DAY SEVEN

Thermochemistry

Learning & Revision for the Day

- Thermochemical Standard State
- Heat or Enthalpy of Reaction
- Hess's Law of Constant Heat Summation
- Bond Energy or Enthalpy
- Calorimetry

Thermochemistry is a branch of chemistry which deals with energy exchange between a chemical system and its surrounding. Heat is generally evolved or absorbed whenever a chemical reaction takes place, or change in the state of matter (vaporisation, fusion, phase transition) occurs.

- Thermochemistry focuses on these energy changes, particularly on the system's energy exchange with its surroundings.
- The heat change accompanying chemical reactions or physical changes are measured experimentally with the help of calorimeter.
- **Chemical Reactions** are invariably associated with transfer of energy and most frequently, energy transfer in chemical reactions takes place in the form of heat. Reactions may be exothermic or endothermic.
  (i) **Exothermic** reactions transfer heat to the surroundings.
  $$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s); \ \Delta H = -1676 \text{ kJ}$$
  (ii) **Endothermic** reactions transfer heat from the surroundings.
  $$N_2(g) + O_2(g) \longrightarrow 2NO(g); \quad \Delta H = +90.4 \text{ kJ}$$

Thermochemical Standard State

- A thermochemical standard state of a substance is its most stable state under 1 atm pressure (standard pressure) and 298 K (standard temperature). Under these conditions, any parameter is designated the superscript θ or 0.
- Purest form for liquids and solids, most stable states are considered with 1 bar pressure condition and with 298 K temperature.
- For a gas, the standard state is considered at a pressure of one atmosphere. In a mixture of gases, its partial pressure must be one atmosphere.
- For a substance in solution, the standard state refers to one molar concentration.

Heat or Enthalpy of Reaction

- It is the amount of heat absorbed or evolved at constant pressure, when the quantities of substance indicated by thermochemical equation have completely reacted. It is denoted by ΔH_r, e.g. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g); \ \Delta H_r = -890.3$ kJ
- ΔH_r° = (sum of enthalpies of products) − (sum of enthalpies of reactants), i.e.

$$\Delta H_r^\circ = \Sigma H_{\text{products}} - \Sigma H_{\text{reactants}}$$

Standard Enthalpy When reaction is carried out at standard conditions (i.e. at 1 atm pressure and 298 K) It is denoted as by $\Delta_r H^\circ$.

(i) If $H_{\text{products}} = H_{\text{reactants}}$; $\Delta H = 0$

(ii) If $H_{\text{products}} > H_{\text{reactants}}$; $\Delta H = +\text{ve}$, reaction is said to be endothermic.

(iii) If $H_{\text{products}} < H_{\text{reactants}}$; $\Delta H = -\text{ve}$, reaction is said to be exothermic.

Factors Influencing Enthalpy of Reaction

Various factors that affect the enthalpy of reaction are :

(i) Physical state of reactants and products
(ii) Allotropic forms of elements involved
(iii) Chemical composition state of reactants and products
(iv) Amount of reactants
(v) Temperature
(vi) Reaction conditions

Types of Standard Enthalpy of Reaction

Different types of standard enthalpy of reactions are given below:

1. Standard Enthalpy of Formation (ΔH_f°)

- It is the standard enthalpy change for the formation of one mole of a compound from its elements in their most stable state of aggregation. e.g.

$$C_{(\text{graphite})} + 2H_2(g) \longrightarrow CH_4(g); \Delta H_f^\circ = -74.8 \text{ kJ mol}^{-1}$$

- Enthalpy of formation of an element at standard state by convention is taken as zero. e.g. enthalpy of formation of Mg, Al, Na, H_2, O_2 etc., is taken as zero.
- The standard enthalpy of the chemical reaction is given by

$$\Delta_r H^\circ = \Delta_f H_P^\circ - \Delta_f H_R^\circ$$

Here, $\Delta_f H^\circ{}_P$ = standard enthalpy of formation for products

$\Delta_f H_R^\circ$ = standard enthalpy of formation for reactants

2. Standard Enthalpy of Combustion (ΔH_c°)

- It is the standard enthalpy change per mole of a substance, when it undergoes complete combustion.

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

$$\Delta H_c^\circ = -192 \text{ kcal mol}^{-1}$$

- ΔH combustion is always negative but for certain reactions it is positive. For example,

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

$$F_2 + \frac{1}{2}O_2 \longrightarrow OF_2; \Delta H = \text{positive}$$

3. Enthalpy of Neutralisation (ΔH_n°)

- It is the amount of heat liberated when 1g equivalent of an acid is completely neutralised by 1g equivalent of a base. ΔH_n is constant for strong acid and strong base,

i.e. $\Delta H_n = -13.7 \text{ kcal mol}^{-1}$ or $-57.27 \text{ kJ mol}^{-1}$

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

$$\Delta H_n = -57.3 \text{ kJ mol}^{-1}$$

- For a weak acid against a strong base or weak base, the numerical value of ΔH_n is always less than 13.7 kcal due to the fact that here the heat is used up in ionisation of weak acid or weak base.
- The absolute value of heat of neutralization of HF is more than 57.3 kJ. This is due to very high heat of hydration of fluoride ion.

4. Standard Enthalpy of Atomisation (ΔH_a°)

It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase. In case of diatomic molecules (X_2), the enthalpy of atomisation, bond dissociation enthalpy and bond enthalpy are same thing.

5. Lattice Enthalpy ($\Delta H_{\text{lattice}}$)

It is the enthalpy change, which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g); \quad \Delta H_{\text{lattice}}^\circ = -787 \text{ kJ mol}^{-1}$$

6. Enthalpy of Hydration (ΔH_{hyd})

It is the enthalpy change, when one mole of anhydrous or partially hydrated salt combines with required number of moles of water to form a specific hydrate.

$$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4 \cdot 5H_2O(s);$$

$$\Delta H_{\text{hydration}} = -78.21 \text{ kJ mol}^{-1}$$

During dissolution, physical state of the compound changes while during hydration, there is no change in the physical state of compound.

7. Standard Enthalpy of Solution ($\Delta H_{\text{sol}}^\circ$)

It is the standard enthalpy change, when one mole of substance dissolves in a specified amount of solvent.

$$\Delta H_{\text{sol}}^\circ = \Delta H_{\text{lattice}} - \Delta H_{\text{hydration}}$$

Integral heat of solution is the enthalpy change when 1 mole of solute is dissolved in a pure solvent to form a solution of desired concentration.

