PROBLEM 6 *Two litre of N_2 at $0°C$ and 5 atm pressure are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming gas to be ideal, calculate work of expansion.*

Solution Since the external pressure is greatly different from the pressure of N_2 and thus, process is irreversible.

$\therefore$
$$W = -P_{ext}(V_2 - V_1)$$
$$W = -1 \times (V_2 - V_1)$$

Given, $\quad V_1 = 2$ litre $\qquad V_2 = ? \qquad\qquad T = 273\,K$

$\qquad\qquad P_1 = 5\,atm \qquad\qquad P_2 = 1\,atm$

$\therefore$
$$P_1 V_1 = P_2 V_2$$

$\therefore$
$$V_2 = \frac{2 \times 5}{1} = 10 \text{ litre}$$

PROBLEM 8 *Calculate the work done in open vessel at 300 K, when 92 g Na reacts with water. Assume ideal gas nature.*

Solution

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$
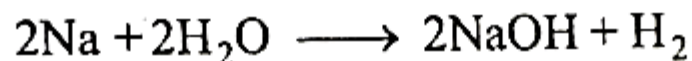
$$\text{Mole of Na} = \frac{92}{23} = 4$$

$$\text{Mole of } H_2 \text{ formed} = \frac{1}{2} \times \text{Mole of Na used}$$

$$= \frac{1}{2} \times 4 = 2$$

Work is done in giving out 2 mole H_2. Thus,

$$W = -P \times V_{H_2} = n_{H_2} RT$$
$$= -2 \times 8.314 \times 300$$
$$= -4988.4 \text{ J}$$

The H_2 liberated pushes the atmospheric gas back and thus, does work in driving back the atmosphere. Note that in case of closed vessel $\Delta V = 0$, $\therefore W = 0$.

PROBLEM 15 *Calculate the maximum work done in expanding 16 g of oxygen at 300 K and occupying a volume of 5 dm³ isothermally until the volume becomes 25 dm³.*

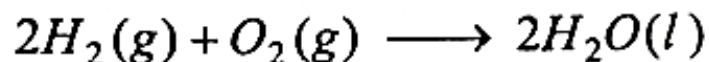**Solution**   Since maximum work and thus, process is reversible

$$n_{O_2} = \frac{w}{m} = \frac{16}{32}, \quad R = 8.314 \, \text{J}, \quad T = 300 \, \text{K}, \quad V_1 = 5 \, \text{dm}^3, \, V_2 = 25 \, \text{dm}^3$$

$$W = -2.303 \, nRT \log_{10} \frac{V_2}{V_1}$$

$$= -2.303 \times \frac{16}{32} \times 8.314 \times 300 \log_{10} \frac{25}{5}$$

$$= -2.01 \times 10^3 \quad \textbf{joule}$$

PROBLEM 44 *Determine the entropy change for the reaction given below;*

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

at 300 *K. If standard entropies of* $H_2(g)$, $O_2(g)$ *and* $H_2O(l)$ *are* 126.6, 201.20 *and* 68.0 $J\ K^{-1}\ mol^{-1}$ *respectively.*

Solution

$$\Delta S_{\text{Reaction}} = \Sigma S_{\text{Product}} - \Sigma S_{\text{Reactants}}$$

$$= 2 \times S_{H_2O} - [2 \times S_{H_2} + S_{O_2}]$$

$$= 2 \times 68 - [2 \times 126.6 + 201.20]$$

$$\Delta S = -318.4 \text{ JK}^{-1}$$

PROBLEM 51 *For a reaction* $M_2O(s) \rightarrow 2M(s) + \frac{1}{2}O_2(g)$;
$\Delta H = 30\ kJ\ mol^{-1}$ *and* $\Delta S = 0.07\ kJ\ K^{-1}\ mol^{-1}$ *at 1 atm. Calculate upto which temperature, the reaction would not be spontaneous?*

(AISSE 1991)

Solution   Given, for the change

$$\Delta H = 30 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta S = 70 \text{ J K}^{-1} \text{ mol}^{-1}$$

