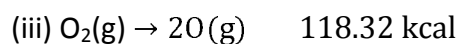
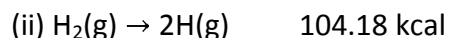
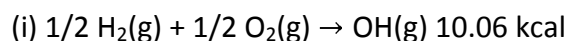


# Thermodynamics

## SUBJECTIVE PROBLEMS:

### Q 1.

The enthalpy for the following reaction ( $\Delta H^\circ$ ) at 25°C are given below:

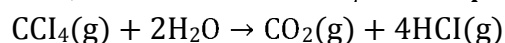


Calculate the O-H bond energy in the hydroxyl radical.

(IIT JEE 1981 – 2 Marks)

### Q 2.

The standard heats of formation at 298 K for  $\text{CCl}_4(\text{g})$ ,  $\text{H}_2\text{O}(\text{g})$ ,  $\text{CO}_2(\text{g})$  and  $\text{HCl}(\text{g})$  are -25.5, -57.8, -94.1 and -22.1 kcal/mol respectively. Calculate  $\Delta H_{298}^\circ$  for the reaction



(IIT JEE 1982 – 2 Marks)

### Q 3.

The molar heats of combustion of  $\text{C}_2\text{H}_2(\text{g})$ , C(graphite) and  $\text{H}_2(\text{g})$  are 310.62 kcal, 94.05 kcal and 68.32 kcal, respectively. Calculate the standard heat of formation of  $\text{C}_2\text{H}_2(\text{g})$ .

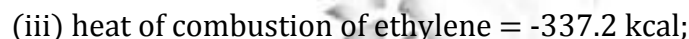
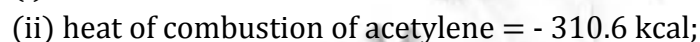
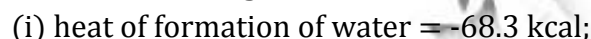
(IIT JEE 1983 – 2 Marks)

Q 4. The heat energy, q, absorbed by a gas  $\Delta H$ , is true at what condition(s).

(IIT JEE 1983 – 2 Marks)

### Q 5.

Give the following standard heats of reaction :



Calculate the heat of reaction for the hydrogenation of acetylene at constant volume (25°C).

(IIT JEE 1984 – 4 Marks)

### Q 6.

The bond dissociation energies of gaseous  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  are 104, 58 and 103 kcal/mole respectively. Calculate the enthalpy of formation of  $\text{HCl}$  gas.

(IIT JEE 1985 – 2 Marks)

### Q 7.

The standard molar heats of formation of ethane, carbon dioxide and liquid water are -21.1, -94.1 and -68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane.

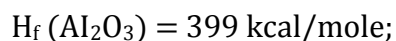
(IIT JEE 1986 – 2 Marks)

### Q 8.

An intimate mixture of ferric oxide,  $\text{Fe}_2\text{O}_3$ , and aluminium, Al, is used in solid fuel rockets.

Calculate the fuel value per gram and fuel value per cc of the mixture. Heats of formation and densities are as follow :

(IIT JEE 1988 – 2 Marks)



$H_f(\text{Fe}_2\text{O}_3) = 199 \text{ kcal/mole}$ ;

Density of  $\text{Fe}_2\text{O}_3 = 5.2 \text{ g/cc}$ ;

Density of Al =  $2.7 \text{ g/cc}$ .

**Q 9.**

An athlete is given 100 gm of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) of energy equivalent to 1560 kJ. He utilizes 50 percent of this gained energy in the event. In order to avoid storage of energy in the body, calculate the weight of water he would need to perspire. The enthalpy of evaporation of water is  $44 \text{ kJ/mole}$ . (IIT JEE 1989 – 2 Marks)

**Q 10.**

The standard enthalpy of combustion at  $25^\circ\text{C}$  of hydrogen, cyclohexene ( $\text{C}_6\text{H}_{10}$ ) and cyclohexane ( $\text{C}_6\text{H}_{12}$ ) are  $-241$ ,  $-3800$  and  $-3920 \text{ kJ/mole}$  respectively. Calculate the heat of hydrogenation of cyclohexene. (IIT JEE 1989 – 2 Marks)

**Q 11.**

Using the data (all values are in  $\text{kcal mol}^{-1}$  at  $25^\circ\text{C}$ ) given below, calculate the bond energy of C-C and C-H bonds. (IIT JEE 1990 – 5 Marks)

$$\Delta H^\circ_{\text{combustion}}(\text{ethane}) = -372.0$$

$$\Delta H^\circ_{\text{combustion}}(\text{propane}) = -530.0$$

$$\Delta H^\circ_{\text{C(s)} \rightarrow \text{C(g)}} = 172.0$$

$$\text{Bond energy of H-H} = 104.0$$

$$\Delta H^\circ_f \text{ of } \text{H}_2\text{O(l)} = -68.0$$

$$\Delta H^\circ_f \text{ of } \text{CO}_2(\text{g}) = -94.0$$

**Q 12.**

A gas mixture of 3.67 litres of ethylene and methane on complete combustion at  $25^\circ\text{C}$  produces 6.11 litres of  $\text{CO}_2$ . Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are  $-1423$  and  $-891 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ . (IIT JEE 1991 – 5 Marks)

**Q 13.**

Determine the enthalpy change of the reaction.

$\text{C}_3\text{H}_8(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{CH}_4(\text{g})$ , at  $25^\circ$ , using the given heat of combustion values under standard conditions

Compound	$\text{H}_2(\text{g})$	$\text{CH}_4(\text{g})$	$\text{C}_2\text{H}_6(\text{g})$	C(graphite)
$\Delta H^\circ$ (kJ/mol)	-285.8	-890.0	-1560.0	-393.5

The standard heat of formation of  $\text{C}_3\text{H}_8(\text{g})$  is  $-103.8 \text{ kJ/mol}$ . (IIT JEE 1992 – 3 Marks)

**Q 14.**

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  $\text{CH}_4$  and  $6x$  litre/hour of  $\text{O}_2$ ) is to be readjusted for butane,  $\text{C}_4\text{H}_{10}$ . In order to get the same calorific output, what should be the rate of supply of butane and oxygen?

