

Thermodynamics-solutions

SUBJECTIVE PROBLEMS

Sol 1.

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. $OH(g) \rightarrow 1/2 H_2(g) + 1/2 O_2(g)$; $\Delta H = + 10.06 \text{ kcal [Reversing eq (i)]}$ $1/2 H_2(g) \rightarrow H(g)$; $\Delta H = -52.09 \text{ kcal [} 1/2 \text{ Eq (ii)]}$ $1/2 O_2(g) \rightarrow O(g)$; $\Delta H = -59.16 \text{ kcal [} 1/2 \text{ Eq (iii)]}$

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

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

<u>Sol 2.</u>

Since we know that Heat content of the compound = Heat of formation ΔH , ΔH^0_{298} . = Total heat contents of the products - Total heat contents of the reactants Writing the given chemical reaction, $CCI_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4HCI(g); \Delta H^0_{298} = ?$ $\Delta H_{298}^{0} = [\Delta H_{CO_2} + 4 * \Delta H_{HCI}] - [\Delta H_{CCI_4} + 2 * \Delta H_{H_2O}]$ Given, ΔH_{CCI_4} = - 25.5 kcal/mole ΔH_{H_2O} = - 57.8 kcal/mole $\Delta H_{HCI} = -22.1 \text{ kcal/mole}$ ΔH_{CO_2} = - 94.1 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 = -41.4 kcal

<u>Sol 3.</u>

The required equation is : $2C_{(s)} + H_{2(g)} \rightarrow C_2H_2;$ $\Delta H = ?$ Write the thermochemical equations for the given data (i) $C_2H_2 + 5/2 O_{2(g)} \rightarrow 2CO_{2(g)} + H_2O_{(\ell)};$ (ii) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)};$ $\Delta H = -94.05$ kcal (iii) $H_{2(g)} + 1/2 O_{2(g)} \rightarrow H_2O_{(\ell)};$ $\Delta H = -68.32$ 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 reactant and thus equation (v) is obtained.

(c) Keep equation (iii) as such.

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

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

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

(iii) $H_2 + 1/2 O_2 \rightarrow H_2O$; $\Delta H = -68.32$ 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

<u>Sol 4.</u>

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

<u>Sol 5.</u>

The given data can be written as follows

(i) $H_2(g) + 1/2 O_2(g) \rightarrow H_2O(I); \quad \Delta = -68.3 \text{ kcal}$

(ii) $C_2H_2(g) + 5/2 O_2(g) \rightarrow H_2O(l) + 2CO_2(g); \quad \Delta H = -310.6 \text{ kcal}$

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

The required thermochemical equation is

 $C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$

The required equation can be obtained by subtracting equation (iii) from the sum of equations (i) and (ii), thus Δ 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 kcal

 $\Delta E = \Delta H - \Delta n R T$

Here $\Delta n = Moles$ of the gaseous products – Moles of the gaseous reactants

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

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

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

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

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

= - 41.7 + 2 * 10⁻³ * 298 = - 41.7 + 0.596 = **41.104 kcal**

<u>Sol 6.</u>

BondH-HCI-CIH-CI ΔH disso.104 kcal58 kcal103 kcalFormation of hydrogen chloride can be represented as $H-H+CI-CI \rightarrow 2H-CI$ Thus the reaction involvesCleavage of one H - H bond, $\Delta H = 104$ kcalCleavage of one CI - CI bond, $\Delta H = 58$ kcal



Formation of two H – CI bonds, $\Delta H = 2 * - 103$ kcal $\therefore \Delta H$ 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 HCI gas = -44/2 = -22 kcal

<u>Sol 7.</u>

The required chemical reaction.

 $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O; \Delta H = x$

Note that since 2 moles of ethane are reacting, the Δ H of the reaction will be $\frac{1}{2}$ x. The thermochemical equations for the given data are written as below.

