Fill Ups of Thermodynamics

Q.1. A system is said to be .... if it can neither exchange matter nor energy with the surroundings. (1993 - 1 Mark)

Ans. isolated

Q.2. The heat content of the products is more than that of the reactants in an .... reaction. (1993 - 1 Mark)

Ans. endotherimic

Q.3. Enthalpy is an .... property. (1997 - 1 Mark)

Ans. extensive

Sol. extensive (because its value does not depend on quantity of substance)

True False of Thermodynamics

Q.1. First law of thermodynamics is not adequate in predicting the direction of a process. (1982 - 1 Mark)

Ans. T

Sol. True; It only tells that if a process occurs the heat gained by one end would be exactly equal to heat lost by the other.

It does not predict the direction.

Q.2. Heat capacity of a diatomic gas is higher than that of a monoatomic gas. (1985 - ½ Mark)

Ans. F

Sol. False; $\frac{C_p}{C_v}$ for monoatomic gas = 1.66

$\frac{C_p}{C_v}$ for diatomic gas = 1.40

Subjective questions of Thermodynamics (Part -1)

Q.1. The enthalpy for the following reaction (ΔH°) at 25°C are given below : (1981 - 2 Marks)

(i) $\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \rightarrow OH(g)$ **10.06 kcal**

(ii) $H_2(g) \rightarrow 2H(g)$ **104.18 kcal**

(iii) $O_2(g) \rightarrow 2O(g)$ **118.32 kcal**

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

Ans. Sol. The required reaction in terms of dissociation energy is $OH(g) \rightarrow O(g) + H(g)$; $\Delta H = ?$

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.

$OH(g) \rightarrow \frac{1}{2}H_2(g) + \frac{1}{2}O_2(g);\ \Delta H$: $\Delta H = +10.06$ kcal [Reversing eq (i)]

$\frac{1}{2}H_2(g) \rightarrow H(g)$ $\Delta H = -52.09$ kcal $\left[\frac{1}{2}\text{Eq (ii)}\right]$

$\frac{1}{2}O_2(g) \rightarrow O(g);$ $\Delta H = -59.16$ kcal $\left[\frac{1}{2}\text{Eq (iii)}\right]$

$OH(g) \rightarrow O(g) + H(g);$ $\Delta H = -101.19$ kcal (adding)

Thus one mole of OH(g) needs 101.19 kcal of energy to break into oxygen and hydrogen gaseous atoms. Hence the bond energy of O–H bond is 101.19 kcal.

Q.2. The molar heats of combustion of $C_2H_2(g)$, C(graphite) and $H_2(g)$ are 310.62 kcal, 94.05 kcal and 68.32 kcal, respectively.

Calculate the standard heat of formation of $C_2H_2(g)$. (1983 - 2 Marks)

Ans. Sol. The required equation is : $2C(s) + H_2(g) \rightarrow C_2H_2$; $\Delta H = ?$

Write the thermochemical equations for the given data

(i) $C_2H_{2\,(g)} + \frac{5}{2} O_{2(g)} \rightarrow 2CO_{2(g)} + H_2O_{(\ell)}$;

$\Delta H = -310.62$ kcal

(ii)$C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -94.05$ kcal

(iii) $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(\ell)}$; $\Delta H = -68.32$ kcal

For getting the above required reaction, we will have to

NOTE :

(a) Bring C_2H_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 reactants and thus equation (v) is obtained.

(c) Keep equation (iii) as such.

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

(iv) $2CO_2 + H_2O \rightarrow C_2H_2 + \frac{5}{2} O_2$; $\Delta H = 310.62$ kcal

(v) $2C + 2O_2 \rightarrow 2CO_2$; $\Delta H = -188.10$ kcal

(vi) $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$; $\Delta H = -68.32$ kcal

On adding, $2C + H_2 \rightarrow C_2H_2$; $\Delta H = 54.20$ kcal Hence the standard heat of formation of $C_2H_2(g) = 54.20$ kcal

Q.3. The heat energy, q, absorbed by a gas ΔH, is true at what condition(s). (1984 - 1 Mark)

Ans. Sol. If heat is absorbed at constant pressure, then $q_p = \Delta E - (-P\Delta V)$ or $q_p = E_2 - E_1 - [-P(V_2 - V_1)]$ or $q_p = (E_2 + PV_2) - (E_1 + PV_1) = H_2 - H_1 = \Delta H$

Q.4. Given the following standard heats of reactions :

(i) heat of formation of water = –68.3 kcal;

(ii) heat of combustion of acetylene = –310.6 kcal;

(iii) heat of combustion of eth ylene = –337.2 kcal; Calculate the heat of reaction for the hydrogenation of acetylene at constant volume (25°C). (1984 - 4 Marks)

Ans. Sol. The given data can be written as follows

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

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

$\Delta H = -310.6$ kcal

(iii) $C_2H_4(g) + 3O_2 \rightarrow 2H_2O(l) + 2CO_2(g); \Delta H = -337.2$ kcal

The required thermochemical equation is C2H2(g) + H2(g) → C2H4(g) The required equation can be obtained by subtracting equation (iii) from the sum of equations (i) and (ii), thus ΔH of the required equation can be calculated as below.