- Differential heat of solution is the enthalpy change when 1 mole of solute is dissolved in such a large volume of solution so that no enthalpy change occurs on further dilution.
- If the solubility of a substance is known at two different temperatures, the mean molar enthalpy of solution over this temperature range can be calculated by applying an equation similar to van't Hoff equation;

$$\frac{\log S_1}{\log S_2} = \frac{\Delta H}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where, S_1 and S_2 are solubilities at T_1 and T_2 temperatures respectively.

8. Standard Enthalpy of Hydrogenation ($\Delta H^\circ_{\text{hydrogenation}}$)

It is the amount of enthalpy change that takes place when one mole of unsaturated organic compound is completely hydrogenated.

9. Standard Enthalpy of Dilution ($\Delta H^\circ_{\text{dil.}}$)

The standard enthalpy change, when 1 mole of a substance is diluted to such an extent that on further dilution no heat is evolved or absorbed is termed as standard enthalpy of dilution.

10. Standard Enthalpy of Transition (ΔH°_t)

It is the enthalpy change when one mole of the substance undergoes transition from one allotropic form to another.

$\text{S(rhombic)} \rightarrow \text{S(monoclinic)}; \Delta H^\circ_t = -13.14\ \text{kJ}$

11. Standard Enthalpy of Fusion ($\Delta H^\circ_{\text{fus}}$)

It is the enthalpy change that accompanies melting of one mole of a solid substance.

$$\Delta H^\circ_{\text{fus}} = -\Delta H^\circ_{\text{freez}}$$

12. Standard Enthalpy of Vaporisation ($\Delta H^\circ_{\text{vap}}$)

It is the amount of heat required to convert one mole of liquid into its vapour state.

$$\Delta H^\circ_{\text{vap}} = -\Delta H^\circ_{\text{cond}}$$

13. Standard Enthalpy of Sublimation ($\Delta H^\circ_{\text{sub}}$)

At standard conditions, change in enthalpy, when one mole of a solid substance sublimes is called the standard enthalpy of sublimation.

$$\Delta_{\text{sub}}H^\circ = \Delta_{\text{fus}}H^\circ + \Delta_{\text{vap}}H^\circ$$

14. Enthalpy of Ionisation (ΔH_{ions})

It is the amount of enthalpy change that take place when one mole of a covalent compound on dissolution in water splits to produce ions in the solution.

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq);$$

$$\Delta H_{\text{ions}} = -55.43\ \text{kJ mol}^{-1}$$

Hess's Law of Constant Heat Summation

The enthalpy change in a particular reaction is always constant and is independent of the path by which the reaction takes place.

$$\begin{tikzcd} A \arrow[r, "\Delta H"] \arrow[d, "\Delta H_1"'] & B \\ C \arrow[r, "\Delta H_2"'] & D \arrow[u, "\Delta H_3"'] \end{tikzcd}$$

In other words, the total heat change (ΔH) accompanying a chemical reaction is the same whether, the reaction takes place in one step or in more steps.

According to Hess's law heat of summation is given as:

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

Some applications of Hess's law are :

- In determination of heat of formation.
- In determination of heat of transition.
- In determination of bond enthalpy
- In determination of resonance energy

Resonance energy = experimental heat of formation − calculated heat of formation

Bond Energy or Enthalpy

- When a bond is formed between two atoms in gaseous state to form a molecule, some heat is always evolved which is called bond energy or bond formation energy.
- **Bond dissociation energy** is the amount of energy required to break/dissociate bond of a particular type present in one molecule of the compound.
- Bond energy is taken as the average value of dissociation energies of same type of bonds present in one mole.
- Since, a chemical reaction involves the breaking of old bonds in reactants and formation of new bonds in products, the enthalpy change of a reaction,

  ΔH_r = Sum of BE of reactants − sum of BE of products
- In a polyatomic molecule containing two or more covalent bonds between same atoms (e.g. CH_4), the term **average bond energy** is preferred in place of bond dissociation energy.

  For CH_4, average BE of C—H bond

  $$= \frac{\text{Bond dissociation energy of } CH_4}{4}$$
- Bond dissociation enthalpy values are negative, if bond formation occurs whereas bond energy values are positive, if bond dissociation occurs.

Factor Affecting Bond Enthalpy

There are various factors affecting bond enthalpy which are as follows:

1. Size of Atoms

- Smaller the size of atom, more closer the atoms to each other during bonding hence, larger is the bond enthalpy. e.g. order of bond enthalpy of halogens is F—F < Cl—Cl > Br—Br > I—I.
- Bond enthalpy of fluorine is smaller than chlorine because of the high degree of lone pair repulsions in F_2 due to its smaller size.

2. Electronegativity

Larger the electronegativity difference between two atoms, more is the polarity in bond and thus, more is the bond strength as well as bond enthalpy.

e.g. F—H > O—H > N—H (Bond enthalpy decreases)

3. Bond Length

Shorter the bond length, more is the bond dissociation enthalpy.

4. Number of Bonding Electrons

As the number of electrons involved in bond increases, strength of the bond increases. This increases the bond enthalpy.

e.g. $C \equiv C > C = C > C - C$ (Bond enthalpy decreases)

Calorimetry

- The experimental measurement of the heat change of reaction or enthalpy change is known as calorimetry. In laboratory, heat changes in physical and chemical processes are measured with a calorimeter which is an insulated container

$$q = mc\Delta t = C\,\Delta t \qquad \text{(Heat capacity, } C = mc)$$
$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

  where, m is the mass of the substance in grams, c is the specific heat and C is the heat capacity.

- For endothermic change, q is positive and for exothermic change, q is negative.

Constant Volume Calorimetry

(Bomb Calorimeter)

- Heat of combustion is measured by placing a known mass of a compound in a **constant volume bomb calorimeter** which is filled with oxygen at about 30 atm pressure.
- On ignition of the sample electrically, there is evolution of heat which can be calculated by recording the rise in temperature of water.
- Heat lost by the sample = Heat gained by the water

$$q_{\text{combustion}} = -[q_{\text{water}} + q_{\text{bomb}}]$$
$$= -[m_{\text{water}} \times c_{\text{water}} + m_{\text{bomb}} \times c_{\text{bomb}}] \times \Delta t$$
$$q_{\text{combustion}} = \Delta E_{\text{combustion}}$$

  (combustion in bomb calorimeter at constant V)

  Therefore, $\Delta H_{\text{combustion}} = \Delta E + \Delta n_g RT$

- The calorific value of a fuel or food is the amount of heat in calories or joules produced from the complete combustion of one gram of the fuel or the food.

$$\text{Calorific value} = \frac{\Delta H_{\text{comb}}}{\text{Molecular mass}}$$

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 $\Delta H^\circ_{f(NO_2)} = 33.84$ kJ mol^{-1} and $\Delta H^\circ_{f(N_2O_4)} = 9.66$ kJ mol^{-1}, hence, dimerisation of NO_2 forming N_2O_4 is

