

Thermodynamics-solutions

SUBJECTIVE PROBLEMS

Sol 1.

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

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.



Thus one mole of OH(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

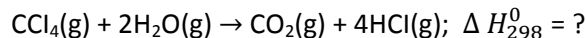
Heat content of the compound

= Heat of formation ΔH , ΔH_{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,

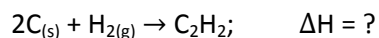
$$\Delta H_{298}^0 = [-94.1 + 4 * - 22.1] - [-25.5 + 2 * - 57.8]$$

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

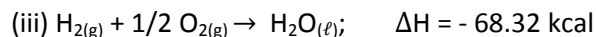
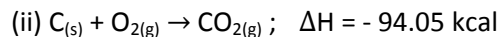
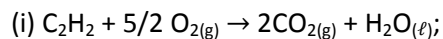
$$= - 182.5 + 141.1 = \mathbf{-41.4 \text{ kcal}}$$

Sol 3.

The required equation is :



Write the thermochemical equations for the given data



For getting the above required reaction, we will have to

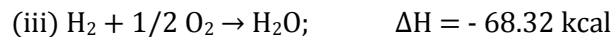
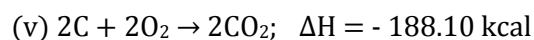
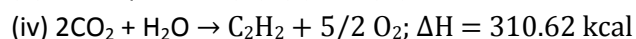
NOTE:

(a) Bring 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 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

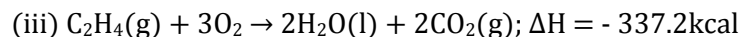
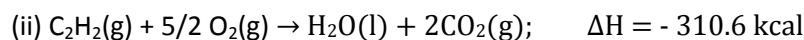
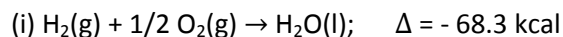
$$q_p = \Delta E - (-P\Delta V)$$

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

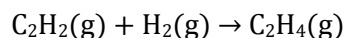
$$\text{or } q_p = (E_2 + PV_2) - (E_1 + PV_1) = H_2 - H_1 = \Delta H$$

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 ΔH of the required equation can be calculated as below.

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

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

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

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

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

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

Substituting the value of ΔH , Δn , R and T in

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

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

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

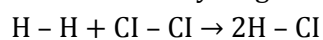
$$= -41.7 + 2 * 10^{-3} * 298$$

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

Sol 6.

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

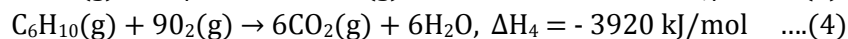
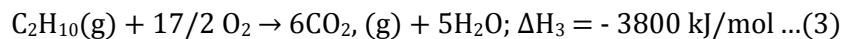
Formation of hydrogen chloride can be represented as



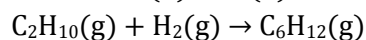
Thus the reaction involves

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).



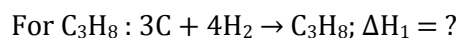
$$\Delta H_1 = (\Delta H_2 + \Delta H_3) - \Delta H_4$$

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

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

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

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

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

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

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

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)

$$x + 6y = 676$$

$$2x + 8y = 956$$

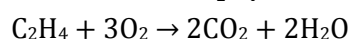
$$\therefore x = 82 \text{ k cal and } y = 99 \text{ k cal}$$

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

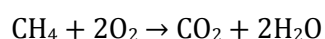
and Bond energy of C - h bond = **99 k cal**

Sol 12.

Combustion of C_2H_4 and CH_4 takes place as follows :



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



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

Let the vol. of CH_4 in mixture = x l

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

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 = $2(3.67 - x) \text{ l}$

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

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

∴ Vol. of CH₄ in the mixture = 1.23 l

and Vol. of C₂H₄ in the mixture = 3.67 - 1.23 = 2.44 l

Vol. of CH₄ per litre of the mixture = 1.23/3.67 = 0.335 l

Vol. of C₂H₄ 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 CH₄ = - 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 C₂H₄

= - 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) H₂ + 1/2 O₂ → H₂O; ΔH₁ = - 285.8 kJ/mol

(ii) CH₄ + 2O₂ → CO₂ + 2H₂O; ΔH₂ = - 890 kJ/mol

(iii) C₂H₆ + 7/2 O₂ → 2CO₂ + 3H₂O; ΔH₃ = - 1560 kJ/mol

(iv) C(s) + O₂ → CO₂; ΔH₄ = - 393.5 kJ/mol

(v) 3C(s) + 4H₂ → C₃H₈(g); ΔH₅ = - 103.8 kJ/mol

The required reaction is C₃H₈(g) + H₂(g) → C₂H₆(g) + CH₄(g), ΔH = ?