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

$= [-68.3 - 310.6] + 337.2$

$= -378.9 + 337.2 = -41.7$ kcal

ΔE, the heat of reaction for the hydrogenation of acetylene at constant volume is given by : $\Delta E = \Delta H - \Delta nRT$

Here Δn = Moles of the gaseous products – Moles of the gaseous reactants

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

Substituting the values of ΔH, Δn, R and T in ΔE

$= \Delta H - \Delta nRT$

$= -41.7 - (-1 \times 2 \times 10^{-3} \times 298)$

$$\left[\begin{array}{l}\because R = 2\text{cal/degree/mole} \\ \quad = 2\times10^{-3}\text{ kcal/deg/mole}\end{array}\right]$$

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

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

Q.5. The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal/mole respectively. Calculate the enthalpy of formation of HCl gas. (1985 - 2 Marks)

Ans. Sol.

Bond	H–H	Cl–Cl	H–Cl
ΔH disso.	104 kcal	58 kcal	103 kcal

Formation of hydrogen chloride can be represented as H – H + Cl – Cl → 2H – Cl

Thus the reaction involves Cleavage of one H – H bond, ΔH = 104 kcal

Cleavage of one Cl – Cl bond, ΔH = 58 kcal

Formation of two H – Cl bonds, ΔH = 2 × – 103 kcal

∴ ΔH of the reaction = (104 + 58) – 2(103)

= 162 – 206 = – 44 kcal

Now since the enthalpy of formation of a compound is the change in heat content accompanied in the formation of one mole of the compound, the enthalpy of formation of

HCl gas = **44/2** = – 22 kcal

Q.6. 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. (1986 - 2 Marks)

Ans. Sol. The required chemical reaction. $2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$; ΔH = x
Note that since 2 moles of ethane are reacting, the ΔH of the reaction will be ½ x.
The thermochemical equations for the given data are written as below.

(i) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -94.1$ kcal

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

(iii) $2C(s) + 3H_2(g) \longrightarrow C_2H_6(g)$; $\Delta H = -21.1$ kcal

We know that $\Delta H = H_{Products} - H_{Reactants}$

$\Delta H = 4\Delta HCO_2 + 6\Delta HH_2O - (2\Delta HC_2H_6 + 7\Delta HO_2)$

$\Delta H = 4 \times -94.1 + 6 \times -68.3 - (2 \times -21.1 + 0)$

$= -376.4 - 409.8 + 42.2 = -744.0$ kcal/2 mole of ethane

$= -372.0$ kcal/mole of ethane

Q.7. An intimate mixture of ferric oxide, Fe_2O_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 follows : (1988 - 2 Marks)

H_f (Al_2O_3) = 399 kcal/mole;

H_f (Fe_2O_3) = 199 kcal/mole;

Density of Fe_2O_3 = 5.2 g/cc;

Density of Al = 2.7 g/cc.

Ans. Sol. $Fe_2O_3 \quad + \quad 2Al \quad \rightarrow \quad 2Fe \quad + \quad Al_2O_3$

$2 \times 56 + 48 = 160 \quad 2 \times 27 = 54$

Heat of reaction = 399 – 199 = 200 kcal

[Al & Fe are in their standard states]

Total weight of reactants = 160 + 54 = 214 g

$\therefore$ Fuel value/gram $= \frac{200}{214} = 0.9346$ kcal/g

Volume of Al $= \frac{54}{2.7} = 20$ cc

Volume of $Fe_2O_3 = \frac{160}{5.2} = 30.77$ cc

Total volume = 20 + 30.77 = 50.77 cc

$\therefore$ Fuel value per cc $= \frac{200}{50.77} = 3.94$ kcal/cc

Q.8. An athlete is given 100 gm of glcuose ($C_6H_{12}O_6$) of energy equivalent to 1560 kJ. He utilizes 50 percent of this gained energy in the event. In order to avoids storage of energy in the body, calculate the weight of water he would need to perspire. The enthalpy of evaporation of water is 44 kJ/ mole. (1989 - 2 Marks)

Ans. Sol. 100 g of glucose = 1560 kJ

Energy utilised in body $= \frac{50}{100} \times 1560 = 780$ kJ

Energy left unutilised in body = 1560 – 780 = 780 kJ

Energy to be given out = 1560 – 780 = 780 kJ

Enthalpy of evaporation of water = 44 kJ/mole = 44 kJ/18 g of water [1 mole H_2O = 18g water]