(a) endothermic (b) isothermic
(c) exothermic (d) isochoric

2 In the reaction, $y \to z, \Delta H = +100$ kcal/mol and for the reaction, $z \to x, \Delta H = -80$ kcal/mol and $y \to x$, $\Delta H = 20$ kcal

Rank the enthalpies of formation of x, y and z in increasing order

(a) y, x, z (b) y, z, x (c) x, z, y (d) x, y, z

3 2.1 g of Fe combines with S evolving 3.77 kJ. The heat of formation of FeS in kJ/mol is

(a) -1.79 (b) -100.5
(c) -3.77 (d) None of these

4 Which of the following is (are) exothermic reactions.

I. Combustion of methane
II. Decomposition of water
III. Dehydrogenation of ethane to ethylene
IV. Conversion of graphite to diamond

(a) (I) and (II) (b) (II) and (III)
(c) (III) and (IV) (d) (II), (III) and (IV)

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

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

(a) 524.1 (b) 41.2 (c) -262.5 (d) -41.2

6 Consider the following,

$$C + O_2 \longrightarrow CO_2;\ \Delta H = x$$
$$CO + \frac{1}{2}O_2 \longrightarrow CO_2;\quad \Delta H = y$$

Then, the heat of formation of CO is

(a) $x - y$ (b) $y - 2x$ (c) $x + y$ (d) $2x - y$

7 On the basis of the following thermochemical data $(\Delta_f H^\circ_{H^+(aq)} = 0)$

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq);\ \Delta H = 57.32 \text{ kJ}$$
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\ \Delta H = -286.20 \text{ kJ}$$

Also $H^\circ(H^+, aq) = 0$

The value of enthalpy of formation of OH^- ion at 25°C is

➞ JEE Main 2009

(a) -22.88 kJ (b) -228.88 kJ
(c) $+228.88$ kJ (d) -343.52 kJ

8 The heat 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

9 If enthalpies of formation of $C_2H_4(g)$, $CO_2(g)$ and $H_2O(l)$ at 250°C and 1 atm pressure be 52, –394 and –286 kJ mol^{-1} respectively, the enthalpy of combustion of $C_2H_4(g)$ will be

(a) 1412 kJ mol^{-1} (b) –1412 kJ mol^{-1}
(c) +141.2 kJ mol^{-1} (d) –141.2 kJ mol^{-1}

10 Heat of combustion of $H_2(g) = -241.8$ kJ mol^{-1}
$C(s) = -393.5$ kJ mol^{-1}, $C_2H_5OH(l) = -1234.7$ kJ mol^{-1}
Hence, heat of formation of $C_2H_5OH(l)$ is

(a) – 2747.1 kJ mol^{-1} (b) –277.7 kJ mol^{-1}
(c) 277.7 kJ mol^{-1} (d) 2747.1 kJ mol^{-1}

11 Combustion of glucose takes place according to the equation,

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$; $\Delta H = -72$ kcal

How much energy will be required for the production of 1.6 g of glucose (molecular mass of glucose = 180) ?

(a) 0.064 kcal (b) 0.64 kcal (c) 6.4 kcal (d) 64 kcal

12 The heat evolved in the combustion of methane is given by the following equation,

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l); \quad \Delta H = -\,890.3\text{ kJ}$$

How many grams of methane would be required to produce 445.15 kJ of heat of combustion?

(a) 4 g (b) 8 g (c) 12 g (d) 16 g

13 Equal volumes of methanoic acid and sodium hydroxide are mixed, if x is the heat of formation of water, heat evolved in neutralisation is

(a) more than x (b) equal to x
(c) twice of x (d) less than x

14 When 1 mole of oxalic acid is treated with excess of NaOH in dilute aqueous solution, 106 kJ of heat is liberated. The enthalpy of ionisation of the acid is

(a) 4.3 kJ mol^{-1} (b) – 4.3 kJ mol^{-1}
(c) – 8.6 kJ mol^{-1} (d) 8.6 kJ mol^{-1}

15 Consider the reaction,

$$4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g); \quad \Delta_r H = -111\text{ kJ}.$$

If $N_2O_5(s)$ is formed instead of $N_2O_5(g)$ in the above reaction, the $\Delta_r H$ value will be
(Given, ΔH of sublimation for N_2O_5 is 54 kJ mol^{-1}) ➞AIEEE 2011

(a) – 165 kJ (b) +54 kJ (c) +219 kJ (d) – 219 kJ

16 The amount of heat absorbed by 70.09 of water for their complete vaporisation is

(a) 23,352 J (b) 7000 J (c) 15,813 J (d) 158,200 J

17 The H_f° of O_3, CO_2, NH_3 and HI are 142.2, – 393.3, – 46.2 and + 25.9 kJ per mol respectively. The order of their increasing stabilities will be

(a) O_3, CO_2, NH_3, HI (b) CO_2, NH_3, HI, O_3
(c) O_3, HI, NH_3, CO_2 (d) NH_3, HI, CO_2, O_3

18 ΔH°_f of atom B is 134.5 kcal / mol and ΔH°_f of atom F is 118.86 kcal / mol. ΔH°_f of $BF_3(g)$ is –271.75 kcal / mol. Average B—F bond energy would be

(a) 97.7 kcal / mol (b) 116.6 kcal / mol
(c) 135.4 kcal / mol (d) 254.3 kcal / mol

19 In a calorimeter, the temperature of the calorimeter increases by 6.12 K, the heat capacity of the system is 1.23 kJ/g /deg. What is the molar heat of decomposition for the ammonium nitrate?

(a) –7.53 kJ / mol (b) –398.1 kJ / mol
(c) –16.1 kJ / mol (d) –602 kJ / mol

20 The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal respectively. The enthalpy of formation of HCl gas would be

(a) –44 kcal (b) 44 kcal (c) –22 kcal (d) 22 kcal

21 Given that, $C(g) + 4H(g) \longrightarrow CH_4(g)$; $\Delta H = -166$ kJ
The bond energy of C—H will be

(a) –415 kJ / mol (b) –41.5 kJ / mol
(c) 832 kJ / mol (d) None of these

22 If at 298 K, the bond energies of C—H, C—C, C=C and H—H bonds are 414, 347, 615 and 435 kJ mol^{-1} respectively,

The value of enthalpy change for the reaction,
$H_2C{=}CH_2(g) + H_2(g) \longrightarrow H_3C{-}CH_3(g)$ at 298 K will be

(a) + 250 kJ mol^{-1} (b) – 250 kJ mol^{-1}
(c) + 125 kJ mol^{-1} (d) – 125 kJ mol^{-1}