It can be obtained by the following calculation.

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

In other words, ΔH = 3ΔH₄ - ΔH₅ + 5ΔH₁ - ΔH₂ - ΔH₃

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

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

Sol 14.

Combustion of CH₄ and C₄H₁₀ takes place as follows

CH₄ + 2O₂ → CO₂ + 2H₂O, ΔH = - 809 kJ mol⁻¹

C₄H₁₀ + 13/2O₂ → 4CO₂ + 5H₂O, ΔH = - 2878 kJ mol⁻¹

In order to get the same calorific output due to C₄H₁₀,

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 CH₄ and C₄H₁₀ can be written as follows :

CH₄ + 2O₂ → CO₂ + 2H₂O; 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 CH₄ gives energy on combustion = 809 kJ

∴ X litre of CH₄ gives energy on combustion = 808(X)/V kJ

∴ 2878 kJ energy is obtained by 1 mole or V litre C₄H₁₀

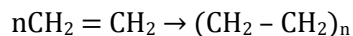
∴ 809(X) * V/V * 2878 litre C₄H₁₀ = 0.281 (X) litre C₄H₁₀

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

∴ C₄H₁₀ + 13/10 O₂ → 4CO₂ + 5H₂O; 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 CH₂ - groups are linked with C - C single bonds thus forming three single bonds (two single bonds are formed when each CH₂ - group of ethylene links with one CH₂ - group of another ethylene molecule). But in the whole unit of polymer, number of single C - C bonds formed/mole of ethylene is 2.

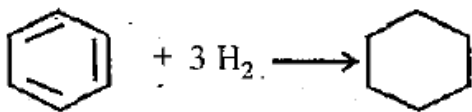
$$\begin{aligned} \text{Energy released} &= \text{Energy due to formation of 2 C - C single bonds} \\ &= 2 * 331 = 662 \text{ kJ/mol of ethylene} \end{aligned}$$

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

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

Sol 16.

Standard enthalpy of hydrogenation of cyclohexen (- 119kJ mol⁻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.

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

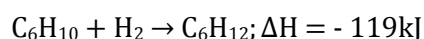
$$= - 156 - (49 + 0)$$

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

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

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

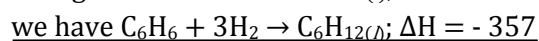
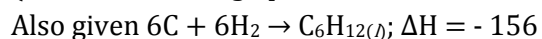
ALTERNATIVE SOLUTION :



(involves breaking up of three double bond and addition of three H₂ molecule)



(involves breaking up of three double bond and addition of three H₂ molecule)



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

Sol 17.

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

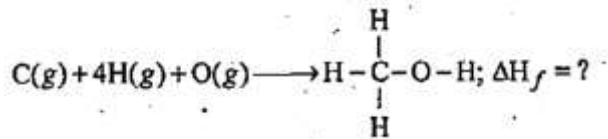
Thus 180 g of glucose (mol. Wt. of glucose) supplies 720 kJ

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

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

Sol 18.

the required thermochemical equation is



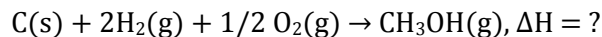
$$\begin{aligned} \Delta H_f &= [\Delta H_{\text{C(s)} \rightarrow \text{C(g)}} + 2\Delta H_{\text{H-H}} + 1/2 \Delta H_{\text{O=O}}] \\ &\quad - [3\Delta H_{\text{C-H}} + \Delta H_{\text{C-O}} + \Delta H_{\text{O-H}} + \Delta H_{\text{vap.CH}_3\text{OH}}] \\ &= [715 + 2 * 436 + 249] - [3 * 415 + 356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

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) $\text{O-H(g)} \rightarrow \text{O(g)} + \text{H(g)}, \Delta H = 463 \text{ kJ mol}^{-1}$