Hence amount water to be perspired to avoid storage of

energy $= \frac{18}{44} \times 780 = 319.1$ g

Q.9. The standard enthalpy of combustion at 25°C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are –241, –3800 and –3920 kJ/mole respectively. Calculate the heat of hydrogenation of cyclohexene. (1989 - 2 Marks)

Ans. Sol. The required reaction is

$$\underset{\text{Cyclohexene}}{C_6H_{10}(g)} + H_2(g) \rightarrow \underset{\text{Cyclohexane}}{C_6H_{12}(g)}, \quad \Delta H_1 = ? \qquad ...(1)$$

The given facts can be written as :

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O, \quad \Delta H_2 = -241$ kJ/mol ...(2)

$C_6H_{10}(g) + \frac{17}{2}O_2 \rightarrow 6CO_2(g) + 5H_2O; \quad \Delta H_3 = -3800$ kJ/mol ...(3)

$C_6H_{12}(g) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O,$

$\Delta H_4 = -3920$ kJ/mol ...(4)

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

$C_6H_{10}(g) + H_2(g) \rightarrow C_6H_{12}(g) \ \Delta H_1 = (\Delta H_2 + \Delta H_3) - \Delta H_4$

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

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

$= -4041 + 3920 = -121$ kJ/mole

Q.10. Using the data (all values are in kcal mol–1 at 25ºC) given below, calculate the bond energy of C–C and C–H bonds. (1990 - 5 Marks)

ΔH°combustion(ethane) = –372.0

ΔH°combustion(propane) = –530.0

$\Delta H^\circ C(s) \rightarrow C(g) = 172.0$

Bond energy of H–H = 104.0

ΔH°_f of $H_2O(l)$ = –68.0

ΔH°_f of $CO_2(g)$ = –94.0

Ans. Sol. For C_3H_8 : $3C + 4H_2 \rightarrow C_3H_8; \ \Delta H_1 = ?$

For C_2H_6 : $2C + 3H_2 \rightarrow C_2H_6; \ \Delta H_2 = ?$

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

∴ $\Delta H_2 = -[1(C\text{–}C) + 6(C\text{–}H)] + [2C_{s\rightarrow g} + 3(H\text{–}H)]$ ...(2)

Let bond energy of C–C be x kcal and bond energy of C–H be y kcal

∴ By eq. (1) $\Delta H_1 = -(2x + 8y) + [3 \times 172 + 4 \times 104]$ ...(3)

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

Also given $C + O_2 \rightarrow CO_2$; $\Delta H = -94.0$ k cal ...(5)

$H_2 + ½O_2 \rightarrow H_2O$; $\Delta H = -68.0$ kcal ...(6)

$C_2H_6 + (7/2)O_2 \rightarrow 2CO_2 + 3H_2O$; $\Delta H = -372$ k cal ...(7)

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$; $\Delta H = -530$ k cal ...(8)

By inspection method : 2 × (5) + 3 × (6) – (7) gives $2C + 3H_2 \rightarrow C_2H_6$; $\Delta H_2 = -20$ k cal ...(9)

and 3 × (5) + 4 × (6) – (8) gives $3C + 4H_2 \rightarrow$ C3H8; $\Delta H_1 = -20$ k cal ...(10)

∴ By eq. (3), (4), (9) and (10)   x + 6y = 6762x + 8y = 956

∴ x = 82 k cal and y = 99 k cal Bond energy of C–C bond = 82 k cal and Bond energy of C–H bond = 99 k cal

Q.11. A gas mixture of 3.67 litres of ethylene and methane on complete combustion at 25°C produces 6.11 litres of 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 kJ mol^{-1} at 25°C. (1991 - 5 Marks)

Ans. Sol. Combustion of C_2H_4 and CH_4 takes place as follows :

$$\underset{1\ \text{vol.}}{C_2H_4} + 3O_2 \rightarrow \underset{2\ \text{vol.}}{2CO_2} + 2H_2O$$

$$\underset{1\ \text{vol.}}{CH_4} + 2O_2 \rightarrow \underset{1\ \text{vol.}}{CO_2} + 2H_2O$$

Let the vol. of CH_4 in mixture = xl

∴ Vol. of C_2H_4 in the mixture = (3.67 – x)l

Vol. of CO_2 produced by x l of CH_4 = x l and

Vol. of CO_2 produced by (3.67 – x) l of C_2H_4 = 2 (3.67 – x) l

∴ Total vol. of CO_2 produced = x + 2 (3.67 – x)

or 6.11 = x + 2 (3.67 – x) or x = 1.23 l

∴ Vol. of CH_4 in the mixture = 1.23 l

and Vol. of C_2H_4 in the mixture = 3.67 – 1.23 = 2.44 l

Vol. of CH_4 per litre of the mixture = $\frac{1.23}{3.67}$ = 0.335 l

Vol. of C_2H_4 per litre of the mixture = $\frac{2.44}{3.67}$ = 0.665 l

Now we know that volume of 1 mol. of any gas at

25°C (298 K) = $\frac{22.4 \times 298}{273}$ = 24.45 l

[∵ Volume at NTP = 22.4L]