23 Given that,

I. $\Delta_f H^\circ$ of N_2O is 82 kJ mol^{-1}

II. Bond energies of N≡N, N=N, O=O and N=O are 946, 418, 498 and 607 kJ mol^{-1} respectively. The resonance energy of N_2O is ➞JEE Main (Online) 2013

(a) – 88 kJ mol^{-1} (b) – 66 kJ mol^{-1}
(c) – 62 kJ mol^{-1} (d) – 44 kJ mol^{-1}

24 Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a C≡C bond in C_2H_2.
The energy is (take the bond energy of a C—H bond as 350 kJ mol^{-1}) ➞AIEEE 2012

$$2C(s) + H_2(g) \longrightarrow C_2H_2(g); \ \Delta H = 225\text{ kJ mol}^{-1}$$
$$2C(s) \longrightarrow 2C(g); \quad \Delta H = 1410\text{ kJ mol}^{-1}$$
$$H_2(g) \longrightarrow 2H(g); \quad \Delta H = 330\text{ kJ mol}^{-1}$$

(a) 1165 kJ mol^{-1} (b) 837 kJ mol^{-1}
(c) 865 kJ mol^{-1} (d) 815 kJ mol^{-1}

25 The standard enthalpy of formation of NH_3 is – 46.0 kJ mol^{-1}. If the enthalpy of formation of H_2 from its atoms is –436 kJ mol^{-1} and that of N_2 is – 712 kJ mol^{-1}, the average bond enthalpy of N—H bond in NH_3 is

➞ AIEEE 2010

(a) – 964 kJ mol^{-1} (b) – 352 kJ mol^{-1}
(c) + 1056 kJ mol^{-1} (d) – 1102 kJ mol^{-1}

26 The heat of combustion of benzoic acid is –2546kJ mol^{-1} at 25°C and 1 atm. The ΔE is

(a) –1555.6 kJ mol^{-1} (b) –2244.7 kJ mol^{-1}
(c) –2544.76 kJ mol^{-1} (d) –2868.66 kJ mol^{-1}

27 ΔH for combustion of ethane and ethyne are – 341.1 and –310.0 kcal respectively. What will be the ratio of calorific values of ethane and ethyne respectively?

(a) 1 : 0.95 (b) 0.65 : 2
(c) 0.95 : 1 (d) 0.002 : 1

28 **Assertion** (A) Combustion of all organic compounds is an exothermic reaction.

Reason (R) The enthalpies of all elements in their standard state are zero.

(a) Assertion and Reason both are correct statements and Reason is the correct explanation of the Assertion
(b) Assertion and Reason both are correct statements but Reason is not the correct explanation of the Assertion
(c) Assertion is correct incorrect and Reason is incorrect
(d) Both Assertion and Reason are incorrect

29 **Statement I** The enthalpy of formation of $H_2O(l)$ is greater than that of $H_2O(g)$.

Statement II The enthalpy change for condensation reaction, i.e. $H_2O(g) \longrightarrow H_2O(l)$ is negative.

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I
(c) Statement I is true; Statement II is false
(d) Both the Statements I and II are false

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 The heat of combustion of carbon to CO_2 is –393.5 kJ/mol. The heat released upon formation of 35.2 g of CO_2 from carbon and oxygen gas is

(a) + 315 kJ (b) – 31.5 kJ
(c) – 315 kJ (d) + 31.5 kJ

2 Which of the reactions defines, ΔH_f°?

(a) $C_{(diamond)} + O_2(g) \longrightarrow CO_2(g)$

(b) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \longrightarrow HF(g)$

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

(d) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$

3 The enthalpy of combustion of H_2, cyclohexene and cyclohexane are –241, –3800 and –3920 kJ mol^{-1} respectively. Heat of hydrogenation of cyclohexene is

(a) 121 kJ mol^{-1} (b) –121 kJ mol^{-1}
(c) +242 kJ mol^{-1} (d) –242 kJ mol^{-1}

4 The enthalpy changes for the following processes are listed below :

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

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

(a) – 14.6 kJ mol^{-1} (b) – 16.8 kJ mol^{-1}
(c) + 16.8 kJ mol^{-1} (d) + 244.8 kJ mol^{-1}

5 On burning 4.0 g of iron to ferric oxide at constant pressure, the heat evolved is 29.28 kJ. The enthalpy of formation of ferric oxide is (At. wt. of Fe = 56)

(a) + 81.98 kJ mol^{-1} (b) – 81.98 kJ mol^{-1}
(c) + 819.8 kJ mol^{-1} (d) – 819.8 kJ mol^{-1}

6 A cooking gas cylinder is assumed to contain 11.2 kg *iso*-butane. The combustion of *iso*-butane is given by

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l);$$
$$\Delta H = -\ 2658\ \text{kJ}$$

If a family needs 15,000 kJ of energy per day for cooking, how long would the cylinder last?

[Assuming that 30% of the gas is wasted due to incomplete combustion.]

(a) 34 days (b) 30 days (c) 31 days (d) 24 days

7 If the heat of neutralisation for a strong acid-base reaction is –57.1 kJ, what would be the heat released when 350 cm^3 of 0.20 M of a dibasic strong acid is mixed with 650 cm^3 of 0.10 M monoacidic base?

(a) 57.1 kJ (b) 3.71 kJ (c) –57.1 kJ (d) 0.317 kJ

8 Consider the reactions given below. On the basis of these reactions find out which of the algebraic relationship given in options (a) to (d) is correct?

I. $C(g)+4H(g) \longrightarrow CH_4(g)$; $\Delta_r H = x$ kJ mol^{-1}

II. $C(\text{graphite})+2H_2(g) \longrightarrow CH_4(g)$; $\Delta_r H = y$ kJ mol^{-1}

(a) $x = y$ (b) $x = 2y$ (c) $x > y$ (d) $x < y$

9 The dissolution of $CaCl_2 \cdot 6H_2O$ in large volume of water is endothermic to the extent of 3.5 kcal mol^{-1}. For the reaction,

$$CaCl_2(s)+6H_2O(l) \longrightarrow CaCl_2 \cdot 6H_2O(s)$$

$\Delta H = -23.2$ kcal. Hence, heat of solution of $CaCl_2$ (anhydrous) in a large volume of water is

(a) 26.7 kcal (b) −26.7 kcal
(c) 19.7 kcal (d) −19.7 kcal

10 The temperature of a bomb calorimeter rises by 1.6 K when a current of 3.2 A is passed for 27s from a 12 V source. Which of the following statements is true?