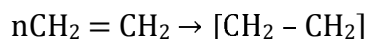
Assume that losses due to incomplete combustion, etc, are the same for both the fuels and the gases behave ideally. (IIT JEE 1993 – 3 Marks)

Heats of combustion :

$\text{CH}_4 = 809 \text{ kJ/mol}$ ;  $\text{C}_4\text{H}_{10} = 2878 \text{ kJ/mol}$

**Q 15.**

The polymerization of ethylene to linear polyethylene is represent by the reaction (IIT JEE 1994 – 2 Marks)



where n has a large integral value. Given that the average enthalpies of bond dissociation for C = C and C-C at 298 K are + 590 and + 331  $\text{kJ mol}^{-1}$ , respectively, calculate the enthalpy of polymerisation per mole of ethylene at 298 K.

**Q 16.**

The standard molar enthalpies of formation of cyclohexane(l) and benzene(l) at 25°C are - 156 and + 49  $\text{kJ mol}^{-1}$  respectively. The standard enthalpy of hydrogenation of cyclohexene(l) at 25°C is - 119  $\text{kJ mol}^{-1}$ . Use these data to estimate the magnitude of the resonance energy of benzene (IIT JEE 1996 – 2 Marks)

**Q 17.**

The enthalpy change involved in the oxidation of glucose is 2800  $\text{kJ mol}^{-1}$ , 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 JEE 1997C – 2 Marks)

**Q 18.**

Compute the heat of formation of liquid methyl alcohol in kilojoules per mole, using the following data. Heat of vaporization of liquid methyl alcohol = 38  $\text{kJ/mol}$ . Heat of formation of gaseous atoms from the elements in their standard states; H, 218  $\text{kJ/mol}$ ; C, 715  $\text{kJ/mol}$ ; O, 249  $\text{kJ/mol}$ . Average bond energies :  
C-H = 415  $\text{kJ/mol}$ , C-O = 365  $\text{kJ/mol}$ , O-H = 463  $\text{kJ/mol}$  (IIT JEE 1997- 5 Marks)

**Q 19.**

Anhydrous  $\text{AlCl}_3$  is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution. (Ionisation energy for Al = 5137  $\text{kJ mol}^{-1}$ ;  $\Delta H_{\text{hydration}}$  for  $\text{Al}^{3+} = 4665 \text{ kJ mol}^{-1}$ ;  $\Delta H_{\text{hydration}}$  for Cl = -381  $\text{kJ mol}^{-1}$ .) (IIT JEE 1997- 2 Marks)

**Q 20.**

From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$  and propene(g) are - 393.5, - 285.8 and 20.42  $\text{kJ mol}^{-1}$  respectively. The enthalpy of isomerisation of cyclopropane to propene is - 33.0  $\text{kJ mol}^{-1}$ . (IIT JEE 1998 - 5 Marks)

**Q 21.**

Estimate the average S-F bond energy in  $\text{SF}_6$ . The values of standard enthalpy of formation of  $\text{SF}_6(\text{g})$ , S(g) and F(g) are : - 1100, 275 and 80  $\text{kJ mol}^{-1}$  respectively. (IIT JEE 1999 - 3 Marks)

**Q 22.**

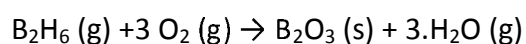
A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm<sup>3</sup> to 2.50 dm<sup>3</sup>. Calculate the enthalpy change in this process.  $C_{v,m}$  for argon is 12.48 JK<sup>-1</sup> mol<sup>-1</sup>.

**(IIT JEE 2000 - 4 Marks)****Q 23.**

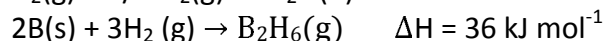
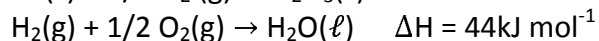
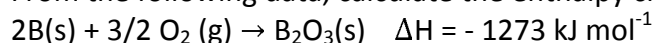
Show that the reaction  $\text{CO(g)} + 1/2 \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$  at 300 K, is spontaneous and exothermic, when the standard entropy change is 4.094 kJ mol<sup>-1</sup> K<sup>-1</sup>. The standard Gibbs free energies of formation for CO<sub>2</sub> and CO are -394.4 and, -137.2 kJ mol<sup>-1</sup>, respectively.

**(IIT JEE 2000 - 3 Marks)****Q 24.**

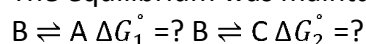
Diborane is a potential rocket fuel which undergoes combustion according to the reaction.

**(IIT JEE 2000 - 2 Marks)**

From the following data, calculate the enthalpy change for the combustion of diborane.

**Q 25.**

When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1,2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate  $\Delta G^\circ$  for the following equilibria :



From the calculated value of  $\Delta G_1^\circ$  and  $\Delta G_2^\circ$  indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C).

**(IIT JEE 2001 - 10 Marks)****Q 26.**

Two moles of a perfect gas undergo the following processes

**(IIT JEE 2002 - 5 Marks)**

(a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L);

(b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L);

(c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L).

(i) Sketch with labels each of the processes on the same P-V diagram.

(ii) Calculate the total work (w) and the total heat change (q) involved in the above processes.

(iii) What will be the values of  $\Delta U$ ,  $\Delta H$  and  $\Delta S$  for the overall process?

**Q 27.**

$C_v$  value of He is always 3R/2 but  $C_v$  value of H<sub>2</sub> is 3R/2 at low temperature and 5R/2 at moderate temperature and more than 5R/2 at higher temperature explain in two to three lines.

**(IIT JEE 2003 - 2 Marks)****Q 28.**

An insulated container contains 1 mol of a liquid, molar volume 100 ml, at 1 bar. When liquid is steeply pressed to 100 bar, volume decreases to 99 ml. Find  $\Delta H$  and  $\Delta U$  for the process.