Heat evolved due to combustion of 0.335 l of CH_4

$= -\frac{0.335 \times 891}{24.45} = -12.20\ \text{kJ}$ [given, heat evolved by combustion of 1l = 891 kJ]

Similarly, heat evolved due to combustion of 0.665 l of C_2H_4

$= -\frac{0.665 \times 1423}{24.45} = -38.70\ \text{kJ}$

∴ Total heat evolved = 12.20 + 38.70 = 50.90 kJ

Q.12. Determine the enthalpy change of the reaction.
$C_3H8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$, at 25°, using the given heat of combustion values under standard conditions:

Compound	**$H_2(g)$**	**$CH_4(g)$**	**$C_2H_6(g)$**	**C(graphite)**
ΔH° (kJ/mol)	**– 285.8**	**–890.0**	**–1560.0**	**–393.5**

The standard heat of formation of C3H8(g) is –103.8 kJ/mol. (1992 - 3 Marks)

Ans. Sol. From the given data, we can write :

(i) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O; \Delta H_1 = -285.8$ kJ/mol

(ii) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O; \Delta H_2 = -890$ kJ mol

(iii) $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O; \Delta H_3 = -1560$ kJ/mol

(iv) $C(s) + O_2 \rightarrow CO_2; \Delta H_4 = -393.5$ kJ/mol

(v) $3C(s) + 4H_2 \rightarrow C_3H_8(g); \Delta H_5 = -103.8$ kJ/mol

The required reaction is $C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) +$

$CH_4(g), \Delta H = ?$

It can be obtained by the following calculations.

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

In other words, $\Delta H = 3\Delta H_4 - \Delta H_5 + 5\Delta H_1 - \Delta H_2 - \Delta H_3$

$\therefore \Delta H = 3(-393.5) - (-103.8) + 5(-285.8) + 890 + 1560$

$= -2609.5 + 2553.8 = -55.7$ kJ/mol

Q.13. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and 6x litre/hour of O_2) is to be readjusted for butane, C_4H_{10}. In order to get 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. (1993 - 3 Marks)

Heats of combustion : CH_4 = 809 kJ / mol; C_4H_{10} = 2878 kJ / mol

Ans. Sol. Combustion of CH_4 and C_4H_{10} takes place as follows

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \Delta H = -809 \text{ kJ mol}^{-1}$

$C_4H_{10} + 13/2O_2 \rightarrow 4CO_2 + 5H_2O$, $\Delta H = -2878$ kJ mol^{-1}

In order to get the same calorific output due to C_4H_{10},

$$\text{the rate of supply of butane} = \frac{x \times 809}{2878} = 0.281\,x\ \text{l/hr}$$

$$= 5.481\,x\ \text{l/hr}$$

$$\text{Rate of supply of oxygen} = 0.2803 \times \frac{13}{2} \times 3 = 5.481\,x\ \text{l/hr}$$

Q.14. The polymerisation of ethylene to linear polyethylene is represented by the reaction (1994 - 2 Marks)

$nCH_2 = CH_2 \longrightarrow$ —[CH_2- CH_2 —]$_n$ 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 kJ mol^{-1}, respectively, calculate the enthalpy of polymerisation per mole of ethylene at 298 K.

Ans. Sol. $nCH_2 = CH_2 \rightarrow (CH_2 - CH_2)n$

NOTE : During the polymerisation of ethylene, one mole of ethylene breaks i.e. one C = C double bond breaks and the two CH_2 – groups are linked with C – C single bonds thus forming three single bonds (two single bonds are formed when each CH_2 – group of ethylene links with one CH_2 – group of another ethylene molecule). But in the whole unit of polymer, number of single C–Cbonds formed/mole of ethylene is 2.

Energy released = Energy due to formation of 2 C–C single bonds

= 2 × 331 = 662 kJ/mol of ethylene

Energy absorbed = Energy due to dissociation of 1 C=C double bond

= 590 kJ/mol of ethylene

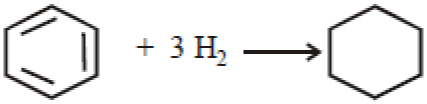
∴Enthalpy of polymerisation/mol of ethylene or

$\Delta H_{\text{polymerisation}} = 590 - 662$ kJ/mol $= -72$ kJ/mole

Subjective questions of Thermodynamics (Part -2)

Q.15. The standard molar enthalpies of formation of cyclohexane(l)and benzene(l) at 25°C are – 156 and + 49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene(l) at 25° C is –119 kJ mol^{-1}. Use these data to estimate the magnitude of the resonance energy of benzene. (1996 - 2 Marks)

Ans. Sol. Standard enthalpy of hydrogenation of cyclohexene (–119kJ mol^{-1}) 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^{-1}



Actual enthalpy of the reaction can be evaluated as follows.