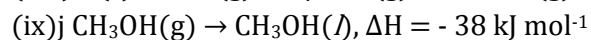
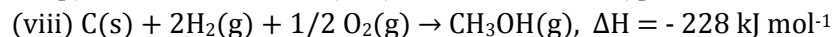
For the calculations of ΔH_f of CH_3OH with the help of above data, following thermochemical equation is written :



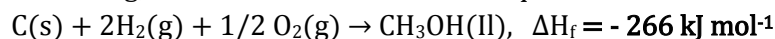
On the basis of bond enthalpy concept ΔH of above reaction is calculated as follows :

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

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



On adding, above two thermochemical equation



Hence standard heat of formation of $\text{CH}_3\text{OH(l)}$ (ΔH_f) = - 266 kJ mol⁻¹

Sol 19.

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

Total hydration energy of Al^{3+} & 3Cl^- ions of AlCl_3 ($\Delta H_{\text{hydration}}$)

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

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

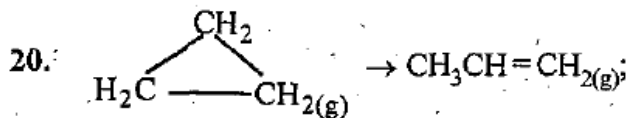
NOTE : This amount of energy is more than that required for the ionization of Al into Al^{3+}

(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



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

Sol 20.



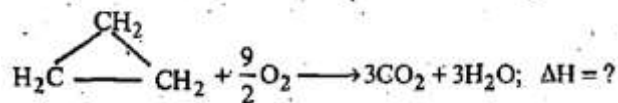
$\Delta H = -33.0 \text{ kJ} \quad \dots(\text{i})$

$\text{C} + \text{O}_2 \rightarrow \text{CO}_{2(\text{g})}; \Delta H = -393.5 \text{ kJ} \quad \dots(\text{ii})$

$\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}_{(\text{l})}; \Delta H = -285.8 \text{ kJ} \quad \dots(\text{iii})$

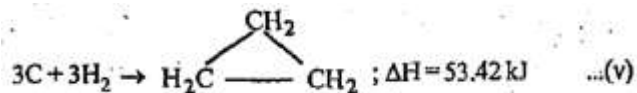
$3\text{C} + 3\text{H}_2 \rightarrow \text{CH}_3 - \text{CH} = \text{CH}_{2(\text{g})}; \Delta H = 20.42 \text{ kJ} \quad \dots(\text{iv})$

The required reaction is

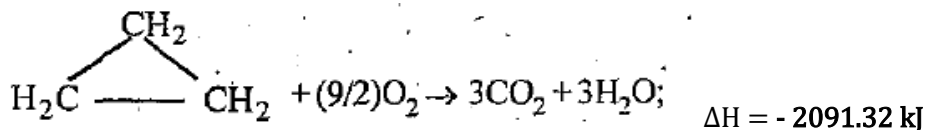


To calculate the value of ΔH follow the following steps.

(iv) - (i) yields



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



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

$\ell n T_1/T_2 = R/C_v \ell n V_2/V_1$

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

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

solving, we get, $T_2 = 188.5$ K

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

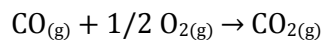
now we know that

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

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

Sol 23.

For following reaction



ΔG° 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,

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

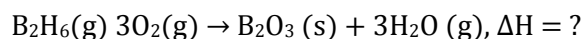
$$\therefore \Delta H^\circ = -285.4 \text{ kJ/mol}$$

Since,

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

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

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

Sol 25.

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

Calculation of ΔG values :

Thus for the equilibrium $B \rightleftharpoons A$

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

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

Similarly for the equilibrium $B \rightleftharpoons C$

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

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

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

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

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

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, $q = 0$ / $\Delta U = w$

$$\Delta U = q + W$$

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

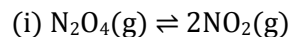
$$= 0 - 100 (99 - 100) = \mathbf{100 \text{ bar mL}}$$

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

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

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

Sol 29.



Initially $P_{N_2O_4} = P_{NO_2} = 10$

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

$$\Delta G^\circ = 2\Delta G_f^\circ(NO_2) - \Delta G_f^\circ(N_2O_4) = 100 - 100 = 0$$

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

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

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

(ii) The negative value of ΔG 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 kJ mol^{-1} .

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

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

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