kJ})$

$\therefore$ $\Delta U = -557.54$ kJ

$\therefore$ Heat liberated at constant volume = 557.54 kJ

11. (a) $\Delta H = \Delta U + P\Delta V$

$$P\Delta V = 76\times 13.6\times 981\times(18-19.6)\,\text{erg}$$
$$= -1.62\times 10^6\ \text{erg}$$
$$= \frac{-1.62\times 10^6}{4.18\times 10^7} = -0.039\,\text{cal}$$

$\therefore$ $\Delta U = 1440 + 0.039\,\text{cal} \simeq \Delta H$

12. (d) Heat supplied to heat water $= ms\Delta T = 10^3\times 1\times 40$

$= 40\times 10^3$

$$\text{Calorific value} = \frac{\Delta H}{\text{Mass of fuel}} = \frac{40\times 10^3}{10} = 4000\,\text{cal}$$

13. (b) $C_p = \left(\frac{\partial H}{\partial T}\right)_p$; At equilibrium T is constant, *i.e.*, $\partial T = 0$; thus, $C_p = \infty$.

14. (d) Standard molar heat enthalpy (H°) of a compound is equal to its standard heat of formation from most stable states of initial components.

15. (b) $2O_3 \xrightarrow{300\,K} 3O_2$; $\Delta H = -68$ kcal; $\Delta S = +$ve.

16. (a) Bond formation shows $\Delta H = -$ve also entropy in liquid state is lesser than gaseous state.

17. (b) By (i) – (ii) + (iii)

18. (b) Carbon in graphite form has $H^\circ = 0$.

19. (a)

$$2C + 3H_2 \rightarrow C_2H_6\,;\ \Delta H = q_2$$
$$\underset{-}{2C} + \underset{-}{2H_2} \rightarrow \underset{-}{C_2H_4}\,;\ \Delta H \underset{-}{=} q_1$$
$$\overline{C_2H_4 + H_2 \rightarrow C_2H_6\,;\ \Delta H = q_2 - q_1}$$

20. (b) $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$; $\Delta H = -46$ kJ

21. (c) e_{H-H} = heat of formation of H atom × 2

$H_{2(g)} \rightarrow 2H;\ e_{H-H}$

$\frac{1}{2}H_2 \rightarrow H;\ \Delta_f H^\circ$ of H

22. (a) Meq. of NaOH $= 20\times 0.5 = 10$

Meq. of HCl $= 100\times 0.1 = 10$

$\therefore$ 10 Meq. (of HCl + NaOH) each reacts to give x kJ

$\therefore$ 1000 Meq. (of HCl + NaOH) each reacts to give $100\cdot x$ kJ

Heat of neutralisation $= -100x$

23. (b) $H_B > H_A$ Also $H_B - H_A = 24$

$H_C < H_B$ $H_B - H_C = 18$

$\therefore$ $H_B > H_C > H_A$

24. (a) $\Delta U = 1.23\times 10^3\times 6.12 = 7.5\times 10^3\,\text{J} = -7.5$ kJ

Heat is given out and thus – 7.5 kJ.

25. (d) C is converted directly from solid to gas.

26. (a) $\Delta H = \Delta U + \Delta nRT$

$\Delta H - \Delta U = \Delta nRT$

$= -3\times 8.314\times 298 = -7432.7\,\text{J} = -7.43$ kJ

27. (b) Thiol is RSH

28. (d) $\Delta H = \Delta U + \Delta nRT$; $\Delta n = -2$ in (d)

29. (d) 50 Meq. of KOH and 50 Meq. of H_2SO_4 will neutralise completely.

30. (b) Initial volume $= a^3\text{cm}^3$

Final volume $= 8a^3\text{cm}^3$

$$\therefore\quad \Delta S = 2.303R\log\frac{V_2}{V_1}$$
$$= 2.303\times 2\log 8$$
$$= 4.15\ \text{cal/}^\circ$$