**(IIT JEE 2004 - 2 Marks)**

**Q 29.** In the following equilibrium  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

**(IIT JEE 2004 - 2 Marks)**

When 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar.

Given :  $\Delta G_f^\circ(\text{N}_2\text{O}_4) = 100\text{kJ}$ ;  $\Delta G_f^\circ(\text{NO}_2) = 50\text{kJ}$

(i) Find  $\Delta G$  of the reaction at 298 K.

(ii) Find the direction of the reaction

**Q 30.**

For the reaction,  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ ;  $\Delta H = -560\text{kJ}$ . Two moles of CO and one mole of  $\text{O}_2$  are taken in a container of volume 1 L. They completely form two moles of  $\text{CO}_2$ , the gases, deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of  $\Delta U$  at 500K. (1 L atm = 0.1 kJ)

**(IIT JEE 2006 - 6Marks)**

# Thermodynamics-solutions

## SUBJECTIVE PROBLEMS

### Sol 1.

The required reaction in terms of dissociation energy is  $\text{OH}(\text{g}) \rightarrow \text{O}(\text{g}) + \text{H}(\text{g}); \Delta H = ?$

This equation can be achieved by (a) reversing the equation (i), (b) dividing equation (ii) and (iii) each by 2, and (c) adding the three resulting equations.



Thus one mole of  $\text{OH}(\text{g})$  needs 101.19 kcal of energy to break into oxygen and hydrogen gaseous atom.

Hence the bond energy of O-H bond is **101.19 kcal**.

### Sol 2.

Since we know that

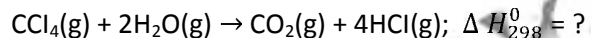
Heat content of the compound

= Heat of formation  $\Delta H, \Delta H_{298}^0$

= Total heat contents of the products

- Total heat contents of the reactants

Writing the given chemical reaction,



$$\Delta H_{298}^0 = [\Delta H_{\text{CO}_2} + 4 * \Delta H_{\text{HCl}}] - [\Delta H_{\text{CCl}_4} + 2 * \Delta H_{\text{H}_2\text{O}}]$$

Given,  $\Delta H_{\text{CCl}_4} = - 25.5 \text{ kcal/mole}$   $\Delta H_{\text{H}_2\text{O}}$

= - 57.8 kcal/mole

$\Delta H_{\text{CO}_2} = - 94.1 \text{ kcal/mole}$   $\Delta H_{\text{HCl}} = - 22.1 \text{ kcal/mole}$

Substituting the values in the above equation,

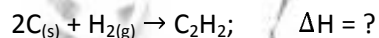
$$\Delta H_{298}^0 = [-94.1 + 4 * - 22.1] - [-25.5 + 2 * - 57.8]$$

$$= [-94.1 - 88.4] - [-25.5 - 115.6]$$

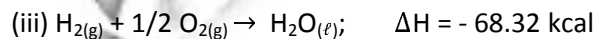
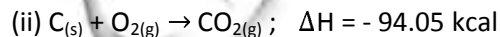
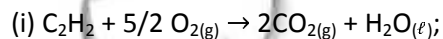
$$= - 182.5 + 141.1 = \mathbf{-41.4 \text{ kcal}}$$

### Sol 3.

The required equation is :



Write the thermochemical equations for the given data



For getting the above required reaction, we will have to

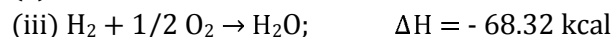
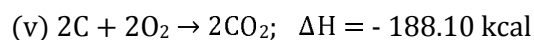
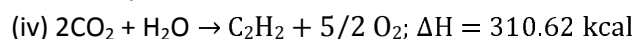
#### **NOTE:**

(a) Bring  $\text{C}_2\text{H}_2$  in the product that can be done by reversing the equation (i) to give equation (iv).

(b) Multiply equation (ii) by 2 to get 2C atoms in the reactant and thus equation (v) is obtained.

(c) Keep equation (iii) as such.

(d) Add equations (iv), (v) and (iii).



On adding,  $2C + H_2 \rightarrow C_2H_2$ ;  $\Delta H = 54.20 \text{ kcal}$

Hence the standard heat of formation of  $C_2H_2(g) = 54.20 \text{ kcal}$

#### **Sol 4.**

If heat is absorbed at constant pressure, then

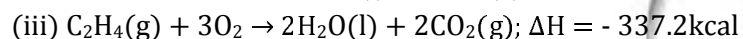
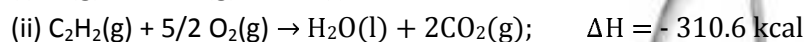
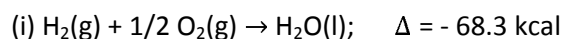
$$q_p = \Delta E - (-P\Delta V)$$

$$\text{or } q_p = E_2 - E_1 - [-P(V_2 - V_1)]$$

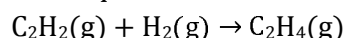
$$\text{or } q_p = (E_2 + PV_2) - (E_1 + PV_1) = H_2 - H_1 = \Delta H$$

#### **Sol 5.**

The given data can be written as follows



The required thermochemical equation is



The required equation can be obtained by subtracting equation (iii) from the sum of equations (i) and (ii), thus  $\Delta H$  of the required equation can be calculated as below.

$$\Delta H = [-68.3 + (-310.6)] - (-337.2)$$

$$= [-68.3 - 310.6] + 337.2$$

$$= -378.9 + 337.2 = -41.7 \text{ kcal}$$

$$\Delta E = \Delta H - \Delta nRT$$

Here  $\Delta n = \text{Moles of the gaseous products} - \text{Moles of the gaseous reactants}$

$$= 1 - (1 + 1) = -1$$

Substituting the value of  $\Delta H$ ,  $\Delta n$ ,  $R$  and  $T$  in

$$\Delta E = \Delta H - \Delta nRT$$

$$\Delta E = -41.7 - (-1 * 2 * 10^{-3} * 298)$$

$$[\because R = 2 \text{ cal/ degree/ mole} = 2 * 10^{-3} \text{ kcal/ deg/ mole}]$$