For a non-spontaneous reaction

$$\Delta G = + \text{ ve}$$

Since $$\Delta G = \Delta H - T\Delta S$$

∴ $$\Delta H - T\Delta S \text{ should be +ve}$$
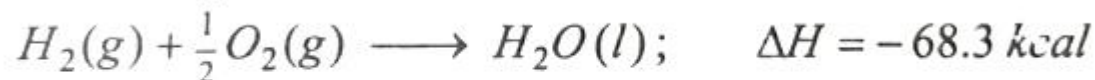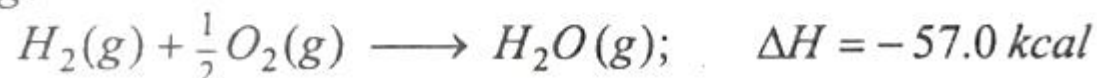
or $$\Delta H > T\Delta S$$

or $$T < \frac{\Delta H}{\Delta S}$$

$$< \frac{30 \times 10^3}{70}$$
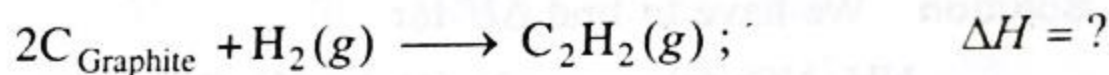
$$T \ < 428.57 \text{ K}$$

PROBLEM 10 *Calculate the enthalpy of vaporisation for water from the following:*

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

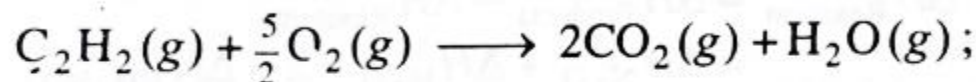$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \qquad \Delta H = -68.3 \ kcal$$

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

PROBLEM 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.*
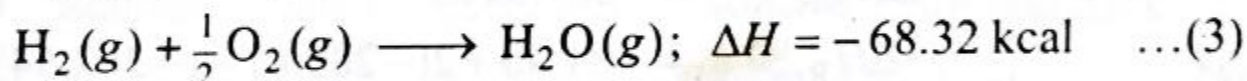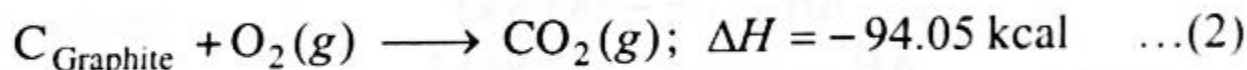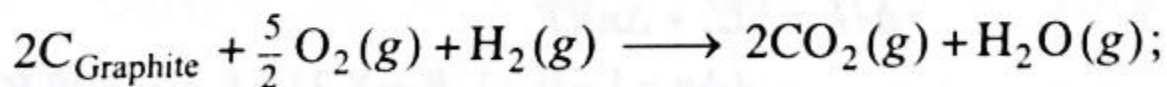
Solution We have to calculate

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

Given,

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

$$\Delta H = -310.62 \text{ kcal} \quad \ldots(1)$$

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

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

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

$$2C_{Graphite} + \frac{5}{2}O_2(g) + H_2(g) \longrightarrow 2CO_2(g) + H_2O(g);$$

$$\Delta H = -256.42 \text{ kcal} \quad \ldots(4)$$

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

$$2C_{Graphite} + H_2(g) \longrightarrow C_2H_2(g); \qquad \Delta H = +54.2 \text{ kcal}$$
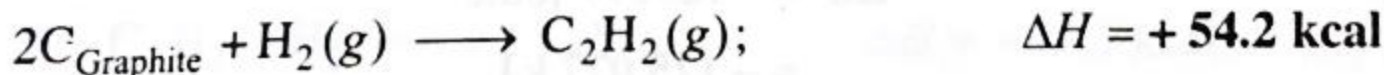
PROBLEM 23 From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of CO_2 (g), $H_2O(l)$ and propene(g) are −393.5, −285.8 and 20.42 kJ mol^{-1} respectively. The enthalpy of isomerisation of cyclopropane to propene is −33.0 kJ mol^{-1}. **(IIT 1998)**

PROBLEM 24 Determine enthalpy change for,

$$C_3H_8(g) + H_2(g) \longrightarrow C_2H_6(g) + CH_4(g)$$
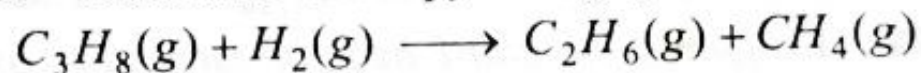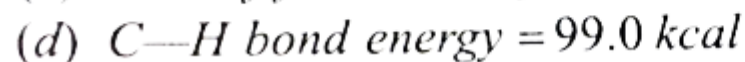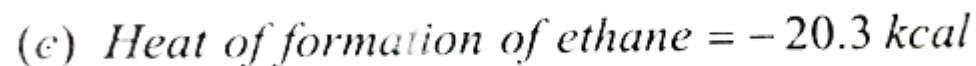
at 25°C using heat of combustion values under standard conditions.