31. (b) $C_3H_8(l) \longrightarrow C_3H_8(g)$; $\Delta H_1 = +15$ kJ

$C_3H_8(g) + 5O_2 \longrightarrow 3CO_2(g) + 4H_2O(l)$; $\Delta H_2 = -2220$ kJ

$C_3H_8(l) + 5O_2 \longrightarrow 3CO_2(g) + 4H_2O(l)$; $\Delta H_3 = ?$

$\therefore$ $\Delta H_3 = \Delta H_1 + \Delta H_2 = 15 - 2220 = -2205$ kJ

Now, $\Delta H = \Delta U + \Delta nRT$

$-2205 = \Delta U + (-2)\times 8.314\times 300\times 10^{-3}$ $(\Delta n = 3 - 5 = -2)$

$\therefore$ $\Delta U = -2200$ kJ

32. (b) $-\Delta G^\circ = 2.303RT\log K$

$72800 = 2.303\times 8.314\times 2400\log K$

$K = 38.39$ at 2400 K

Also at $2.303\log\frac{K_2}{K_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

$$2.303\log\frac{K_2}{38.39} = \frac{205000}{8.314}\times\left[\frac{2600-2400}{2600\times 2400}\right]$$
$$\frac{K_2}{38.39} = 2.20$$
$$\therefore\quad K_2 = 84.46$$

• PREVIOUS YEARS PROBLEMS •

1. 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 given reaction is : **(IIT 2000)**

$CO_{2(g)} + H_{2(g)} \longrightarrow CO_{(g)} + H_2O_{(g)}$

(a) +524.1 (b) +41.2

(c) –262.5 (d) – 41.2

2. Which of the reaction defines $\Delta_f H^\circ$: **(IIT 2003)**

(a) $C_{(Diamond)} + O_2 \longrightarrow CO_{2(g)}$

(b) $1/2H_{2(g)} + 1/2F_{2(g)} \longrightarrow HF_{(g)}$

(c) $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

(d) $CO_{(g)} + 1/2O_{2(g)} \longrightarrow CO_{2(g)}$

3. For which reaction ΔH_r° is equal to ΔH_f°: **(IIT 2002)**

(a) $CH_{4(g)} + 2Cl_{2(g)} \longrightarrow CH_2Cl_{2(l)} + 2HCl_{(g)}$

(b) $Xe_{(g)} + 2F_{2(g)} \longrightarrow XeF_{4(g)}$

(c) $2CO + O_{2(g)} \longrightarrow 2CO_{2(g)}$

(d) $N_{2(g)} + O_{3(g)} \longrightarrow N_2O_{3(g)}$

4. $\Delta H_{vap} = 30$ kJ/mol and $\Delta S_{vap} = 75$ J $mol^{-1}K^{-1}$. Find temperature of vapour at one atmosphere: **(IIT 2004)**

(a) 400 K (b) 350 K

(c) 298 K (d) 250 K

5. The bond energy (in kcal mol^{-1}) of a C—C single bond is approximately : **(IIT 2010)**

(a) 1 (b) 10

(c) 100 (d) 1000

6. The species which by definition has zero standard molar enthalpy of formation at 298 K : **(IIT 2010)**

(a) $Br_2(g)$ (b) $Cl_2(g)$

(c) $H_2O(g)$ (d) $CH_4(g)$

7. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a $C\equiv C$ bond in C_2H_2. Given that the heat of formation of $C_2H_2 = 225$ kJ mol^{-1}. (take the bond energy of a C–H bond as 350 kJ mol^{-1}):

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

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

(IIT 2012)

(a) 1165 (b) 837

(c) 865 (d) 815

8. 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 and –1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25°C is : **[JEE (Advanced-I) 2013]**

(a) +2900 kJ (b) –2900 kJ

(c) –16.11 kJ (d) +16.11 kJ

9. For complete combustion of ethanol, $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$, 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, $\Delta_C H$, for the reaction will be : **[JEE (Main) 2014]**

($R = 8.314$ kJ mol^{-1})

(a) –1366.95 kJ mol^{-1} (b) –1361.95 kJ mol^{-1}

(c) –1460.50 kJ mol^{-1} (d) –1350.50 kJ mol^{-1}

10. The heats of combustion of carbon and carbon monoxide are – 393.5 and – 283.5 kJ mol^{-1}, respectively. The heat of formation (in kJ) of carbon monoxide per mole is : **[JEE (Main) 2016]**

(a) 676.5 (b) – 676.5

(c) – 110.5 (d) 110.5

11. Given :

$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g)$;