(a) The calorimeter constant is 648 JK^{-1}
(b) This calorimeter constant will be same if the calorimeter is open
(c) The information is insufficient for calculating calorimeter constant
(d) The calorimeter constant is independent of calorimeter content

11 For the 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 $(R = 8.314$ JK^{-1}mol$^{-1})$ ➞ JEE Main 2015

(a) −1366.95 kJ mol^{-1} (b) −1361.95 kJ mol^{-1}
(c) −1460.50 kJ mol^{-1} (d) −1350.50 kJ mol^{-1}

12 The enthalpy of dissolution of $BaCl_2(s)$ and $BaCl_2 \cdot 2H_2O(s)$ are −20.6 and 8.8 kJ per mol respectively. The enthalpy of hydration for,

$$BaCl_2(s)+2H_2O \longrightarrow BaCl_2 \cdot 2H_2O(s),\text{ is}$$

(a) 29.4 kJ (b) −29.4 kJ (c) −11.8 kJ (d) 38.2 kJ

13 The standard enthalpy of formation (ΔH_f°) at 298 K for methane, $CH_4(g)$ is – 74.8 kJ mol^{-1}. The addition information required to determine the average energy for C—H bond formation would be

(a) the dissociation energy of H_2 and enthalpy of sublimation of carbon
(b) latent heat of vaporisation of methane
(c) the first four ionisation energies of carbon and electron gain enthalpy of hydrogen
(d) the dissociation energy of hydrogen molecule, H_2

14 What will be the enthalpy change for the combustion of cyclopropane at 298 K? The enthalpies 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}.

(a) 844.63 kJ
(b) – 844.63 kJ
(c) – 2090.342 kJ
(d) 1893.44 kJ

15 If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1:1: 0.5 and ΔH_f for the formation of XY is −200 kJ mol^{-1}. The bond dissociation energy of X_2 will be

(a) 400 kJ mol^{-1}
(b) 300 kJ mol^{-1}
(c) 200 kJ mol^{-1}
(d) None of the above

16 1.0 L sample of mixture of CH_4 and O_2 measured at 25°C and 740 torr, was allowed to react at constant pressure in a calorimeter, together with its contents had a heat capacity of 1260 cal K^{-1}. The complete combustion of CH_4 to CO_2 and water caused a temperature rise in calorimeter of 0.667 K. What will be the mole % of CH_4 in the original mixture?

[Heat of combustion of CH_4 is – 215 kcal mol]

(a) 25% (b) 15%
(c) 40% (d) 10%

ANSWERS

SESSION 1	**1** (c)	**2** (a)	**3** (b)	**4** (d)	**5** (b)	**6** (a)	**7** (b)	**8** (c)	**9** (b)	**10** (b)
	11 (b)	**12** (b)	**13** (d)	**14** (d)	**15** (a)	**16** (d)	**17** (b)	**18** (d)	**19** (d)	**20** (c)
	21 (b)	**22** (d)	**23** (a)	**24** (d)	**25** (b)	**26** (c)	**27** (c)	**28** (b)	**29** (d)	
SESSION 2	**1** (c)	**2** (b)	**3** (b)	**4** (c)	**5** (d)	**6** (d)	**7** (b)	**8** (c)	**9** (c)	**10** (a)
	11 (a)	**12** (b)	**13** (a)	**14** (c)	**15** (d)	**16** (d)				

Hints and Explanations

SESSION 1

1 $2NO_2 \longrightarrow N_2O_4$

$\Delta H^\circ = \Delta H^\circ_{f\,(N_2O_4)} - 2 \times \Delta H^\circ_{f\,(NO_2)}$

$\Delta H^\circ = 9.66 - 2 \times 33.84 = -58.02$ kJ

Since, $\Delta H = -$ve thus, reaction is exothermic.

2 $\Delta H_{\text{reaction}} = \Sigma \Delta H_{f\,(\text{Products})} - \Sigma \Delta H_{f\,(\text{reactants})}$

$\Rightarrow \quad \Delta H^\circ_{f(z)} - \Delta H^\circ_{f(y)} = 100$ kcal

i.e. $\quad \Delta H^\circ_{f(z)} > \Delta H^\circ_{f(y)}$

also, $\Delta H^\circ_{f(x)} - \Delta H^\circ_{f(z)} = -80$ kcal

i.e. $\quad \Delta H^\circ_{f(z)} > \Delta H^\circ_{f(x)}$

Also $\quad y \rightarrow x, \Delta H = 20$ kcal

i.e. $\quad \Delta H^\circ_{f(x)} > \Delta H^\circ_{f(y)}$

$\Rightarrow$ Overall order is $y < x < z$.

3 When 2.1 g Fe combines with S, heat evolved = 3.77 kJ

When 56 g (atomic mass) combines with S, then heat evolved.

$$\Delta H / \text{mole of FeS} = \frac{3.77 \times 56}{2.1} = 100.5$$

Since, the heat is evolved in the formation of FeS, thus, the heat of formation of FeS is – 100.5 kJ mol^{-1}.

4 $CH_4(g) + O_2 \xrightarrow{\Delta} 2CO_2(g) + H_2O(l)$

$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}O_2(g) + \text{Heat}$

$C_2H_6 \longrightarrow CH_2{=}CH_2 + H_2 + \text{Heat}$

$\text{C(graphite)} + \frac{1}{2}O_2(g) \longrightarrow CO(g) + \text{Heat}$

(II), (III) and (IV) are exothermic reactions because they proceeds by the evolution of heat.

5. $C + O_2 \longrightarrow CO_2(g)\,;$

$\Delta H_f^\circ = -393.5 \text{ kJ mol}^{-1}$ ...(i)

$C + \frac{1}{2}O_2 \longrightarrow CO(g)\,;$

$\Delta H_f^\circ = -110.5 \text{ kJ mol}^{-1}$ ...(ii)

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O(g)\,;$

$\Delta H_f^\circ = -241.8 \text{ kJ mol}^{-1}$ ...(iii)

Eq. (ii) + Eq. (iii) – Eq. (i)

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

$\Delta H_r = \Delta H^\circ_{f(CO)} + \Delta H^\circ_{f(H_2O)} - \Delta H^\circ_{f(CO_2)}$

$= -110.5 - 241.8 - (-393.5)$

$= -352.3 + 393.5 = 41.2$ kJ

6 $C + O_2 \longrightarrow CO_2;\ \Delta H = x$

$CO + \frac{1}{2}O_2 \longrightarrow CO_2\ ;\ \Delta H = y$

$C + \frac{1}{2}O_2 \longrightarrow CO\ ;\ \Delta H = x - y$

7 Consider the heat of formation of H_2O.

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

$\Delta H = -286.20$ kJ

i.e. $\Delta H_{f(H_2O,\,l)} = -286.20$ kJ

Now, consider the ionisation of H_2O.