Compounds	$H_2(g)$	$CH_4(g)$	$C_2H_6(g)$	$C_{(Graphite)}$
$\Delta H°$ 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)

PROBLEM 50 *Calculate the C—C bond energy from the following data:*

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

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

(c) *Heat of formation of ethane* $= -20.3 \ kcal$

(d) *C—H bond energy* $= 99.0 \ kcal$

Solution $$2C + 3H_2 \longrightarrow C_2H_6; \quad \Delta H = -20.3 \text{ kcal}$$
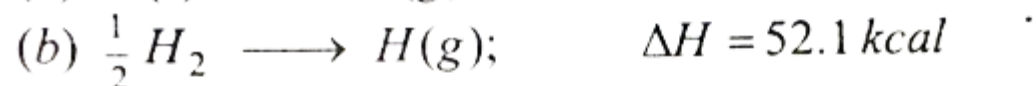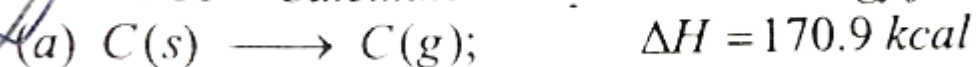
Also, $\quad \Delta H = -[1e_{C-C} + 6e_{C-H}] + [2(C(s) \rightarrow C(g)) + 3e_{H-H}]$

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

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

$\qquad$ C—C bond energy = **80.7 kcal**

PROBLEM 53   *The dissociation energy of CH_4 is 360 kcal/mol and of ethane is 620 kcal/mol. Calculate C—C bond energy.*

Solution Given, $CH_4 \longrightarrow C + 4H$; $\Delta H = 360$ kcal

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

$\therefore$ " " " C—H bond $= \dfrac{360}{4} = 90$ kcal

In $C_2H_6 \longrightarrow 2C + 6H$

Bond energy of $C_2H_6 = 1(C\text{—}C) + 6(C\text{—}H)$

$620 = 1(C\text{—}C) + 6 \times 90$

PROBLEM 56 *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.*

Solution

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

$$N_2H_4 \longrightarrow 2N(g) + 4H(g); \quad \Delta H_2 = y \text{ kcal mol}^{-1}$$
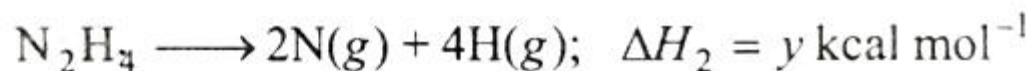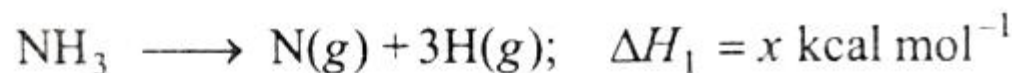
$$\Delta H_1 = 3 \times e_{N-H} = x \qquad \qquad \qquad \dots(1)$$

$$\Delta H_2 = 4 \times e_{N-H} + e_{N-N} = y \qquad \qquad \dots(2)$$

From Eqs. (1) and (2)

$$\therefore \qquad y = 4 \cdot \frac{x}{3} + e_{N-N}$$

$$\therefore \qquad e_{N-N} = y - \frac{4x}{3}$$

$$= \frac{3y - 4x}{3} \text{ kcal mol}^{-1}$$

PROBLEM 59 *Calculate the resonance energy of N_2O from the following data: ΔH_f° of N_2O is $82\ kJ\ mol^{-1}$.*

$N\equiv N$	$946\ kJ\ mol^{-1}$
$N=N$	$418\ kJ\ mol^{-1}$
$O=O$	$498\ kJ\ mol^{-1}$
$N=O$	$607\ kJ\ mol^{-1}$

(Roorkee 1991)

Solution Given, for N_2O

$$N_2 + \frac{1}{2}O_2 \longrightarrow N_2O ; \quad \Delta H_{exp} = 82 \text{ kJ}$$
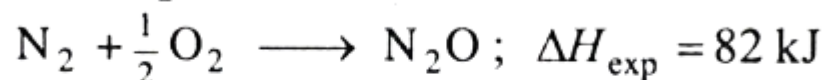
Also from bond energy data, using $N{=}N{=}O$ structure for N_2O

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

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

$$= +170 \text{ kJ}$$

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

$$= 82 - 170$$

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

PROBLEM 62 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 $C = 716.8 \ kJ \ mol^{-1}$