$\Delta_r H^\circ = -393.5$ kJ mol^{-1}

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

$\Delta_r H^\circ = -285.8$ kJ mol^{-1}

$CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g)$;

$\Delta_r H^\circ = +890.3$ kJ mol^{-1}

Based on the above thermochemical equations, the value of $\Delta_r H^\circ$ at 298 K for the reaction :

$C_{(graphite)} + 2H_2(g) \longrightarrow CH_4(g)$ will be : **[JEE (Main) 2017]**

(a) + 74.8 kJ mol^{-1} (b) + 144.0 kJ mol^{-1}

(c) – 74.8 kJ mol^{-1} (d) – 144.0 kJ mol^{-1}

SOLUTIONS (Previous Year Problems)

1. (b) Given,

$$C + O_2 \longrightarrow CO_2\,;\quad \Delta H^\circ = -393.5\text{ kJ} \quad \text{...(1)}$$
$$C + 1/2O_2 \longrightarrow CO;\quad \Delta H^\circ = -110.5\text{ kJ} \quad \text{...(2)}$$
$$H_2 + 1/2O_2 \longrightarrow H_2O;\quad \Delta H^\circ = -241.8\text{ kJ} \quad \text{...(3)}$$

By Eqs. (2) + (3) − (1) $CO_2 + H_2 \longrightarrow CO + H_2O;$

$$\Delta H^\circ = +41.2$$

2. (b) No doubt (a) and (b) both represents heat of formations but standard heat of formation $\Delta_f H^\circ$ for CO_2 will be formed from carbon graphite.

$C_{\text{Graphite}} + O_2 \longrightarrow CO_2$ as graphite is most stable form of carbon.

3. (b) It is based on definitions of heat of formation of $XeF_{4(g)}$.

4. (a) $\Delta H = \Delta S \cdot T$

$$\therefore\quad T = \frac{\Delta H}{\Delta S} = \frac{30 \times 10^3}{75} = 400\text{ K}$$

5. (c) e_{C-C} ranges between 85 to 150 kcal mol^{-1}.

6. (b) Standard molar enthalpy of elements in their most stable state is zero.

$$H^\circ_{Br_2(l)} = 0;\quad H^\circ_{Cl_2(g)} = 0;\quad H^\circ_{I_2(s)} = 0$$

7. (d) (i) $2C(s) + H_2(g) \longrightarrow H-C \equiv C-H(g)$,

$$\Delta H = 225\text{ kJ mol}^{-1}$$

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

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

From equation (i) :

$$225 = [2 \times \Delta H_{C(s) \to C(g)} + 1 \times e_{H-H}] - [2 \times e_{C-H} + 1 \times e_{C\equiv C}]$$
$$225 = [1410 + 1 \times 330] - [2 \times 350 + 1 \times e_{C\equiv C}]$$
$$225 = [1410 + 330] - [700 + e_{C\equiv C}]$$
$$225 = 1740 - 700 - e_{C\equiv C}$$
$$e_{C\equiv C} = 1040 - 225 = 815\text{ kJ mol}^{-1}$$
$$BE_{C\equiv C} = 815\text{ kJ mol}^{-1}$$

8. (c) $C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$

$$\Delta_{f\,\text{comb.}C_6H_{12}O_6} H^\circ = 6\Delta_f H^\circ_{CO_2} + 6\Delta_f H^\circ_{H_2O(l)} - \Delta_f H^\circ_{C_6H_{12}O_6(s)}$$
$$= 6 \times (-400) + 6 \times (-300) - (-1300) = -2900\text{ kJ/mol}$$

∴ Standard enthalpy of combustion per gram of glucose

$$= \frac{-2900}{180} = -16.11\text{ kJ}$$

9. (a) $\Delta_C H = \Delta_C U + \Delta n_{(g)} RT$

$$\Delta_C U = -1364.47\text{ kJ mol}^{-1},\ \Delta n_{(g)} = 2 - 3 - 1$$
$$\therefore\quad \Delta_C H = -1364.47 \times 10^3 + (-1) \times 8.314 \times 298$$
$$= -1364470 - 2477.57 = -1366.95\text{ J}$$
$$= -1366.95\text{ kJ mol}^{-1}$$

The value of R given in question is wrong, it is 8.314 J mol^{-1}.