$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq);$

$\Delta H = 57.32$ kJ

$\Delta H_r = \Delta H_{f(H^+,\,aq)} + \Delta H_{f(OH^-,\,aq)} - \Delta H_{f(H_2O,\,l)}$

$57.32 = 0 + \Delta H_{f(OH^-,\,aq)} - (-286.20)$

Thus, $\Delta H_{f(OH^-,\,aq)} = 57.32 - 286.20$

$= -228.88$ kJ

8 $C(s) + O_2(g) \longrightarrow CO_2(g)\,;$

$\Delta H = -393.5 \text{ kJ mol}^{-1}$ ...(i)

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

$\Delta H = -283.5 \text{ kJ mol}^{-1}$ ...(ii)

On subtracting Eq. (ii) from Eq. (i), we get

$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g);$

$\Delta H = (-393.5 + 283.5) \text{ kJ mol}^{-1}$

$= -110 \text{ kJ mol}^{-1}$

9. $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

$\Delta H_{\text{reaction}} = [2 \times \Delta H^\circ_{f\,(CO_2)} + 2 \times \Delta H^\circ_{f\,(H_2O)}] - [\Delta H^\circ_{f\,(C_2H_4)} + 3 \times \Delta H^\circ_{f\,(O_2)}]$

$= [2(-394) + 2(-286)] - [52 + 0]$

$= -1412 \text{ kJ mol}^{-1}$

10 $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);$

$\Delta H^\circ = -241.8 \text{ kJ mol}^{-1}$

$\therefore \quad \Delta H^\circ_{f\,(H_2O)} = -241.8 \text{ kJ mol}^{-1}$

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

$\Delta H^\circ = -393.5 \text{ kJ mol}^{-1}$

$\therefore \quad \Delta H^\circ_{f\,(CO_2)} = -393.5 \text{ kJ mol}^{-1}$

$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l);$

$\Delta H^\circ = -1234.7 \text{ kJ mol}^{-1}$

$\Delta H^\circ = 2\Delta H^\circ_{f(CO_2)} + 3\Delta H^\circ_{f\,(H_2O)} - \Delta H^\circ_{f\,(C_2H_5OH)}$

$-1234.7 = -2 \times 393.5 - 3 \times 241.8 - \Delta H^\circ_{f\,(C_2H_5OH)}$

$\therefore \quad \Delta H^\circ_{f\,(C_2H_5OH)} = -277.7 \text{ kJ mol}^{-1}$

11 ΔH per 1.6 g of glucose

$$= \frac{72 \times 1.6}{180} = 0.64 \text{ kcal}$$

12 CH_4 required $= \dfrac{445.15 \times 16}{890.3} = 8$ g

13 As methanoic acid is a weak acid, heat of neutralisation is less than x.

14 $H_2C_2O_4(aq) \longrightarrow 2H^+(aq) + C_2O_4^{2-}(aq);$

$\Delta_{\text{ion}} H = x$ kJ

$[H^+(aq) + OH^-(aq) \longrightarrow H_2O(l);$

$\Delta_{\text{heat}} H = -57.3 \text{ kJ}] \times 2$

$H_2C_2O_4 + 2OH^- \longrightarrow 2H_2O(l) + C_2O_4^{2-};$

$\Delta H = x - 114.6$ kJ

Also, $\Delta H_i = -106$ kJ (given) heat is liberated

But $\quad x - 114.6 = -106$

$\therefore \quad x = 8.6 \text{ kJ mol}^{-1}$

15

$$\begin{tikzcd}
4NO_2(g) + O_2(g) \arrow[rr, "\Delta H = -111\,KJ"] \arrow[dr, "\Delta H = ?"'] & & 2N_2O_5(g), \\
& 2N_2O_5(s) \arrow[ur, "+54\,kJ"'] &
\end{tikzcd}$$

From Hess law,

$\Delta H_f + \Delta H_{\text{sub}} = \Delta H_{\text{reaction}}$

$\Delta H_f = \Delta H_{\text{reaction}} - \Delta H_{\text{sub}}$

$= -111 \text{ kJ} - (54 \text{ kJ})$

$= -111 - 54 \text{ kJ} = -165 \text{ kJ}$

Thus, the enthalpy of formation, ΔH_f for N_2O_5 (s) is –165 kJ.

16 The heat absorbed, Q is given by

$Q = \text{mass} \times \text{latent heat of vaporisation}\,(L_v)$

mass = 70.09 g = 0.07 kg

$L_v = 2260$ kJ

$\therefore Q = 0.07 \times 2260 = 158.2 \text{ kJ} = 158{,}200$ J

17 Energy absorbed

$$\propto \frac{1}{\text{stability of compound}}$$

Energy released ∝ stability of compound.

Thus, the correct order of increasing stabilities will be

$$CO_2 < NH_3 < HI < O_3$$

18 The dissociation of BF_3 *(g)* can be written as

$$BF_3(g) \longrightarrow B(g) + 3F(g);$$

$$\Delta H_f^\circ = -271.75 \text{ kcal/mol}$$

$$\Delta H = [\Delta H_B^\circ + 3 \times \Delta H^\circ_F] - [\Delta H^\circ_{BF_3}]$$

$$= -271.75 \text{ kcal/mol}$$

$$\Delta H = 134.5 + 3 \times 118.86 - (-271.75)$$

$$= 762.83 \text{ kcal}$$

$$= 3 \times \text{Avg B—F bond energy}$$

$$\text{B—F bond energy} = 254.3 \text{ kcal/mol}$$

19 Molecular weight of $NH_4NO_3 = 80$

Heat evolved $= 1.23 \times 6.12$

Molar heat of decomposition

$= 1.23 \times 6.12 \times 80$

$= -602 \text{ kJ mol}^{-1}$ (as heat is evolved)