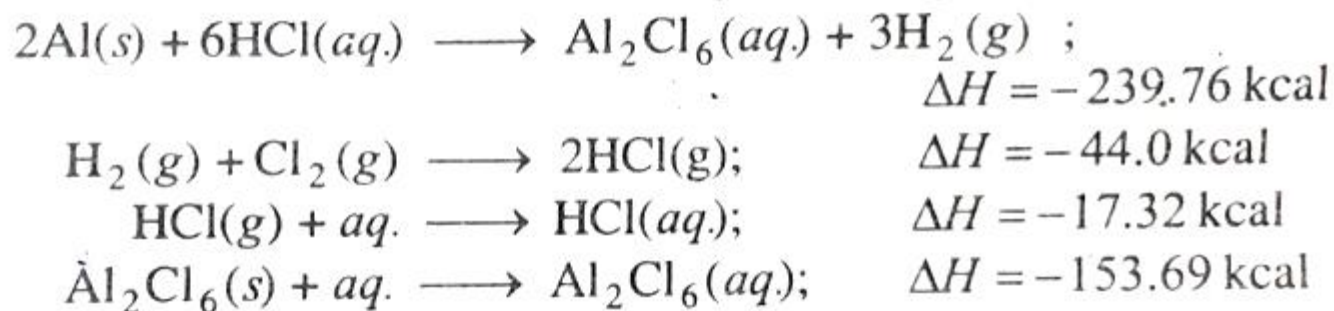(3) Bond energy of C—H, C—C, C=C and H—H are 490, 340, 620 and 436.9 $kJ \ mol^{-1}$ respectively.

Solution

For C_6H_6: $\quad 6C(s) + 3H_2(g) \longrightarrow C_6H_6$; $\quad \Delta H_{exp} = -358.5$ kJ
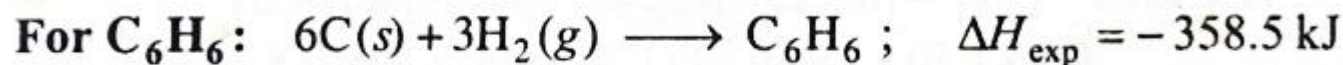
$\therefore \quad \Delta H_{cal} = $ [B.E. data for formation of bonds

$\quad\quad\quad\quad\quad + $ B.E. data for dissociation of bonds]

$\quad\quad\quad = -[3(C\!-\!C) + 3(C\!=\!C) + 6(C\!-\!H)] + [6C_{s \to g} + 3(H\!-\!H)]$

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

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

$\therefore \quad$ Resonance energy $= $ Exp. $\Delta H_f - $ Calculated ΔH_f

$\quad\quad\quad\quad\quad\quad\quad = -358.5 - (-208.5)$

$\quad\quad\quad\quad\quad\quad\quad = \mathbf{-150.0 \ kJ \ mol^{-1}}$

*34. Calculate the heat of formation of anhydrous Al_2Cl_6 from:

$$2Al(s) + 6HCl(aq.) \longrightarrow Al_2Cl_6(aq.) + 3H_2(g) \; ;$$
$$\Delta H = -239.76 \text{ kcal}$$

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g); \qquad \Delta H = -44.0 \text{ kcal}$$
$$HCl(g) + aq. \longrightarrow HCl(aq.); \qquad \Delta H = -17.32 \text{ kcal}$$
$$\dot{A}l_2Cl_6(s) + aq. \longrightarrow Al_2Cl_6(aq.); \qquad \Delta H = -153.69 \text{ kcal}$$

[Ans.   −321.99 kcal]

31. Calculate the heat of formation of sulphuric acid from

$$S(s) + O_2(g) \longrightarrow SO_2(g); \qquad \Delta H = -70.96 \text{ kcal}$$

$$SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g); \qquad \Delta H = -23.49 \text{ kcal}$$

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l); \qquad \Delta H = -31.14 \text{ kcal}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \qquad \Delta H = -68.40 \text{ kcal}$$
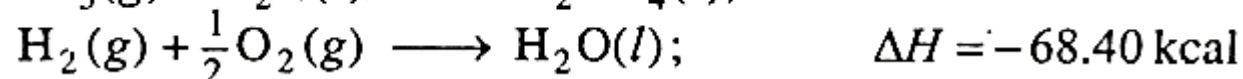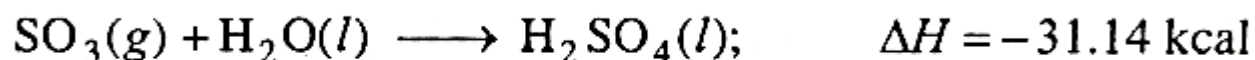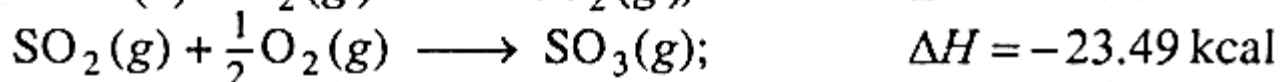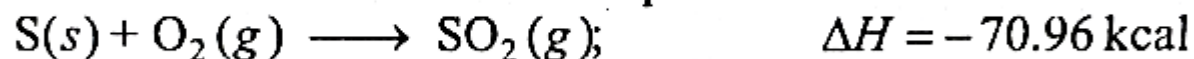
[Ans.   −193.99 kcal]