10. (c) Given,

$$C(s) + O_2(g) \longrightarrow CO_2(g);\quad \Delta H = -393.5\text{ kJ/mol} \quad \text{...(1)}$$
$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g);\ \Delta H = -283.5\text{ kJ/mol} \quad \text{...(2)}$$

By eq. (1) − eq. (2)

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g);$$
$$\Delta H = -393.5 + 283.5\text{ kJ/mol} = -110\text{ kJ/mol}$$

Note : However choice (c) shows − 110.5 kJ/mol

11. (c)

$$C_{(\text{graphite})} + O_2(g) \longrightarrow CO_2(g);$$
$$\Delta_r H^\circ = -393.5\text{ kJ mol}^{-1} \quad \text{...(i)}$$
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);$$
$$\Delta_r H^\circ = -285.8\text{ kJ mol}^{-1} \quad \text{...(ii)}$$
$$CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g);$$
$$\Delta_r H^\circ = 890.3\text{ kJ mol}^{-1} \quad \text{...(iii)}$$

By

(i) + 2 × (ii) + (iii), we get

$$C_{(\text{graphite})} + 2H_2(g) \longrightarrow CH_4(g);\ \Delta_r H^\circ$$
$$\Delta_r H^\circ = -393.5 - 285.8 \times 2 + 890.3$$
$$= -74.8\text{ kJ mol}^{-1}$$

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Which of the following mixtures on neutralisation will show a same rise in temperature ?
(a) 60 mL of 0.1 M HCl + 60 mL of 0.1 M NaOH
(b) 30 mL of 0.1 M HCl + 30 mL of 0.1 M NaOH
(c) 40 mL of 0.1 M HCl + 30 mL of 0.1 M NaOH
(d) 60 mL of 0.1 M HCl + 100 mL of 0.1 M NaOH

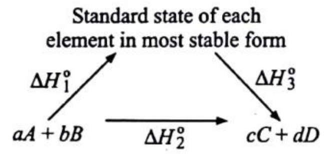
2. If $\Delta_f H^\circ_{(C_2H_6)g} = -85\ \text{kJ mol}^{-1}$, $\Delta H^\circ_{f(C_3H_8)g} = -104\ \text{kJ mol}^{-1}$, ΔH° for $C_{(s)} \longrightarrow C_{(g)}$ is 718 kJ mol^{-1} and heat of formation of H-atom is 218 kJ mol^{-1}, then :
(a) $e_{C-C} = 345$ kJ (b) $e_{C-H} = 414$ kJ
(c) $e_{H-H} = 436$ kJ (d) $e_{H-H} = 218$ kJ

3. For which reaction $\Delta H < \Delta U$:
(a) $COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$
(b) $NH_4Cl_{(s)} \rightleftharpoons NH_{3(v)} + HCl_{(v)}$
(c) $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$
(d) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

4. Melting of ice at –1°C shows :
(a) $\Delta S = +$ ve (b) $\Delta H = +$ ve
(c) $\Delta G = +$ ve (d) process is spontaneous

5. Select the correct statements :
(a) All combustion reactions are exothermic
(b) Heat of combustion are always exothermic
(c) $N_2 + O_2 \longrightarrow 2NO; \Delta H = +$ ve
(d) $F_2 + \frac{1}{2}O_2 \longrightarrow F_2O; \Delta H = +$ ve

6. Which of the following are incorrect ?



(a) $\Delta H_1^\circ = -aH_A^\circ - bH_B^\circ$
(b) $\Delta H_2^\circ = cH_C^\circ + dH_D^\circ$
(c) $\Delta H_3^\circ = cH_C^\circ + dH_D^\circ - aH_A^\circ - bH_B^\circ$
(d) $\Delta H_3^\circ = \Delta H_2^\circ - \Delta H_1^\circ$

7. Which of the following reactions are exothermic ?
(a) Rusting of iron (b) Burning of wax
(c) Synthesis of NH_3 (d) Condensation of steam

8. Select the correct statements :
(a) A good fuel has higher calorific value
(b) Endothermic reactions always becomes faster as we approach absolute zero
(c) Enthalpy of vaporisation increases from F_2 to I_2
(d) Bond enthalpy of X—X bond has the order :
F—F > Cl—Cl > Br—Br > I—I