20 $\frac{1}{2} H_2 + \frac{1}{2} Cl_2 \longrightarrow HCl$

$$\Delta H = \Sigma BE_{\text{reactants}} - \Sigma BE_{\text{products}}$$

$$= \left[\frac{1}{2} BE(H_2) + \frac{1}{2} BE(Cl_2)\right] - BE(HCl)$$

$$= \left[\left(\frac{1}{2} \times 104\right) + \left(\frac{1}{2} \times 58\right)\right] - 103$$

$$= (52 + 29) - 103 = -22 \text{ kcal}$$

21 The bond energy $C—H = -166/4$

$$= -41.5 \text{ kJ mol}^{-1}$$

22 $CH_2{=}CH_2 + H_2 \longrightarrow CH_3—CH_3$

$$\Delta H = (BE)_{\text{reactants}} - (BE)_{\text{products}}$$

$$= 4\,(BE)_{C—H} + (BE)_{C=C} + (BE)_{H—H} - [6(BE)_{C—H} + (BE)_{C—C}]$$

$$= -125 \text{ kJmol}^{-1}$$

23 $N_2 + \frac{1}{2} O_2 \longrightarrow N_2O$

or $N{\equiv}N + \frac{1}{2} O{=}O \longrightarrow N{=}N{=}O$

$$\therefore\ \Delta H = BE_{N\equiv N} + \frac{1}{2} BE_{O=O} - [BE_{N=N} + BE_{N=O}]$$

$$= 946 + \frac{1}{2} \times 498 - [418 + 607]$$

$$= 1195 - 1025 = +170$$

Resonance energy = Experimental value − calculated value

$$= 82 - 170 = -88 \text{ kJ}$$

24 For calculation of $C{\equiv}C$ bond energy, we must first calculate dissociation energy of C_2H_2 as

$$C_2H_2(g) \longrightarrow 2C(g) + 2H(g) \quad \ldots\text{(i)}$$

By using the given bond energies and enthalpies,

$$C_2H_2(g) \longrightarrow 2C(g) + H_2(g);\ \Delta H = -225 \text{ kJ mol}^{-1} \quad \ldots\text{(ii)}$$

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

$$H_2(g) \longrightarrow 2H(g);\ \Delta H = 330 \text{ kJ mol}^{-1} \quad \ldots\text{(iv)}$$

On adding Eqs. (ii), (iii) and (iv) gives Eq. (i) $C_2H_2(g) \longrightarrow 2C(g) + 2H(g);$

$$\Delta H = 1515 \text{ kJ mol}^{-1}$$

$$1515 \text{ kJ mol}^{-1} = 2 \times (C—H)\ BE + (C{\equiv}C)\ BE$$

$$= 2 \times 350 + (C{\equiv}C)\ BE$$

$$(C{\equiv}C)\ BE = 1515 - 700 = 815 \text{ kJ mol}^{-1}$$

25 Given, $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \longrightarrow NH_3(g);$

$$\Delta H_f^\circ = -46.0 \text{ kJ mol}^{-1}$$

$\therefore$ Bond enthalpy of $N—H = 46 \text{ kJ mol}^{-1}$ (+ve sign is taken because energy is supplied to break N—H bonds).

$$2H(g) \longrightarrow H_2(g);$$

$$\Delta H_f^\circ = -436 \text{ kJ mol}^{-1}$$

$$BE_{(H—H)} = 436 \text{ kJ mol}^{-1}$$

$$2N(g) \longrightarrow N_2(g);$$

$$\Delta H_f^\circ = -712 \text{ kJ mol}^{-1}$$

$$BE_{(N—N)} = 712 \text{ kJ mol}^{-1}$$

$$\Delta H_r = \frac{1}{2} BE_{N_2} + \frac{3}{2} BE_{H_2} - 3BE_{N-H}$$

$$\Rightarrow -46 = \left[\frac{1}{2} \times 712 + \frac{3}{2} \times 436\right] - 3BE_{(N-H)}$$

$$3BE_{(N-H)} = 1010 + 46$$

$$3E_{(N-H)} = 1056$$

$$BE_{(N-H)} = \frac{1056}{3} = 352 \text{ kJ mol}^{-1}$$

26 $C_6H_5COOH(s) + 7.5O_2(l)$

$$\longrightarrow 7CO_2(g) + 3H_2O(l)$$

$$\Delta n_g = -0.5$$

$$\Delta H = \Delta E + \Delta n_g RT$$

$$-2546 = \Delta E - 0.5 \times 8.314 \times 10^{-3} \times 298$$

$$\Delta E = -2544.76 \text{ kJ mol}^{-1}$$

27 Calorific value of heat produced by 1 g of fuel.

Calorific value of ethane

$$= \frac{-341.1}{30} = -11.37 \text{ kcal/g}$$

Calorific value for ethyne

$$= \frac{-310.0}{26} = -11.92 \text{ kcal/g}$$

$\therefore$ Ratio of calorific values of ethane and ethyne = 11.37 : 11.92 = 0.95 : 1

28 In a combustion reaction,sum of enthalpies of reactants is greater than the sum of the enthalpies of products. Therefore, combustion of all organic compounds is an exothermic reaction. Also, enthalpies of all elements in their standard state are zero.

So, both A and R are true but R is not the correct explanation of A.

29 Both the Statements I and II are correct and Statement II is the correct explanation for Statement I.

SESSION 2

1 $C + O_2 \longrightarrow CO_2;\ \Delta H = -393.5 \text{ kJ/mol}$

$\because$ Heat released during the formation of 44 g of $CO_2 = -393.5$ kJ

Heat released during the formation of 1 g of $CO_2 = \frac{-393.5}{44}$ kJ

Heat released during the formation of 35.2 g (given) of CO_2

$$= -\frac{393.5 \times 35.2}{44} = -315 \text{ kJ}$$

2 ΔH_f°,standard heat of formation is the amount of heat evolved or absorbed when one gram mole of a substance is formed from its constituent elements. For the formation of a compound the constituent must be in elemental form therefore formation of HF represents the standard heat of formation of HF.

3 $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O;$

$$\Delta H = -241 \text{ kJ mol}^{-1} \quad \ldots\text{(i)}$$

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

$$\Delta H = -3800 \text{ kJ mol}^{-1} \quad \ldots\text{(ii)}$$

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

$$\Delta H = -3920 \text{ kJ mol}^{-1} \quad \ldots\text{(iii)}$$

For the reaction,

$$C_6H_{10} + H_2 \longrightarrow C_6H_{12}$$

Eq. (i) + Eq. (ii) – Eq. (iii)

$$\Delta H = -241 - 3800 - (-3920)$$

$$= -121 \text{ kJ mol}^{-1}$$

4 $\frac{1}{2} I_2(s) + \frac{1}{2} Cl_2(g) \longrightarrow ICl(g)$

$$\Delta H = \left[\frac{1}{2} \Delta H_{s \to g(I_2)}\right.$$

$$+\frac{1}{2}\Delta H_{\text{diss}(\text{Cl}_2)}+\frac{1}{2}\Delta H_{\text{diss}(\text{I}_2)}\Big]-\Delta H_{\text{ICl}}$$

$$=\left(\frac{1}{2}\times 62.76+\frac{1}{2}\times 242.3+\frac{1}{2}\times 151.0\right)$$

$$-211.3$$

$$=228.03-211.3$$

$$=16.73\approx 16.8\ \text{kJ/mol}$$

5 $\underset{2\text{ mol}}{2\text{Fe}(s)}+\frac{3}{2}O_2(g)\longrightarrow \underset{1\text{ mol}}{Fe_2O_3(s)}$