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

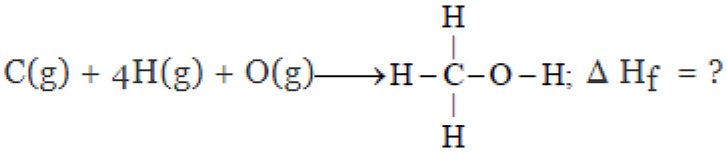
$$-156 - (49\ 0) - 205 \text{ kJ mol}$$

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

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

Q.16. 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 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states; H, 218 kJ/mol; C, 715 kJ/mol; O, 249kJ / mol.
Average bond energies : C – H = 415kJ/mol, C – O = 365 kJ/mol, O – H = 463 kJ/mol (1997 - 5 Marks)

Ans. Sol. The required thermochemical equation is



$$C(g) + 4H(g) + O(g) \longrightarrow H-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-O-H;\ \Delta H_f = ?$$

$$\Delta H_f = \left[\Delta H_{C(s)\rightarrow C(g)} + 2\Delta H_{H-H} + \frac{1}{2}\Delta H_{O=O}\right]$$

$$-\left[3\Delta H_{C-H}+\Delta H_{C-O}+\Delta H_{O-H}+\Delta H_{vap.CH_3OH}\right]$$

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

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

Q.17. Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution. (Ionisation energy for Al = 5137 kJ mol^{-1}; $\Delta H_{hydration}$ for Al3+ = –4665 kJ mol^{-1}; $\Delta H_{hydration}$ for Cl– = – 381 kJ mol^{-1}.) (1997 - 2 Marks)

Ans. Sol. TIPS/Formulae : For ionisation $\Delta H_{ionisation} > \Delta H_{Hydration}$

Total hydration energy of Al^{3+} & 3Cl– ions of $AlCl_3$ ($\Delta H_{hydration}$) = (Hydration energyof Al^{3+} + 3 x Hydration energy of Cl–) = [–4665 + 3 (–381)]kJ $mole^{-1}$ = –5808 kJ $mole^{-1}$ **NOTE :** This amount of energy is more than that required for the ionisation of Al into Al^{3+} (Ionisation energy of Al to Al^{3+}= 5137 kJ mol^{-1}).

Due to this reason, $AlCl_3$ becomes ionic in aqueous solution. In aqueous solution it exists in ionic form as below $AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$ $AlCl_3$ + aq. → $AlCl_3$(aq.); ΔH = ?

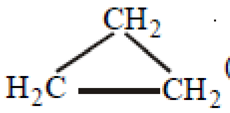
ΔH = Energy released during hydration – Energy used during ionisation

= –4665 – 3 x 381 + 5137 = – 671 kJ/mol

Thus formation of ions will take place.

Q.18. 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}. (1998 - 5 Marks)

Ans. Sol.



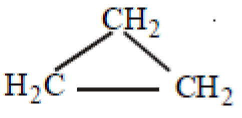
$(g) \rightarrow (g) \rightarrow CH_3CH=CH_2(g);\ \Delta H=-33.0\ \text{kJ}$ ...(i)

$C + O_2 \rightarrow CO_2(g)$; ΔH = – 393.5kJ ...(ii)

$H_2 + 1/2O_2 \rightarrow H_2O(l)$; ΔH = – 285.8 kJ ...(iii)

$3C + 3H_2 \rightarrow CH_3–CH = CH_2(g)$; ΔH = 20.42 kJ ...(iv)

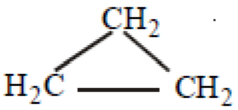
The required reaction is



$+ \frac{9}{2}O_2 \longrightarrow 3CO_2 + 3H_2O;\ \ \Delta H = ?$

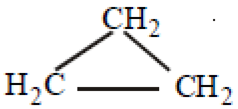
To calculate the value of ΔH follow the following steps. (iv) – (i) yields

$3C + 3H_2 \rightarrow$



; ΔH = 53.42 kJ ...(v)

[3 x (ii) + 3 x (iii)] – (v) yields]



$+ (9/2)O_2 \rightarrow 3CO_2 + 3H_2O;$

ΔH = −2091.32 kJ

Q.19. Estimate the average S–F bond energy in SF_6. The values of standard enthalpy of formation of $SF_6(g)$, S(g)and F(g) are : – 1100, 275 and 80 kJ mol^{-1} respectively. (1999 - 3 Marks)

Ans. Sol. Given $S(s) + 3F_2(g) \rightarrow SF_6(g)$; ΔH = –1100 kJ .....(i)

$S(S) \rightarrow S(g)$; ΔH = 275 kJ .....(ii)

$1/2\ F_2(g) \rightarrow F(g)$; ΔH = 80 kJ .....(iii)

To get $SF_6(g) \rightarrow\ S(g) + 6F(g)$ we can proceed as (ii) + 6 x (iii) - (i)

∴ $SF_6(g) \rightarrow S(g) + 6F(g)$; ΔH= 1855 kJ

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

Q.20. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3.