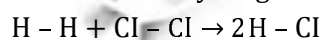
$$= -41.7 + 2 * 10^{-3} * 298$$

$$= -41.7 + 0.596 = 41.104 \text{ kcal}$$

#### **Sol 6.**

Bond	H - H	Cl - Cl	H - Cl
$\Delta H$ disso.	104 kcal	58 kcal	103 kcal

Formation of hydrogen chloride can be represented as



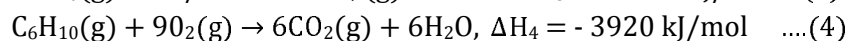
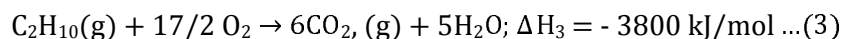
Thus the reaction involves

Cleavage of one H - H bond,  $\Delta H = 104 \text{ kcal}$

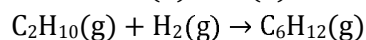
Cleavage of one Cl - Cl bond,  $\Delta H = 58 \text{ kcal}$







The required reaction (1) can be obtained by adding equations (2) and (3) and subtracting (4) from the sum of (2) and (3).



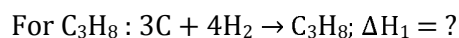
$$\Delta H_1 = (\Delta H_2 + \Delta H_3) - \Delta H_4$$

$$= [-241 + (-3800)] - (-3920)$$

$$= (-241 - 3800) - (-3920)$$

$$= -4041 + 3920 = -121 \text{ kJ/mole}$$

### **Sol 11.**



$$\therefore \Delta H_1 = -[2(\text{C}-\text{C}) + 8(\text{C}-\text{H})] + [3\text{C}_{\text{s} \rightarrow \text{g}} + 4(\text{H}-\text{H})] \dots(1)$$

$$\therefore \Delta H_2 = -[1(\text{C}-\text{C}) + 6(\text{C}-\text{H})] + [2\text{C}_{\text{s} \rightarrow \text{g}} + 3(\text{H}-\text{H})] \dots(2)$$

Let bond energy of C - C be x kcal and bond energy of C - H by y kcal

$$\therefore \text{By eq. (1)} \Delta H_1 = -(2x + 8y) + [3 * 172 + 4 * 104] \dots(3)$$

$$\Delta H_2 = -(x + 6y) + [2 * 172 + 3 * 104] \dots(4)$$

Also given  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ ;  $\Delta H = -94.0 \text{ k cal} \dots(5)$

$$\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}; \Delta H = -68.0 \text{ k cal} \dots(6)$$

$$\text{C}_2\text{H}_6 + (7/2)\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}; \Delta H = -372 \text{ k cal} \dots(7)$$

$$\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}; \Delta H = -530 \text{ k cal} \dots(8)$$

By inspection method:  $2 * (5) + 3 * (6) - (7)$  gives

$$2\text{C} + 3\text{H}_2 \rightarrow \text{C}_2\text{H}_6; \Delta H_2 = -20 \text{ k cal} \dots(9)$$

And  $3 * (5) + 4 * (6) - (8)$  gives

$$3\text{C} + 4\text{H}_2 \rightarrow \text{C}_3\text{H}_8; \Delta H_1 = -20 \text{ k cal} \dots(10)$$

$\therefore$  By eq. (3), (4), (9) and (10)

$$X + 6y = 676$$

$$2x + 8y = 956$$

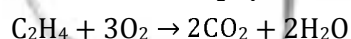
$$\therefore x = 82 \text{ k cal and } y = 99 \text{ k cal}$$

Bond energy of C - C bond = **82 k cal**

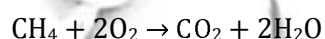
and Bond energy of C - h bond = **99 k cal**

### **Sol 12.**

Combustion of  $\text{C}_2\text{H}_4$  and  $\text{CH}_4$  takes place as follows :



$$1 \text{ vol.} \quad 2 \text{ vol.}$$



$$1 \text{ vol.} \quad 1 \text{ vol.}$$

Let the vol. of  $\text{CH}_4$  in mixture = x /

$$\therefore \text{Vol. of } \text{C}_2\text{H}_4 \text{ in the mixture} = (3.67 - x) /$$

Vol. of  $\text{CO}_2$  produced by x / of  $\text{CH}_4 = x /$  and

Vol. of  $\text{CO}_2$  produced by (3.67 - x) / of  $\text{C}_2\text{H}_4 = 2(3.67 - x) /$

$$\therefore \text{Total vol. of } \text{CO}_2 \text{ produced} = x + 2(3.67 - x)$$

$$\text{Or } 6.11 = x + 2(3.67 - x) \text{ or } x = 1.23 /$$

∴ Vol. of CH<sub>4</sub> in the mixture = 1.23 l

and Vol. of C<sub>2</sub>H<sub>4</sub> in the mixture = 3.67 - 1.23 = 2.44 l

Vol. of CH<sub>4</sub> per litre of the mixture = 1.23/3.67 = 0.335 l

Vol. of C<sub>2</sub>H<sub>4</sub> per litre of the mixture = 2.44/3.67 = 0.665 l

Now we know that volume of 1 mol. Of any gas at 25°C (298 K) = 22.4 \* 298/273 = 24.45 l

[∴ Volume at NTP = 22.4L]

Heat evolved due to combustion of 0.335 l of CH<sub>4</sub> = - 0.335 \* 891/24.45 = - 12.20 kJ [given, heat evolved by combustion of 1 l = 891 kJ]

Similarly, heat evolved due to combustion due to combustion of 0.665 l of C<sub>2</sub>H<sub>4</sub>  
= - 0.665 \* 1423/24.45 = - 38.70 kJ