9. Select the correct statements :
(a) Bond energy of $e_{H-H} = 2 \times \Delta_f H$ of H-atom
(b) The ratio of heat of vaporisation and the normal boiling point of a liquid is $\simeq 88\ \text{J mol}^{-1}$
(c) Heat of neutralisation for HF is – 16.4 kcal eq.$^{-1}$
(d) Hess's law can be proved experimentally

10. Which of the following are endothermic reactions ?
(a) Combustion of CH_4
(b) Decomposition of H_2O
(c) Dehydrogenation of ethane
(d) Conversion of graphite to diamond

SOLUTIONS (More Than One Answer Correct)

1. (a,b) (a) Generates $\frac{60 \times 0.1 \times 13.7}{1000}$ kcal heat which is used by 120 mL solution.
(b) Generates $\frac{30 \times 0.1 \times 13.7}{1000}$ kcal heat which is used by 60 mL solution.

2. (a,b,c) $\frac{1}{2}H_2 \longrightarrow H; \Delta H^\circ = 218$ kJ; Let e_{C-C} be a and e_{C-H} be b kJ.

$$\therefore \quad e_{H-H} = 436\ \text{kJ}$$

$$2C + 3H_2 \longrightarrow C_2H_6; \Delta_f H^\circ$$

Also, $\Delta_f H^\circ C_2H_6 = -[e_{C-C} + 6e_{C-H}] + [2C_{s \to g} + 3e_{H-H}]$

$$-85 = -[e_{C-C} + 6b] + [2 \times 718 + 3 \times 436] \text{ or}$$

$$a + 6b = 2829$$

$$3C + 4H_2 \longrightarrow C_3H_8; \Delta H^\circ$$

$$\Delta_f H^\circ C_3H_8 = -[2e_{C-C} + 8e_{C-H}] + [3C_{s \to g} + 4e_{H-H}]$$

$$-104 = -[2a + 8b] + [3 \times 718 + 4 \times 436] \text{ or}$$

$$2a + 8b = 4002$$

$$\therefore \quad a = 345\ \text{kJ}, \quad b = 414\ \text{kJ}$$

3. (c,d) $\Delta H = \Delta U + \Delta nRT$ if Δn is – ve, then $\Delta H < \Delta U$.

4. (a,b,c) ΔH and ΔS both increase on melting of ice.

5. (b,c,d) Only three combustions are endothermic. The third one is $N_2 + \frac{1}{2}O_2 \longrightarrow N_2O; \Delta H = +$ ve.

6. (b,c) $\Delta H_1^\circ = \Sigma H_{s.s}^\circ - \Sigma H_R^\circ$ and so on.

7. (a,b,c,d) All are exothermic.

8. (a,c) $e_{Cl-Cl} > e_{F-F}$

9. (a,b,c) $\frac{1}{2}H_2 \longrightarrow H; \Delta_f H \therefore e_{H-H} = 2 \times \Delta_f H$; Also, HF has higher ΔH neutralisation due to extensive hydration of F^- ions. Also, Hess's law has been proved theoretically. Trouton's rule $\frac{\Delta H_V}{T_b} \simeq 88\ \text{J mol}^{-1}$

10. (b,c,d) Heat of combustion is always – ve.

COMPREHENSION BASED PROBLEMS

Comprehension 1 : Chemical reactions are usually exothermic or endothermic. A balanced thermochemical equation involving physical states of reactants and products expresses the chemical changes as well as heat of reaction. Heat changes are usually expressed in terms of ΔH (at constant P) or ΔU (at constant V). The heats of reactions varies with physical state of reactants and products, conditions of constant pressure or volume and temperature. Heats of combustion and heat of neutralization, heat of condensation are always exothermic. Standard heat enthalpy of a compound is its heat of formation at 1 atm P and 25°C.