Calculate the enthalpy change in this process. CV, m for argon is 12.48 JK^{-1} mol^{-1}. (2000 - 4 Marks)

Ans. Sol. TIPS/Formulae : For adiabatic expansion, we have

$$\ell n\frac{T_1}{T_2}=\frac{R}{C_v}\ell n\frac{V_2}{V_1} \quad \text{and} \quad \Delta H=nC_p\Delta T.$$

$$\ell n\frac{300}{T_2}=\frac{8.31}{12.48}\ell n\frac{2.50}{1.25}$$ Solving, we get, T_2 = 188.5 K

No. of moles of argon gas, $n = \frac{PV}{RT} = \frac{1\times1.25}{0.082\times300} = 0.05$

Now we know that $\Delta H = nC_p\Delta T$ = 0.05 x 20.8(188.5 - 300) =-115.41 Joules

[$\because C_p=C_v+R=12.48 + 8.314 = 20.8$]

Q.21. Show that the reaction $CO(g)+\frac{1}{2}O_2(g)\longrightarrow CO_2(g)$ **at 300 K, is spontaneous and exothermic, when the standard entropy change is –0.094 kJ mol^{-1} K^{-1}. The standard Gibbs free energies of formation for CO_2 and CO are –394.4 and –137.2 kJ mol^{-1}, respectively. (2000 - 3 Marks)**

Ans. Sol. For following reaction

$$CO_{(g)}+\frac{1}{2}O_{2(g)}\longrightarrow CO_{2(g)}$$

ΔG° can be calculated as follows :

$$\Delta G° = DG_p° - \Delta G°_R = \left[\Delta G°CO_2-\left(\Delta G°CO+\frac{1}{2}\Delta G°O_2\right)\right]$$

$$=-394.4-(-137.2+\frac{1}{2}\times0) = -257.2 \text{ kJ mol}^{-1}$$

Since, $\Delta G° = \Delta H°-T\Delta S_o$ or $-257.2 = \Delta H - 300(0.094)$

$\therefore \Delta H° = -285.4$ kJ/mol Since,

NOTE : ∴ΔH° is negative, so the reaction is exothermic and since ΔG° is negative so the reaction is spontaneous.

Q.22. Diborane is a potential rocket fuel which under goes combustion according to the reaction. (2000 - 2 Marks) $B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O\ (g)$ From the following data, calculate the enthalpy change for the combustion of diborane.

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

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(\ell)\ \Delta H = -\ 286\ \text{kJ mol}^{-1}$$

$$H_2O\ (l) \longrightarrow H_2O(g)\ \Delta H = 44\ \text{kJ mol}^{-1}$$

$$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g)\ \Delta H = 36\ \text{kJ mol}^{-1}$$

Ans. Sol. The chemical reaction for combustion of diborane is $B_2H_6\ (g) + 3O_2(g) \longrightarrow B_2O_3\ (s) + 3H_2O\ (g)$, $\Delta H = ?$

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

$\Delta H = [\Delta H B_2O_3\ (s) + 3\Delta H H_2O(g)\ ] - \Delta H B_2H_6\ (g)$; ($\because$ $\Delta H_f°$ of $O_2 = 0$)

$\Delta H H_2O(g)$ can be obtained by adding $\Delta H H_2O(l)$ and $\Delta H\ H_2O(g)$, i.e. $-\ 286 + 44 = -\ 242\ \text{kJ mol}^{-1}$

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

$= -2035\ \text{kJ mol}^{-1}$

Q.23. 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 $\Delta G°$ for the following equilibria :

$$B \rightleftharpoons A \quad \Delta G_1^\circ = ? \qquad B \rightleftharpoons C \quad \Delta G_2^\circ = ?$$

From the calculated value of ΔG_1° and ΔG°_2 indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C). (2001 - 10 Marks)

Ans. Sol. TIPS/Formulae :

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

Calculation of ΔG values :

Thus for the equilibrium $B \rightleftharpoons \mathbf{A}$

$\Delta G_1{}^{\circ} = (-2.303 \times 8.314 \times 448) \log \frac{1.3}{95.2}$

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

Similarly for the equilibrium $B \rightleftharpoons C$

$\Delta G^{\circ}{}_2 = (-2.303 \times 8.314 \times 448) \log \frac{3.5}{95.2}$

or $\Delta G^{\circ}{}_2 = 12.312$kJ mole^{-1}

Similarly for equilibrium, $A \rightleftharpoons C$

$\Delta G^{\circ} = -8.314 \times 448 \times 2.303 \times \log_{10} \frac{3.5}{1.3} = = -3.688$ kJ mole^{-1}