∴ Total heat evolved = 12.20 + 338.70 = **50.90 kJ**

### **Sol 13.**

From the given data, we can write :

(i) H<sub>2</sub> + 1/2 O<sub>2</sub> → H<sub>2</sub>O; ΔH<sub>1</sub> = - 285.8 kJ/mol

(ii) CH<sub>4</sub> + 2O<sub>2</sub> → CO<sub>2</sub> + 2H<sub>2</sub>O; ΔH<sub>2</sub> = - 890 kJ mol

(iii) C<sub>2</sub>H<sub>6</sub> + 7/2 O<sub>2</sub> → 2CO<sub>2</sub> + 3H<sub>2</sub>O; ΔH<sub>3</sub> = - 1560 kJ/mol

(iv) C(s) + O<sub>2</sub> → CO<sub>2</sub>; ΔH<sub>4</sub> = - 393.5 kJ/mol

(v) 3C(s) + 4H<sub>2</sub> → C<sub>3</sub>H<sub>8</sub>(g); ΔH<sub>5</sub> = - 103.8 kJ/mol

The required reaction is C<sub>3</sub>H<sub>8</sub>(g) + H<sub>2</sub>(g) → C<sub>2</sub>H<sub>6</sub>(g) + CH<sub>4</sub>(g), ΔH = ?

It can be obtained by the following calculation.

3 \* (iv) - (v) + 5(i) - (iii) - (ii)

In other words, ΔH = 3ΔH<sub>4</sub> - ΔH<sub>5</sub> + 5ΔH<sub>1</sub> - ΔH<sub>2</sub> - ΔH<sub>3</sub>

∴ ΔH = 3(- 393.5) - (-103.8) + 5(-285.8) + 890 + 1560

= - 2609.5 + 2553.8 = **-55.7 kJ.mol**

### **Sol 14.**

Combustion of CH<sub>4</sub> and C<sub>4</sub>H<sub>10</sub> takes place as follows

CH<sub>4</sub> + 2O<sub>2</sub> → CO<sub>2</sub> + 2H<sub>2</sub>O, ΔH = - 809 kJ mol<sup>-1</sup>

C<sub>4</sub>H<sub>10</sub> + 13/2O<sub>2</sub> → 4CO<sub>2</sub> + 5H<sub>2</sub>O, ΔH = - 2878 kJ mol<sup>-1</sup>

In order to get the same calorific output due to C<sub>4</sub>H<sub>10</sub>,

The rate of supply of butane = x \* 809/2878 = **0.281 x/hr**

Rate of supply of oxygen = 0.2803 x \* 13/2 \* 3 = **5.481 x/hr**

### **ALTERNATIVE SOLUTIONS :**

The reaction of combustion of CH<sub>4</sub> and C<sub>4</sub>H<sub>10</sub> can be written as follows :

CH<sub>4</sub> + 2O<sub>2</sub> → CO<sub>2</sub> + 2H<sub>2</sub>O; ΔH = - 809

X        6X

Initial volume (in litre)

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

∴ V litre of 1 mole CH<sub>4</sub> gives energy on combustion = 809 kJ

∴ X litre of CH<sub>4</sub> gives energy on combustion = 808(X)/V kJ

∴ 2878 kJ energy is obtained by 1 mole or V litre C<sub>4</sub>H<sub>10</sub>

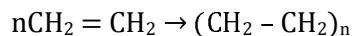
∴ 809(X) \* V/V \* 2878 litre C<sub>4</sub>H<sub>10</sub> = 0.281 (X) litre C<sub>4</sub>H<sub>10</sub>

Thus, butane supplied for same calorific output = 0.281 (X) litre

∴ C<sub>4</sub>H<sub>10</sub> + 13/10 O<sub>2</sub> → 4CO<sub>2</sub> + 5H<sub>2</sub>O; ΔH = - 2878 kJ/mol

$$\begin{aligned} \text{Volume of O}_2 \text{ required} &= 3 * \text{volume of O}_2 \text{ for combustion of C}_4\text{H}_{10} \\ &= 3 * 13/2 * \text{volume of C}_4\text{H}_{10} \\ &= 3 * 13/2 * 0.281 \text{ (X) litre O}_2 \end{aligned}$$

### **Sol 15.**



**NOTE :** During the polymerization of ethylene, one mole of ethylene breaks i.e. one C = C double bond breaks and the two CH<sub>2</sub> - groups are linked with C - C single bonds thus forming three single bonds (two single bonds are formed when each CH<sub>2</sub> - group of ethylene links with one CH<sub>2</sub> - group of another ethylene molecule). But in the whole unit of polymer, number of single C - C bonds formed/mole of ethylene is 2.

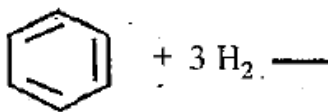
$$\begin{aligned} \text{Energy released} &= \text{Energy due to formation of 2 C - C single bonds} \\ &= 2 * 331 = 662 \text{ kJ/mol of ethylene} \end{aligned}$$

$$\begin{aligned} \text{Energy absorbed} &= \text{energy due to dissociation of 1 C = C double bond} \\ &= 590 \text{ kJ/mol of ethylene} \end{aligned}$$

$$\therefore \text{Enthalpy of polymerization/mol of ethylene or } \Delta H_{\text{polymerisation}} = 590 - 662 \text{ kJ/mol} = -72 \text{ kJ/mole}$$

### **Sol 16.**

Standard enthalpy of hydrogenation of cyclohexen (- 119kJ mol<sup>-1</sup>) means the enthalpy of hydrogenation of one C = C double bond. Now benzene has three C = C double bonds, the enthalpy of the reaction would be = 3 \* - 119 = - 357 kJ mol<sup>-1</sup>



Actual enthalpy of the reaction can be evaluated as follows.

$$\Delta H_{\text{(Reaction)}} = \Delta H_f^\circ (\text{Product}) - \Delta H_f^\circ (\text{Reactants})$$