[1] The heat energy released during neutralization of 1 eq. of HF with 1 eq. of NaOH and with 1 eq. of CH_3COOH and 1 eq. of NaOH are respectively :
(a) −16.4 kcal, −12.0 kcal (b) −12.0 kcal, −10 kcal
(c) −13.7 kcal in both (d) −12.0 kcal, −16.4 kcal

[2] Heat of dissociation for H_2O in H^+ and OH^- ions is :
(a) −57.27 kJ/mol (b) +57.27 kJ/mol
(c) −50 kJ/mol (d) +50 kJ/mol

[3] In which case of mixing a strong acid and a base each of 1 N concentration, temperature rise is highest :
(a) 20 mL acid + 30 mL alkali
(b) 10 mL acid + 40 mL alkali
(c) 25 mL acid + 25 mL alkali
(d) 30 mL acid + 20 mL alkali

[4] Heat of combustion of CH_4, C_2H_4, C_2H_2 and C_2H_6 are $-890, -1411, -1300$ and -1560 kJ mol^{-1}. The best fuel is :
(a) CH_4 (b) C_2H_4
(c) C_2H_6 (d) C_2H_2

[5] The enthalpy of which form of carbon has been supposed to be zero at 25°C and 1 atm :
(a) Graphite (b) Diamond
(c) Coke (d) Charcoal

[6] Molar heat capacity of diamond carbon in equilibrium with graphite carbon at constant pressure is :
(a) zero (b) infinity
(c) 3.4 kJ/mol (d) −3.4 kJ/mol

Comprehension 2 : 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 (Advanced II) 2015]**

[1] 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

[2] The pH of the solution after **Expt-2 :**
(a) 2.8 (b) 4.7
(c) 5.0 (d) 7.0

SOLUTIONS

Comprehension 1

[1] (a) Heat released during neutralization of weak acid < -13.7. In HF, hydration of F^- ion is responsible for higher value.

[2] (b) $H^+ + OH^- \longrightarrow H_2O; \quad \Delta H = -13.7 \times 4.18\,kJ$

[3] (c) 25 Meq. of acid and 25 Meq. of alkali reacts to give $\frac{13.7 \times 25}{1000}$ kcal heat

[4] (a) Best fuel is CH_4 as its calorific value $= \frac{890}{16} = 55.63\,kJ$

[5] (a) Graphite is the most stable form of carbon.

[6] (b) $C_p = \left[\frac{\Delta H}{\Delta T}\right]_p$. At equilibrium during phase transition

$\Delta T = 0$

Comprehension 2

[1] (a)

$$\begin{array}{lcccccc} & HCl & + & NaOH \longrightarrow & NaCl & + & H_2O \\ \text{m.mol before reaction} & 100 & & 100 & - & & - \\ \text{m.mol after reaction} & - & & - & 100 & & 100 \end{array}$$

Heat released by the reaction of 100 m.mol of HCl and NaOH each $= [200 \times 4.2 + C] \times 5.7$ ...(1)

Heat of neutralisation for 100 m. mol of NaOH and HCl each $= 57 \times 1000 \times \frac{100}{1000}$ ...(2)

By (1) and (2)

$$\therefore \quad 57 \times 1000 \times \frac{100}{1000} = [200 \times 4.2 + C] \times 5.7 \qquad \text{...(3)}$$

Similarly for the neutralisation of 100 m.mol of NaOH and CH_3COOH each is given by

$$\begin{array}{ccccccc} CH_3COOH & + & NaOH & \longrightarrow & CH_3COONa & + & H_2O \\ 200 & & 100 & & - & & - \\ 100 & & - & & 100 & & - \end{array}$$

$$\Rightarrow |\Delta H| \times 1000 \times \frac{100}{1000} = [200 \times 4.2 + C] \times 5.6 \qquad \text{...(4)}$$

By eq. (3) eq. (4)

$$|\Delta H| = 56\,kJ/mol$$
$$\Delta H_{\text{neutralisation}} = -56\,kJ/mol$$
$$-56 = -57 + \Delta H_{IE}$$
$$\Delta H_{IE} = 1\,kJ/mol$$

[2] (b) Solution is buffer which cantains 100 m.mol of CH_3COOH and 100 m.mol of CH_3COONa

$$pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$
$$= -\log(2 \times 10^{-5}) + \log\frac{100/1000}{100/1000}$$
$$= 5 - \log 2$$
$$= 4.7$$

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement (S) and explanation (E) is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) S is correct but E is wrong
(b) S is wrong but E is correct
(c) Both S and E are correct and E is correct explanation of S
(d) Both S and E are correct but E is not correct explanation of S

1. S : Heat of neutralization for HF is – 68.552 kJ/eq. where as for HCl it is –57.26 kJ/eq.
E : The acid HF is weak acid.