Hence, we have that

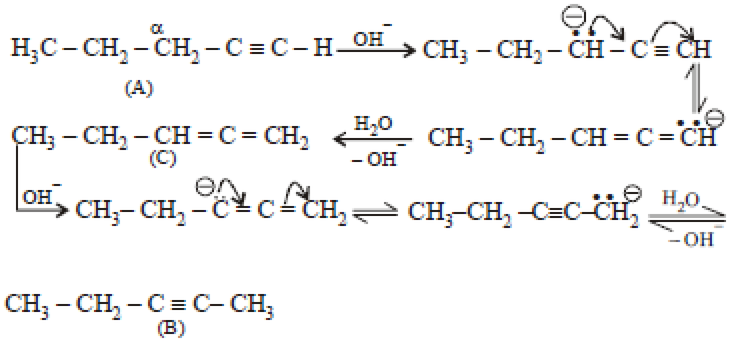
$B \rightleftharpoons A, \ \Delta G_1^{\circ} = +15.992 \text{ kJ mole}^{-1}$

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

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

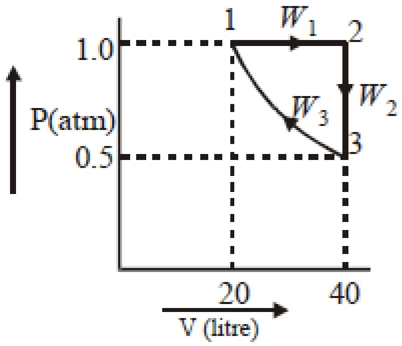
Thus, the correct order of stability, B > C > A

NOTE : Mechanism of isomerisation



Q.24. Two moles of a perfect gas undergo the following processes: (2002 - 5 Marks) (a) a reversible isobaric expansion from (1.0 atm, 20.0L) 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 ΔU, ΔH and ΔS for the overall process?

Ans. Sol.



(ii) Total work (W) = $W_1 + W_2 + W_3$

$$= - P\Delta V + 0 + 2.303RT \log\frac{V_2}{V_1}$$

$$= -1 \times 20 + 2.303 \times 2 \times 0.082 \times 121.95 \log 2$$

$$= -20 + 13.87 = -6.13 \text{ L atm}$$

$$\left[\begin{array}{l} PV = nRT \\ T = \dfrac{PV}{nR} = \dfrac{.5 \times 40}{2 \times 0.082} \end{array}\right] = 121.95 \text{ K}$$

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

$\Delta U = q + W = 0$, so $q = -W = -(-6.13)$ L.atm = 620.7 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 values in a given state of a system.

Q. 25. C_v value of He is always 3R/2 but C_v value of H_2 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. (2003 - 2 Marks)

Ans. Sol. Helium molecule is monoatomic so it has just three degrees of freedom corresponding to the three translational motion at all temperature and hence Cv 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 translational 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.

Q. 26. 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. ΔH and ΔU for the pr ocess. (2004 - 2 Marks)

Ans. Sol. TIPS/Formulae : 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, $q = 0 \therefore \Delta U = w$

$\Delta U = q + W = q - P(V_2 - V_1)$

since $W = -P(V_2 - V_1) = 0 - 100(99 - 100) = 100$ bar mL

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

$= 100 + [(100 \times 99) - (1 \times 100)]$

= 100 + (9900 – 100) = 9900 bar mL

Q. 27. In the following equilibrium $N_2O_4(g)$ $2NO_2(g)$ (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 : ΔG_f^o (N_2O_4) = 100kJ; ΔG_f^o (NO_2) = 50 kJ (i) Find ΔG of the reaction at 298 K. (ii) Find the direction of the reaction

Ans. Sol. (i) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Initially p N2O4 = p NO2= 10

$$\text{Reaction quotient} = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{100}{10} = 10$$

$\Delta G° = 2\ \Delta G°_f\ (NO_2) - \Delta G°_f\ (N_2O_4) = 100 - 100 = 0$

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

$= 0 - 2.303 \times 298 \log 10 = - 56.0304$ L atm.

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

Q.28. For the reaction, $2CO + O_2 \longrightarrow 2CO_2$; ΔH = -560kJ. Two moles of CO and one mole of O_2 are taken in a container of volume 1 L. They completely form two moles of 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 ΔU at 500 K. (1 L atm = 0.1 kJ) (2006 - 6M)

Ans. Sol. $\Delta H = \Delta U + \Delta(PV) = \Delta U + V\ \Delta P$ ($\because \Delta V = 0$)

or $\Delta U = \Delta H - V\ \Delta P = -560 - [1(40 - 70) \times 0.1]$

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

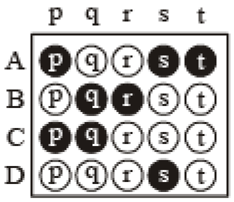
So the magnitude is 557 kJ mol^{-1}.