(i) $C(s) + O_2(g) \rightarrow Co_2(g)$; $\Delta H = -94.1$ kcal (ii) $H_2(g) \frac{1}{2}O_2(g) \rightarrow H_2O(g)$; $\Delta H = -68.3$ kcal (iii) $2C(s) + 3H_2(g) \rightarrow C_2H_6(g)$; $\Delta H = -21.1$ kcal We know that $\Delta H = H_{Products} - H_{Reactants}$ $\Delta H = 4\Delta H_{CO_2} + 6\Delta H_{H_2O} - (2\Delta H_{C_2H_6} + 7\Delta H_{O_2})$ $\Delta H = 4^* - 94.1 + 6^* - 68.3 - (2^* - 21.1 + 0)$ = -376.4 - 409.8 + 42.2 = -744.0 kcal/2 mole of ethane = -372.0 kcal/mole of ethane

<u>Sol 8.</u>

Fe₂O₃ + 2AI → 2Fe + AI₂O₃ 2 * 56 + 48 = 160 2 * 27 = 54 Heat of reaction = 399 - 199 = 200 kcal [Al & Fe are in their standard states] Total weight of reactans = 160 + 54 = 214 g \therefore Fuel value/gram = 200/214 = 0.9346 kcal/g Volume of Al = 54/2.7 = 20 cc Volume of Fe₂O₃ = 160/5.2 = 30.77 cc Total volume = 20 + 30.77 = 50.77 cc \therefore Fuel value per cc = 200/50.77 = **3.94 kcal/cc Sol O**

<u>Sol 9.</u>

100 g of glucose = 1560 kJ Energy utilized in body = 50/100 * 1560 = 780 kJEnergy left unutilized in body = 1560 - 780 = 780 kJEnergy to be given out = 1560 - 780 = 780 kJEnthalpy of evaporation of water = 44 kJ/mole = 44 kJ/18 gOf water [1 mole H₂O = 18g water] Hence amount water to be perspired to avoid storage of energy = 18/44 * 780 = 319.1 g

<u>Sol 10.</u>

The required reaction is $C_6H_{10}(g) + H_2(g) \rightarrow C_2H_{12},(g), \Delta H_1 = ?$(1)CyclohexeneCyclohexaneThe given facts can be written as : $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O,$ $\Delta H_2 = -241 \text{ kJ/mol}$...(2)



 $\begin{array}{l} C_{2}H_{10}(g) + 17/2 \ O_{2} \rightarrow 6CO_{2}, (g) + 5H_{2}O; \\ \Delta H_{3} = - 3800 \ \text{kJ/mol} \ ...(3) \\ C_{6}H_{10}(g) + 9O_{2}(g) \rightarrow 6CO_{2}(g) + 6H_{2}O, \\ \Delta H_{4} = - 3920 \ \text{kJ/mol} \(4) \\ \text{The required reaction (1) can be obtained by adding equations (2) and (3) and subtracing (4) from the sum of (2) and (3). \\ C_{2}H_{10}(g) + H_{2}(g) \rightarrow C_{6}H_{12}(g) \\ \Delta H_{1} = (\Delta H_{2} + \Delta H_{3}) - \Delta H_{4} \\ = [-241 + (-3800)] - (-3920) \\ = (-241 - 3800) - (-3920) \\ = -4041 + 3920 = -121 \ \text{kJ/mole} \\ \hline \begin{array}{c} \text{Sol 11.} \\ \text{For } C_{3}H_{8} : 3C + 4H_{2} \rightarrow C_{3}H_{8}; \\ \Delta H_{1} = ? \\ \text{For } C_{2}H_{6} : 2C + 3H_{2} \rightarrow C_{2}H; \\ \Delta H_{2} = ? \end{array}$