2. S : In a diatomic molecule involving two like atoms covalently bonded with each other, bond energy = 2 × heat of formation of atom.
E : $H_2 \longrightarrow 2H; e_{H—H} = \Delta H.$

3. S : Bond energy for breaking up a bond is endothermic.
E : Heat is required to overpower the attractions between two atoms.

4. S :

$$C+\frac{1}{2}O_2 \longrightarrow CO; \qquad \Delta H = -26.0 \text{ kcal}$$

$$CO+\frac{1}{2}O_2 \longrightarrow CO_2; \qquad \Delta H = -68.3 \text{ kcal}$$

$$\therefore \quad C+O_2 \longrightarrow CO_2; \qquad \Delta H = -94.3 \text{ kcal}$$

E : This is an experimental proof of Hess's law.

5. S : Heat of combustion are always exothermic.
E : Combustion of N_2 to give NO is exothermic.

6. S : Combustion of N_2 to give NO is endothermic.
E : Bond energy of N_2 is very high.

7. S : The ratio of heat of vaporisation and the normal boiling point of a liquid is approximately 88 J/mol.
E : This is Trouton's rule derived by experimental data.

8. S : Standard heat enthalpy of a compound is its heat of formation at 25°C and 1 atm.
E : Standard heat enthalpy of pure elements have arbitrarily assumed to be zero.

9. S : The variation of heat of reaction with temperature are given in terms of Kirchhoff's equation.
E : The Kirchhoff's equation is : $\Delta H = \Delta U + \Delta nRT$.

10. S : Heat of neutralization can be given as :

$$H^+ + OH^- \longrightarrow H_2O; \quad \Delta H = -13.6 \text{ kcal}$$

E : Heat of neutralization can be alternatively defined as heat of formation of water.

11. S : The dissolution of NaCl in water is endothermic, though it is spontaneous process.
E : ΔG for the process is –ve because ΔH_{sol} is very low and thus $T\Delta S > \Delta H$.

12. S : Heat of combustion of C_2H_6 is –341.1 kcal mol^{-1} and heat of combustion of C_2H_2 is –310 kcal mol^{-1} but C_2H_2 is better fuel.
E : The better fuel has high calorific value.

ANSWERS (Statement Explanation Problems)

1. (d) No doubt HF is weak acid but the higher values are due to extensive hydration of F^- ion being smallest anion (only H^- is smaller than F^-)
2. (c) Heat of formation of H atom = $\Delta H = \frac{e_{H—H}}{2}$.
3. (c) Explanation is correct reason for statement.
4. (a) This is an application of Hess's law and not an experimental proof. Hess's law has been verified theoretically.
5. (a) $\frac{1}{2}N_2 + \frac{1}{2}O_2 \longrightarrow NO; \Delta H = +$ ve. It is due to high bond energy of N_2. Note this equation does not represent heat of combustion of N_2 (Partial combustion).
6. (c) Explanation is correct reason for statement.
7. (c) This is Trouton's rules derived from exp. data.
8. (c) Explanation is correct reason for statement.
9. (a) Kirchhoff's equation is $\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$.
10. (a) Heat of formation of water is $H_2 + 1/2O_2 \longrightarrow H_2O$; ΔH_{for}.
11. (c) Explanation is correct reason for statement.
12. (c) Calorific value is defined as the heat given out by burning 1 g fuel.

$$\text{Calorific value for } C_2H_6 = \frac{-341.1}{30} = -11.37 \text{kcal/g}$$

$$\text{Calorific value for } C_2H_2 = \frac{-310}{26} = -11.92 \text{kcal/g}$$

MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

1.	List A		List B
A.	$HCl + NH_4OH \rightarrow NH_4Cl + H_2O$	(a)	$\Delta H = -13.7\,\text{kcal}$
B.	$H^+ + OH^- \rightarrow H_2O$	(b)	$\Delta H > -13.7\,\text{kcal}$
C.	$HF + NaOH \rightarrow NaF + H_2O$	(c)	$\Delta H < -13.7\,\text{kcal}$