Moles of Fe $=\frac{4}{56}=\frac{1}{14}$ mol

Moles of Fe_2O_3 formed $=\frac{1}{28}$ mol

Heat released = 29.28 kJ

$\therefore \Delta_f H^\circ (Fe_2O_3)=\frac{-29.28}{1/28}\ \text{kJ mol}^{-1}$

$=-819.84\ \text{kJ mol}^{-1}$

6 $\because$ 58 g *iso*-butane provides energy

$=2658\ \text{kJ}$

11.2×10^3 g *iso*-butane will provide energy

$=\frac{2658\times 11.2\times 10^3}{58}=513268.9$ kJ

The daily requirement of energy

$=15000\ \text{kJ}$

$\because$ Loss of energy = 30%

$\therefore$ Total energy used for work

$=\frac{513268.9\times 70}{100}$

$\therefore$ Cylinder will last

$=\frac{513268.9\times 70}{100\times 15000}=24$ days

7 Millimoles of dibasic strong acid

$=M\times V=0.20\times 350=70$ mmol

$\therefore$ Amount of H^+ ions in the acid

$=2\times 70=140$ mmol

Similarly, amount of OH^- ions in monobasic strong base

$=0.10\times 650\times 1=65$ mmol

[Here, OH^- is the limiting reactant].

$\because$ 1 mole of OH^- ions produces

$=57.1$ kJ heat 65×10^{-3} moles of OH^- ions will produce

$=57.1\times 65\times 10^{-3}=3.71$ kJ

8 Same bonds are formed in reaction (1) and (2) but no bonds are broken in reaction (1) whereas, bonds in the reactant molecules are broken in reaction (2).

As energy is absorbed when bonds are broken, energy released in reaction (1) is greater than that in reaction (2) hence, $x > y$.

9 $CaCl_2(s)+6H_2O\longrightarrow CaCl_2\cdot 6H_2O(s);$

$\Delta H=-23.2$ kcal

$CaCl_2\cdot 6H_2O(s)+(aq)\longrightarrow CaCl_2\cdot 6H_2O;$

$\Delta H=+3.5$ kcal

Thus, $CaCl_2(s)+(aq)$ (excess)

$\longrightarrow CaCl_2\cdot 6H_2O(aq),$

$\Delta H=-23.2+3.5=19.7$ kcal

10 $Q=It=3.2\times 27$

Energy produced

$=QV=3.2\times 27\times 12=1036.8$ J

Calorimeter constant

$=\frac{1036.8}{1.6}=648\ \text{JK}^{-1}$

11 $C_2H_5OH(l)+3O_2(g)\longrightarrow 2CO_2(g)+3H_2O(l)$

$\Delta U=-1364.47$ kJ/mol

$\Delta H=\Delta U+\Delta n_g RT$

$\Delta n_g=-1$

$\Delta H=-1364.47+\frac{-1\times 8.314\times 298}{1000}$

[Here, value of R is unit of J must be converted into kJ]

$=-1364.47-2.4776$

$=-1366.95$ kJ/mol

12 $BaCl_2(s)+2H_2O(l)$

$\longrightarrow BaCl_2\cdot 2H_2O(aq);$

$\Delta H=H_1=-20.6$ kJ ...(i)

$BaCl_2(s)+2H_2O(aq)$

$\longrightarrow BaCl_2\cdot 2H_2O(aq);$

$\Delta H=H_2=+8.8$ kJ ...(ii)

For the reaction,

$BaCl_2(s)+2H_2O\longrightarrow BaCl_2\cdot 2H_2O(s)$

Eq (i) – Eq (ii)

$\Delta H=\Delta H_1-\Delta H_2=-20.6-8.8$

$=-29.4$ kJ

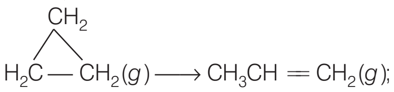
13 Carbon is found in solid state. The state of substance affects the enthalpy change. For formation of CH_4, the equation of can be written as

$C(s)+H_2(g)\longrightarrow CH_4(g)$

$C(s)\longrightarrow C(g)$ sublimation

and $H_2(g)\longrightarrow 2H(g)$ dissociation are required for the average energy of C—H formation

14 Given,



$\Delta H=-33.0$ kJ ...(i)

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

$\Delta H=-393.5$ kJ ...(ii)

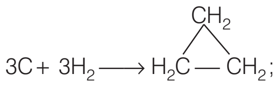
$H_2+\frac{1}{2}O_2\longrightarrow H_2O(l);$

$\Delta H=-285.8$ kJ ...(iii)

$3C+3H_2\longrightarrow CH_3-CH=CH_2(g);$

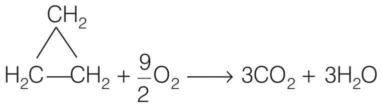
$\Delta H=20.42$ kJ ...(iv)

Eq. (iv) – Eq. (i) yields



$\Delta H=53.42$ kJ ...(v)

3 Eq (ii) + 3 Eq (iii) – Eq (v) yields



$\Delta_r H=[3\times(-393.5)]+[3\times(-285.5)]-53.42=-2090.342$ kJ

15 $X_2+Y_2\longrightarrow 2XY$

$\Delta H=(BE)_{X-X}+(BE)_{Y-Y}-2(BE)_{X-Y}$

If BE of $X—Y=a$,

(BE) of $(X—X)=a$ and (BE) of $(Y—Y)=a/2$

and BE of $X-Y=a$

$\Delta H_{f(X-Y)}=200$ kJ

$-400=a+\frac{a}{2}-2a$

$-400=-\frac{a}{2}\quad a=+800$ kJ

The bond dissociation energy of $X_2=800\ \text{kJmol}^{-1}$

16 Heat generated $=C\times \Delta T$

$=1260\times 0.667=840.4$ cal

Molar mass of $CH_4=16$ g/mol

Enthalpy of combustion for 16 g $CH_4=-215$ kcal/mol

$=-215000$ cal/mol

Thus, enthalpy equal to -840.42 cal

$=\frac{16}{215000}\times 840.42=0.0625$ g

Number. of moles of CH_4 in the reaction

$=\frac{0.0625}{16}=3.91\times 10^{-3}$ mol

$pV=nRT=0.973\times 1$

$=n\times 0.082\times 298$

$n=3.92\times 10^{-2}$ mol

$\therefore$ mol% of $CH_4=\frac{3.91\times 10^{-3}}{3.92\times 10^{-2}}\times 100$

$=9.97\approx 10\%$