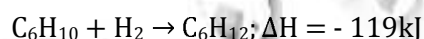
$$= -156 - (49 + 0)$$

$$= -205 \text{ kJ mol}^{-1}$$

$$\therefore \text{Resonance energy} = \Delta H_{\text{Exp}} - \Delta_{\text{cal}}$$

$$= -357 - (-205) = -152 \text{ kJ mol}^{-1}$$

### **ALTERNATIVE SOLUTION :**



(involves breaking up of three double bond and addition of three H<sub>2</sub> molecule)

$$\therefore \text{C}_6\text{H}_6 + 3\text{H}_2 \rightarrow \text{C}_6\text{H}_{12}; \Delta H = 3 * (-119) = -357 \text{ kJ}$$

(involves breaking up of three double bond and addition of three H<sub>2</sub> molecule)

$$\text{Also given } 6\text{C} + 6\text{H}_2 \rightarrow \text{C}_6\text{H}_{12(l)}; \Delta H = -156$$

$$\text{we have } \text{C}_6\text{H}_6 + 3\text{H}_2 \rightarrow \text{C}_6\text{H}_{12(l)}; \Delta H = -357$$

$$\underline{6\text{C} + 3\text{H}_2 \rightarrow \text{C}_6\text{H}_6; \Delta H = +201 \text{ kJ}}$$

$$\text{Therefore, resonance energy} = 49 - 201 = -152 \text{ kJ}$$

### **Sol 17.**

$$\text{Energy available for muscular work by 1 mole of glucose} = 2880 * 25/100 = 720 \text{ kJ mol}^{-1}$$

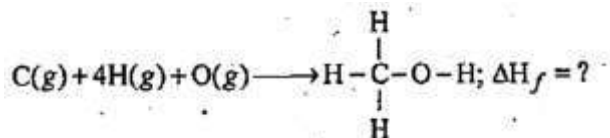
Thus 180 g of glucose (mol. Wt. of glucose) supplies 720 kJ

$$120 \text{ g of glucose will supply} = 720/180 * 120 = 480 \text{ kJ}$$

$$100 \text{ kJ is needed to walk 1 km, Hence, 480 kJ is needed to walk } 1/100 * 480 = \mathbf{4.8 \text{ km}}$$

### Sol 18.

the required thermochemical equation is



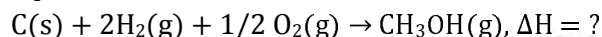
$$\begin{aligned} \Delta H_f &= [\Delta H_{\text{C(s)} \rightarrow \text{C(g)}} + 2\Delta H_{\text{H-H}} + 1/2 \Delta H_{\text{O=O}}] \\ &\quad - [3\Delta H_{\text{C-H}} + \Delta H_{\text{C-O}} + \Delta H_{\text{O-H}} + \Delta H_{\text{vap, CH}_3\text{OH}}] \\ &= [715 + 2 * 436 + 249] - [3 * 415 + 356 + 463 + 38] = - 266 \text{ kJ mol}^{-1} \end{aligned}$$

#### ALTERNATIVE SOLUTION :

The given data is as follows :

- (i)  $\text{CH}_3\text{OH(l)} \rightarrow \text{CH}_3\text{OH(g)}, \Delta H = 38 \text{ kJ mol}^{-1}$
- (ii)  $1/2 \text{H}_2(\text{g}) \rightarrow \text{H(g)}, \Delta H = 218 \text{ kJ mol}^{-1}$
- (iii)  $\text{C(graphite)} \rightarrow \text{C(g)}, \Delta H = 715 \text{ kJ mol}^{-1}$
- (iv)  $1/2 \text{O}_2(\text{g}) \rightarrow \text{O(g)}, \Delta H = 249 \text{ kJ mol}^{-1}$
- (v)  $\text{C-H(g)} \rightarrow \text{C(g)} + \text{H(g)}, \Delta H = 415 \text{ kJ mol}^{-1}$
- (vi)  $\text{C-O(g)} \rightarrow \text{C(g)} + \text{O(g)}, \Delta H = 356 \text{ kJ mol}^{-1}$
- (vii)  $\text{O-H(g)} \rightarrow \text{O(g)} + \text{H(g)}, \Delta H = 463 \text{ kJ mol}^{-1}$

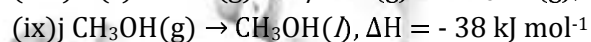
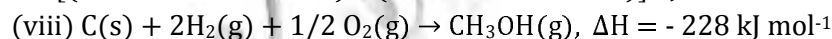
For the calculations of  $\Delta H_f$  of  $\text{CH}_3\text{OH}$  with the help of above data, following thermochemical equation is written :



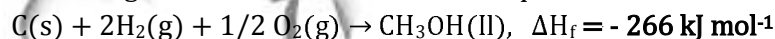
On the basis of bond enthalpy concept  $\Delta H$  of above reaction is calculated as follows :

$\Delta H = - [(\text{sum of bond enthalpies of all bonds of products} - \text{Sum of bond enthalpies of all bonds of reactants.})]$

$$\begin{aligned} \Delta H &= - \left[ (3 * E_{\text{C-H}} + E_{\text{C-O}} + E_{\text{O-H}}) \right. \\ &\quad \left. - \left( E_{\text{C(g)} \rightarrow \text{C(g)}} + 4 * E_{\frac{1}{2}(\text{H-H})(\text{g})} + E_{\frac{1}{2}\text{O}_2(\text{g})} \right) \right] \\ &= - [(3 * 415 + 356 + 463) - (715 + 4 * 218 + 249)] \text{ kJ mol}^{-1} = - 228 \text{ kJ mol}^{-1} \end{aligned}$$



On adding, above two thermochemical equation



Hence standard heat of formation of  $\text{CH}_3\text{OH(l)}$  ( $\Delta H_f$ ) = - 266 kJ mol<sup>-1</sup>