$\because \Delta G° = - 2.303RT \log K_p$ at equilibrium $\Delta G° = 0$

$\therefore - 2.303RT \log K_p = 0 \Rightarrow \log K_p = 0$ or $K_p = 1$

Match the following of Thermodynamics

DIRECTION : Question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example :



If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

Q.1. Match the transformations in column I with appropriate options in column II (2011)

Column-I	**Column-II**
(A) CO_2 (s) → CO_2 (g)	**(p) phase transition**
(B) $CaCO_3$ (s) → CaO(s)+ CO_2 (g)	**(q) allotropic change**
(C) 2Hg → H_2 (g)	**(r) ΔH is positive**
(D) $P_{(white,\ solid)}$ → $P_{(red,\ solid)}$	**(s) ΔS is positive (t) ΔS is negative**

Ans. Sol. A – p, r, s ; B – r, s ; C – t ; D – p, q, t

(A) CO_2 (s) → CO_2 (g) It is phase transition. The process is endothermic (sublimation). Gas is produced, so entropy increases.

(B) On heating $CaCO_3$ decomposes. So, process is endothermic.
The entropy increases as gaseous product is formed.

(C) 2H• → H2(g) Entropy decreases as number of gaseous particles decreases.

(D) It is phase transition.

White and red P are allotropes.

Red P is more stable than white.

So ΔH is –ve.

DIRECTION : Question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example :

Q.2. Match the thermodynamic processes given under Column-I with the expressions given under Column-II. (JEE Adv. 2015)

Column-I	**Column-II**
(A) Freezing of water at 273 K and 1 atm	**(p) $q = 0$**
(B) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	**(q) $w = 0$**
(C) Mixing of equal volumes of two ideal gases at constant temperature and pressure container	**(r) $\Delta S_{sys} < 0$ in an isolated**
(D) Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K, followed by reversible	**(s) $\Delta U = 0$ cooling to 300 K at 1 atm**

Ans. Sol. A- (r, t); B -(p, q, s); C -(p, q, s); D- (p, q, s, t) (A) → r,t

$H_2O(\ell) \rightleftharpoons H_2O(s)$

It is at equilibrium at 273 K and 1 atm So ΔS_{sys} is negative As it is equilibrium process so $\Delta G = 0$

(B) → p, q, s

Expansion of 1 mole of an ideal gas in vacuum under isolated condition

Hence, $w = 0$ and $q_p = C_p dT$ $(\because dT = 0) \Rightarrow q = 0$

$\Delta U = C_v dT$ $\quad (\because dT = 0) \quad \Delta U = 0$

(C) → p, q, s

Mixing of two ideal gases at constant temperature

Hence, DT = 0

$\therefore q = 0; \; \Delta U = 0$ also $w = 0$

$(\Delta U = q + w)$

(D) → p, q, s, t

Reversible heating and cooling of gas follows same path also initial and final position is same.

$$\text{Hence, } \left.\begin{aligned} q &= 0 \\ w &= 0 \end{aligned}\right\} \text{Path same}$$

$$\left.\begin{aligned} \Delta U &= 0 \\ \Delta G &= 0 \end{aligned}\right\} \text{State function}$$

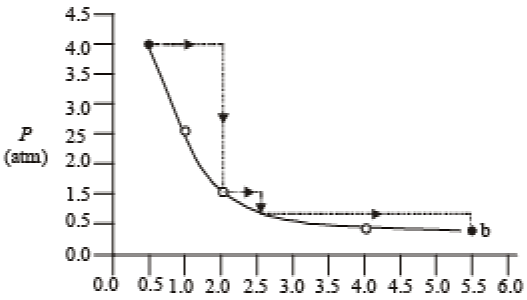
Integer Type ques of Thermodynamics

Q.1. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1}, the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is (2009 - 6M)

Ans. Sol. Energy released by combustion of 3.5 g gas = 2.5 × (298.45 – 298) kJ

Energy released by 1 mole of gas $= \frac{2.5 \times 0.45}{3.5/28} = 9\ \text{kJmol}^{-1}$

Q.2. One mole of an ideal gas is taken from a to b along two paths denoted by the solid and the dashed lines as shown in the graphs below. If the work done along the solid line path w_s and that along the dotted line path is w_d, then the integer closest to the ratio w_d / w_s is : (2010)



Ans. 2

Sol. $w_d = \left(-4 \times \frac{3}{2}\right) + (-1 \times 1) + \left(-\frac{2}{3} \times \frac{5}{2}\right) = -\left(6 + 1 + \frac{5}{3}\right)$

$w_d = -\frac{26}{3}\ \text{L atm}$

$w_S = -\ 2.303\ RT \log \frac{5.5}{1/2} = -2.303\ PV \log 11$

$w_S = -\ 4.606 \times 1.04 = -\ 4.8\ \text{L atm}$

$\frac{w_d}{w_s} = \frac{-\frac{26}{3}}{-4.8} = 1.80 \simeq 2.0$