 $\therefore \Delta H_1 = -[2 (C - C) + 8(C - H)] + [3C_{s \to g} + 4(H - H)]$(1) $\therefore \Delta H_2 = -[1 (C - C) + 6(C - H)] + [2C_{s \to g} + 3(H - H)]$(2) Let bond energy of C – C be x kcal and bond energy of C – H by y kcal : By eq. (1) $\Delta H_1 = -(2x + 8y) + [3 * 172 + 4 * 104]$(3) $\Delta H_2 = -(x + 6y) + [2 * 172 + 3 * 104]$(4) Also given $C + O_2 \rightarrow CO_2$; $\Delta H = -94.0$ k cal(5) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O; \Delta H = -68.0 \text{ k cal}$(6) $C_2H_6 + (7/2)O_2 \rightarrow 2CO_2 + 3H_2O; \Delta H = -372 \text{ k cal}$(7) $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O; \Delta H = -530 \text{ k cal} \dots (8)$ 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 $3C + 4H_2 \rightarrow C_3H_8$; $\Delta H_1 = -20$ k cal ...(10) ∴ By eq. (3), (4), (9) and (10) X + 6y = 6762x + 8y = 956 \therefore 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

<u>Sol 12.</u>

Combustion of C₂H₄ and Ch₄ takes place as follows : C₂H₄ + 3O₂ \rightarrow 2CO₂ + 2H₂O 1 vol 2 vol. CH₄ + 2O₂ \rightarrow CO₂ + 2H₂O 1 vol 1 vol Let the vol. of CH₄ in mixture = x *I* \therefore Vol. of C₂H₄ in the mixture = (3.67 - x) *I* Vol. of CO₂ produced by x *I* of CH₄ = x *I* and Vol. of CO₂ produced by (3.67 - x) *I* of C₂H₄ = 2(3.67 - x) *I* \therefore Total vol. of CO₂ produced = x + 2 (3.67 - x) Or 6.11 = x + 2(3.67 - x) or x = 1.23 *I*



 \therefore Vol. of CH₄ in the mixture = 1.23 *I* and Vol. of C_2H_4 in the mixture = 3.67 - 1.23 = 2.44 *I* Vol. of CH₄ per litre of the mixture = 1.23/3.67 = 0.335 IVol. of C_2H_4 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) = $22.4 \times 298/273 = 24.45$ / [: Volume at NTP = 22.4L] Heat evolved due to combustion of 0.335 /of $CH_4 = -0.335 * 891/24.45 = -12.20 \text{ k}$ [given, heat evolved by combustion of 1 I = 891 kmSimilarly, heat evolved due to combustion due to combustion of 0.665 / of C₂H₄ = -0.665 * 1423/24.45 = -38.70 kJ∴ Total heat evolved = 12.20 + 338.70 = 50.90 kI

Sol 13.

From the given data, we can write : (i) $H_2 + 1/2 O_2 \rightarrow H_2O; \Delta H_1 = -285.8 \text{ kJ/mol}$ (ii) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$; $\Delta H_2 = -890$ kJ mol (iii) $C_2H_6 + 7/2 O_2 \rightarrow 2CO_2 + 3H_2O; \Delta H_3 = -1560 \text{ kJ/mol}$ (iv) $C(s) + O_2 \rightarrow CO_2$; $\Delta H_4 = -393.5 \text{ kJ/mol}$ (v) $3C(s) + 4H_2 \rightarrow C_3H_8(g); \Delta H_5 = -103.8 \text{ kJ/mol}$ 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 calculation. 3 * (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

Sol 14.

Combustion of CH_4 and C_4H_{10} takes place as follows $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_1 \Delta H = -809 \text{ kJ mol}^{-1}$ $C_4H_{10} + 13/2O_2 \rightarrow 4CO_2 + 5H_{2=0}$, $\Delta H = -2878 \text{ kJ mol}^{-1}$ In order to get the same calorific output due to C_4H_{10} , The rate of supply of butane = x *809/2878 = 0.281 x//hrRate of supply of oxygen = 0.2803 x * 13/2 * 3 = 5.481 x//hr

ALTERNATIVESOLUTIONS:

The reaction of combustion of CH₄ and C₄H₁₀ can be written as follows :

 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O; \Delta H = -809$

Initial volume (in litre)

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

 \therefore V litre of 1 mole CH₄ gives energy on combustion = 809 kJ

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

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

 \therefore 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



Volume of O_2 required = 3 * volume of O_2 for combustion of C_4H_{10} = 3 * 13/2 * volume of C_4H_{10} = 3 * 13/2 * 0.281 (X) litre O_2

Sol 15.