### Sol 19.

For ionization  $\Delta H_{\text{ionisation}} > \Delta H_{\text{Hydration}}$

Total hydration energy of  $\text{Al}^{3+}$  &  $3\text{Cl}^-$  ions of  $\text{AlCl}_3$  ( $\Delta H_{\text{hydration}}$ )

= (Hydration energy of  $\text{Al}^{3+}$  + 3 \* Hydration energy of  $\text{Cl}^-$ )

$$= [- 4665 + 3 (-381)] \text{ kJ mole}^{-1} = - 5808 \text{ kJ mole}^{-1}$$

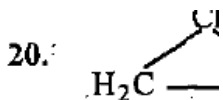
**NOTE :** This amount of energy is more than that required for the ionization of Al into  $\text{Al}^{3+}$

(Ionisation energy of Al to  $\text{Al}^{3+}$  = 5137 kJ mol<sup>-1</sup>). Due to this reason,  $\text{AlCl}_3$  becomes ionic in aqueous solution. In aqueous solution it exists in ionic form as below



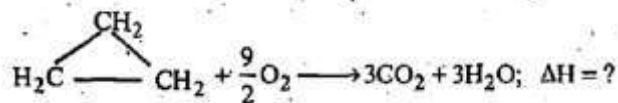
$\text{AlCl}_3 + \text{aq.} \rightarrow \text{AlCl}_{3(\text{aq.})}; \Delta H = /$   
 $\Delta H = \text{Energy released during hydration}$   
 $- \text{Energy used during ionization}$   
 $= -4665 - 3 * 381 + 5137 = -671 \text{ kJ/mol}$   
 Thus formation of ions will take place.

**Sol 20.**



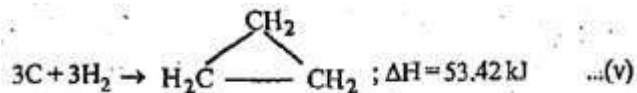
- $\Delta H = -33.0 \text{ kJ} \quad \dots \text{(i)}$   
 $\text{C} + \text{O}_2 \rightarrow \text{CO}_2(\text{g}); \Delta H = -393.5 \text{ kJ} \quad \dots \text{(ii)}$   
 $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}(\text{l}); \Delta H = -285.8 \text{ kJ} \quad \dots \text{(iii)}$   
 $3\text{C} + 3\text{H}_2 \rightarrow \text{CH}_3 - \text{CH} = \text{CH}_2(\text{g}); \Delta H = 20.42 \text{ kJ} \quad \dots \text{(iv)}$

The required reaction is

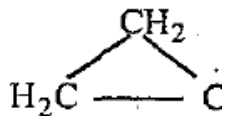


To calculate the value of  $\Delta H$  follow the following steps.

(iv) - (i) yields



[3 \* (ii) + 3 \* (iii)] - (v) yields



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

**Sol 21.**

Given  $\text{S}_{(\text{s})} + 3\text{F}_{2(\text{g})} \rightarrow \text{SF}_{6(\text{g})}; \Delta H = -1100 \text{ kJ} \quad \dots \text{(i)}$

$\text{S}_{(\text{s})} \rightarrow \text{S}_{(\text{g})}; \Delta H = 275 \text{ kJ} \quad \dots \text{(ii)}$

$1/2 \text{F}_{2(\text{g})} \rightarrow \text{F}_{(\text{g})}; \Delta H = 80 \text{ kJ} \quad \dots \text{(iii)}$

To get  $\text{SF}_{6(\text{g})} \rightarrow \text{S}_{(\text{g})} + 6\text{F}_{(\text{g})}$  we can proceed as

(ii) + 6 \* (iii) - (i)

$\therefore \text{SF}_{6(\text{g})} \rightarrow \text{S}_{(\text{g})} + 6\text{F}_{(\text{g})}; \Delta H = 1855 \text{ kJ}$

Thus average bond energy for S-F bond =  $1855/6 = 309.16 \text{ kJ}$

**Sol 22.**

For adiabatic expansion, we have

$\ln T_1/T_2 = R/C_v \ln V_2/V_1$

and  $\Delta H = nC_p \Delta T$ .

$$\ln 300/T_2 = 8.31/12.48 \ln 2.50/1.25$$

solving, we get,  $T_2 = 188.5 \text{ K}$

$$\text{No. of moles of argon gas, } N = PV/RT = 1 * 1.25 / 0.082 * 300 = 0.05$$

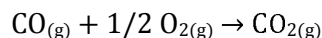
now we know that

$$\Delta H = nC_p \Delta T = 0.05 * 20.8(188.5 - 300) = -115.41 \text{ joules}$$

$$[\because C_p = C_v + R = 12.48 + 3.314 = 20.8]$$

### **Sol 23.**

For following reaction



$\Delta G^\circ$  can be calculated as follows :

$$\begin{aligned} \Delta G^\circ &= \Delta G_p^\circ - \Delta G_R^\circ = [\Delta G^\circ \text{CO}_2 - (\Delta G^\circ \text{CO} + 1/2 \Delta G^\circ \text{O}_2)] \\ &= -394.4 - (-137.2 + 1/2 * 0) = -257.2 \text{ kJ mol}^{-1} \end{aligned}$$

Since,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \text{ or } -257.2 = \Delta H - 300(0.094)$$

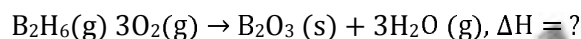
$$\therefore \Delta H^\circ = -285.4 \text{ kJ/mol}$$

Since,

**NOTE :**  $\Delta H^\circ$  is negative, so the reaction is exothermic and since  $\Delta G^\circ$  is negative so the reaction is spontaneous.