2.	List A		List B
A.	$2P_W + 5O_2 \rightarrow P_2O_5$	(a)	$\Delta_f H$ of P_2O_5
B.	$2P_G + 5O_2 \rightarrow P_2O_5$	(b)	$\Delta_f H^\circ$ of P_2O_5
C.	$C_A + O_{2(g)} \rightarrow CO_{2(g)}$	(c)	$\Delta_f H^\circ$ of CO_2
D.	$C_G + O_{2(g)} \rightarrow CO_{2(g)}$	(d)	$\Delta_f H$ of CO_2

3.	List A		List B
A.	$O_{2(g)} \rightarrow O_{2(l)}$	(a)	$\Delta_r H^\circ = \Delta_{\text{cond}} H^\circ$
B.	$Br_{2(l)} \rightarrow Br_{2(g)}$	(b)	$\Delta_r H^\circ = \Delta_v H^\circ$
C.	$I_{2(s)} \rightarrow I_{2(l)}$	(c)	$\Delta_r H^\circ = \Delta_s H^\circ$
D.	$H_2O_{(s)} \rightarrow H_2O_{(v)}$	(d)	$\Delta_r H = \Delta_s H$

4.	List A		List B
A.	$H_2 \rightarrow 2H$	(a)	$\Delta H = \Delta_f \text{H of H} \times 2$
B.	$CH_4 \rightarrow C + 4H$	(b)	$\Delta H =$ Average bond energy ×4
C.	$C_2H_2 + 2H_2 \rightarrow C_2H_6$	(c)	$\Delta H = -e_{C\equiv C} - 4e_{C-H} + 2e_{H-H} + e_{C-C}$
D.	$C_2H_4 + H_2 \rightarrow C_2H_6$	(d)	$\Delta H = -e_{C=C} - e_{H-H} + e_{C-H} + e_{C-C}$

Type II : More Than One Match Are Possible

5.	List A		List B
(A)	$C_6H_{12}O_6 + (aq) \rightleftharpoons C_6H_{12}O_6(aq)$	(i)	Exothermic
(B)	$CaO + (aq) \rightleftharpoons Ca(OH)(aq)$	(ii)	Endothermic
(C)	$C + O_2 \rightarrow CO_2$; at 298 K	(iii)	ΔH is heat of reaction
(D)	$C_{\text{graphite}} + O_2 \rightarrow CO_2$; $\Delta H_{298\,K}$ at 298 K	(iv)	ΔH is heat of formation of CO_2
		(v)	ΔH is standard heat of formation of CO_2
		(vi)	ΔH is standard heat enthalpy of CO_2

6.	List A		List B
(A)	$\Delta_f H^\circ(O_2, g)$	(i)	Zero
(B)	$\Delta_f H^\circ(S_R)$	(ii)	Not equal to zero
(C)	$\Delta_f H^\circ(S_M)$	(iii)	Most stable form
(D)	$\Delta_f H^\circ(P_{\text{white}})$	(iv)	Less stable form
(E)	$\Delta_f H^\circ(P_{\text{black}})$		

7.	List A		List B
(A)	$CO_2(s) \longrightarrow CO_2(g)$	(p)	Phase transition
(B)	$CaCO_3(s) \longrightarrow CaO(s) + CO(g)$	(q)	Allotropic change
(C)	$2H \longrightarrow H_2(g)$	(r)	$\Delta H = +ve$
(D)	$\underset{\text{(White, solid)}}{P} \longrightarrow \underset{\text{(red, solid)}}{P}$	(s)	$\Delta S = +ve$
		(t)	$\Delta S = -ve$

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8.	List A		List B
(A)	$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$	(p)	Standard enthalpy of $CO_2(g)$
(B)	$C_{\text{graphite}} + O_2(g) \rightarrow CO_2(g)$	(q)	Enthalpy of reaction
(C)	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	(r)	Enthalpy of combustion of $CO(g)$
(D)	$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$	(s)	Standard enthalpy of $H_2O(l)$

ANSWERS

1. A – c; B – a; C – b
2. A – b; B – a; C – d; D – c
3. A – a; B – b; C – c; D – d
4. A – a; B – b; C – c; D – d
5. A – ii, iii; B – i, iii; C – i, iii, iv; D – i, iii, v, vi
6. A – i, iii; B – i, iii; C – ii, iv; D – i, iv; e – ii, iii
7. A –p,r,s; B –r,s; C – t; D – p,q,r
8. A – q,r; B – p,q; C – q,s; D – q