Q.14 The enthalpy is maximum for

(A) 10 gms of water   (B) 10 gms of ice   (C) 10 gms of steam   (D) Same for all

Q.15 When $50 cm^3$ of 0.2 N H_2SO_4 is mixed with $50 cm^3$ of 1 N KOH, the heat liberated is

(A) 11.45 KJ   (B) 57.3 KJ   (C) 573 J   (D) 573 KJ

Q.16 The heats of neutralisation of HCl with NH_4OH and that of NaOH with CH_3COOH are repectively -51.4 and -50.6 KJ eq^{-1}. The heat of neutralisation of acetic acid with NH_4OH will be

(A) -44.6 KJ eq^{-1} (B) -50.6 KJ eq^{-1} (C) -51.4 KJ eq^{-1} (D) -57.4 KJ eq^{-1}

Q.17 In which of the following combinations of HCl and NaOH, the heat energy liberated is maximum

(A) 10ml of 0.1M HCl+40 ml of 0.1 M NaOH   (B) 30ml of 0.1M HCl+20 ml of 0.1 M NaOH

(C) 25ml of 0.1M HCl+25 ml of 0.1 M NaOH   (D) 35ml of 0.1M HCl+15 ml of 0.1 M NaOH
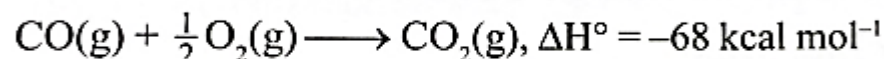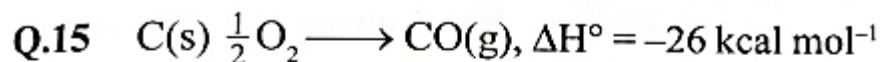
Q.3 Under the same conditions how many mL of 1MKOH and $0.5MH_2SO_4$ solutions, respectively when mixed for a total volume of 100 mL produce the highest rise in temperature:

(A) 67:33   (B) 33:67   (C) 40:60   (D) 50:50

Q.15 $C(s) \frac{1}{2}O_2 \longrightarrow CO(g)$, $\Delta H° = -26$ kcal mol^{-1}

$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$, $\Delta H° = -68$ kcal mol^{-1}

Which is/are correct statement(s)?

(A) heat of formation of CO_2 is -68 kcal mol^{-1}

(B) heat of combustion of $C(s)$ is -26 kcal mol^{-1}

(C) heat of combustion of $CO(g)$ -68 kcal mol^{-1}

(D) heat of formation of $CO(g)$ is -26 kcal mol^{-1}

Q.9   The favourable conditions for a spontaeous reaction are

(A) $T\Delta S > \Delta H$, $\Delta H = +ve$, $\Delta S = +ve$

(B) $T\Delta S > \Delta H$, $\Delta H = +ve$, $\Delta S = -ve$

(C) $T\Delta S = \Delta H$, $\Delta H = +ve$, $\Delta S = -ve$

(D) $T\Delta S = \Delta H$, $\Delta H = +ve$, $\Delta S = +ve$

Q.19 For the reaction at 300 K

$A(g) + B(g) \longrightarrow C(g)$

$\Delta E = -3.0 \text{ kcal}$; $\Delta S = -10.0 \text{ cal/K}$

value of ΔG is

(A) −600 cal   (B) −6600 cal   (C) −6000 cal   (D) None

Q.20 What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure?

(A) 80cal   (B) 540 cal   (C) 620 cal   (D) zero

Ex. 49. *Two moles of a perfect gas undergo the following processes:*

(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 the labels of 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* ΔE, ΔH *and* ΔS *for the overall process?*

(IIT 2002)

Ex. 52. The heat of formation of methane is -17.9 kcal. If the heats of atomisation of carbon and hydrogen are 170.9 and 52.1 kcal per mole, calculate the C—H bond energy in methane.