### **Sol 24.**

The chemical reaction for combustion of diborane is



For this the enthalpy change can be calculated in the following way.

$$\begin{aligned} \Delta H &= [\Delta H_{\text{B}_2\text{O}_3(s)} + 3\Delta H_{\text{H}_2\text{O}(g)}] - \Delta H_{\text{B}_2\text{H}_6(g)} ; \\ &(\because \Delta H_f^\circ \text{ of O}_2 = 0) \end{aligned}$$

$\Delta H_{\text{H}_2\text{O}(g)}$  can be obtained by adding  $3\Delta H_{\text{H}_2\text{O}(\ell)}$  and

$$\Delta H_{\text{H}_2\text{O}(g)}, \text{ i.e. } -286 + 44 = -242 \text{ kJ mol}^{-1}$$

$$\Delta H = [-1273 + 3 * -242] - 36 \text{ kJ mol}^{-1} = -1273 - 726 - 36 = -2035 \text{ kJ mol}^{-1}$$

### **Sol 25.**

$$\Delta G^\circ = -2.303RT \log [\text{Product}]/[\text{Reactant}]$$

Calculation of  $\Delta G$  values :

Thus for the equilibrium  $B \rightleftharpoons A$

$$\Delta G_1^\circ = (-2.303 * 8.314 * 448) \log 1.3/95.2$$

$$\text{Or } \Delta G_1^\circ = 15.992 \text{ kJ mole}^{-1}$$

Similarly for the equilibrium  $B \rightleftharpoons C$

$$\Delta G_2^\circ = (-2.303 * 8.314 * 448) \log 3.5/95.2$$

$$\text{Or } \Delta G_2^\circ = 12.312 \text{ kJ mole}^{-1}$$

Similarly for equilibrium,  $A \rightleftharpoons C$

$$\Delta G_3^\circ = -8.314 * 448 * 2.303 * \log_{10} 3.5/1.3 = -3.688 \text{ kJ mole}^{-1}$$

Hence, we have that

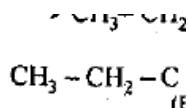
$$B \rightleftharpoons A, \quad \Delta G_1^\circ = +15.992 \text{ kJ mole}^{-1}$$

$$B \rightleftharpoons C, \quad \Delta G_2^\circ = +12.312 \text{ kJ mole}^{-1}$$

$$B \rightleftharpoons C, \quad \Delta G_3^\circ = -3.688 \text{ kJ mole}^{-1}$$

Thus, the correct order of stability, **B > C > A**

**NOTE :** Mechanism of isomerisation



**Sol 26.**

(ii) Total work (W) =  $W_1 + W_2 + W_3$   
 $W_3 = -P\Delta V + 0 + 2.303nRT \log V_2/V_1$   
 $= -1 * 20 + 2.303 * 2 * 0.082 * 121.95 \log 2$   
 $= -20 + 13.87 = -6.13 \text{ L atm}$

$$\left[ \begin{array}{l} PV = nRT \\ T = \frac{PV}{nR} = \frac{5 * 40}{2 * 0.082} \end{array} \right] = 121.95 \text{ k}$$

Since the system has returned to its initial state i.e. the process is cyclic, so  $\Delta U = 0$

$$\Delta U = q + W = 0, \text{ so } q = -W = -(-6.13) \text{ L.atm} = \mathbf{620.7 \text{ J}}$$

**NOTE :** In a cyclic process heat absorbed is completely converted into work.

(iii) Entropy is a state function and since the system has returned to its initial state, so  $\Delta S = 0$ .

Similarly  $\Delta H = 0$  and  $\Delta U = 0$  for the same reason i.e. U and H are also state functions having definite value in a given state of a system.

**Sol 27.**

Helium molecule is monoatomic so it has just three degrees of freedom corresponding to the three translational motion at all temperature and hence  $C_v$  value is always  $3/2 R$ . Hydrogen molecule is diatomic which are not rigidly held so they vibrate about a well defined average separation. For hydrogen molecule we have rotational and vibrational motion both besides translation motion.

These two additional contributions increase its total heat capacity. Contribution from vibrational motion is not appreciable at low temperature but increases from 0 to R on raising temperature.

**Sol 28.**

For adiabatic process,  $W = P(V_2 - V_1)$

Here  $P_1 = 1$  bar,  $P_2 = 100$  bar,  $V_1 = 100$  mL,  $V_2 = 99$  mL; For adiabatic process,  $q = 0$  /  $\Delta U = w$

$$\Delta U = q + W$$

$$= q - P(V_2 - V_1) \text{ since } W = -P(V_2 - V_1)$$

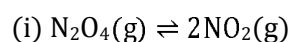
$$= 0 - 100(99 - 100) = \mathbf{100 \text{ bar mL}}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + (P_2V_2 - P_1V_1)$$

$$100 + [(100 * 99) - (1 * 100)]$$

$$= 100 + (9900 - 100) = \mathbf{9900 \text{ bar mL}}$$

**Sol 29.**



Initially  $P_{\text{N}_2\text{O}_4} = P_{\text{NO}_2} = 10$

$$\text{Reaction quotient} = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = 100/10 = 10$$

$$\Delta G^\circ = 2\Delta G_f^\circ(\text{NO}_2) - \Delta G_f^\circ(\text{N}_2\text{O}_4) = 100 - 100 = 0$$

$$\Delta G = \Delta G^\circ - 2.303 RT \log K_p$$

$$= 0 - 2.303 * 298 \log 10$$

$$= \mathbf{- 56.0304 \text{ L atm}}$$

(ii) The negative value of  $\Delta G$  indicates that the reaction is spontaneous & will lie in the right direction, (forward).

**Sol 30.**

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + V \Delta P \quad (\because \Delta V = 0)$$

$$\text{or } \Delta U = \Delta H - V \Delta P = -560 - [1(40 - 70) * 0.1]$$

$$= -560 + 3 = -557 \text{ kJ mol}^{-1}$$

So the magnitude is  $557 \text{ kJ mol}^{-1}$ .

$$\because \Delta G^\circ = -2.303RT \log K_p \text{ at equilibrium } \Delta G^\circ = 0$$

$$\therefore -2.303RT \log K_p = 0$$

$$\text{Log } K_p = 0 \text{ or } K_p = 1$$