 $nCH_2 = CH_2 \rightarrow (CH_2 - CH_2)_n$

NOTE : During the polymerization 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 – C bonds 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 polymerization/mol of ethylene or $\Delta H_{polymerisation} = 590 - 662 \text{ kJ/mol} = -72 \text{ kJ/mol}$

<u>Sol 16.</u>

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

$$+ 3 H_2 \longrightarrow$$

Actual enthalpy of the reaction can be evaluated as follows.

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

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

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

= -357 - (-205) = -152kJ mol⁻¹

ALTERNATIVESOLUTION :

 $C_6H_{10} + H_2 \rightarrow C_6H_{12}; \Delta H = -119 kJ$

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

 \div C_6H_6 + 3H_2 \rightarrow C_6H_{12} ; ΔH = 3 * (-119) = - 357 kJ

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

Also given $6C + 6H_2 \rightarrow C_6H_{12(l)}$; $\Delta H = -156$

we have $C_6H_6 + 3H_2 \rightarrow C_6H_{12(\hbar)}$; $\Delta H = -357$

 $6C + 3H_2 \rightarrow C_6H_6; \Delta H = +201 \text{ kJ}$

Therefore, resonance energy = 49 - 201 = -152 kJ

<u>Sol 17.</u>

Energy available for muscular work by 1 mole of glucose = 2880 * 25/100 = 720 kJ mol⁻¹ Thus 180 g of glucose (mol. Wt. of glucose) supplies 720 kJ 120 g of glucose will supply = 720/180 * 120 = 480 kJ 100 kJ is needed to walk 1 km, Hence, 480 kJ is needed to walk 1/100 * 480 = 4.8 km



<u>Sol 18.</u>

the required thermochemical equation is

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

 $\begin{aligned} \Delta H_{f} &= [\Delta H_{C(s) \to C(g)} + 2\Delta H_{H-H} + 1/2 \ \Delta H_{0=0}] \\ &- [3\Delta H_{C-H} + \Delta H_{C-0} + \Delta H_{0-H} + \Delta H_{vap.CH_{3}OH}] \\ &= [715 + 2 * 436 + 249] - [3 * 415 + 356 + 463 + 38] = - 266 \text{ kJ mol}^{-1} \\ &\text{ALTERNATIVESOLUTION :} \end{aligned}$

The diven data is as follows :

(i) $CH_3OH(\Lambda) \rightarrow Ch_3OH(g), \Delta H = 38 \text{ kJ mol}^{-1}$

(ii) $1/2 H_2(g) \rightarrow H(g)$, $\Delta H = 218 \text{ kJ mol}^{-1}$

(iii) C(graphite) \rightarrow C(g), Δ H = 715 kJ mol⁻¹

(iv) $1/2 O_2(g) \rightarrow O(g)$, $\Delta H = 249 \text{ kJ mol}^{-1}$

(v) C – H(g) \rightarrow C(g) + H(g), Δ H = 415 kJ mol⁻¹

(vi) C – O(g) \rightarrow C(g) + O(g), Δ H = 356 kJ mol⁻¹

(vii) 0 – H(g)
$$\rightarrow$$
 0(g) + H(g), Δ H = 463 kJ mol⁻¹

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

 $C(s) + 2H_2(g) + 1/2 O_2(g) \rightarrow CH_3OH(g), \Delta H = ?$

On the basis of bond enthalpy concept ΔH of above reaction is calculated as follows : $\Delta H = - [(\text{sum of bond enthalpies of all bonds of products - Sum of bonds enthalpies of all bonds of reactants.)]$

$$\Delta H = - \begin{bmatrix} (3 * E_{C-H} + E_{C-O} + E_{O-H}) \\ - \left(E_C(g) \operatorname{toC}(g) E + 4 * E_{\frac{1}{2}(H-H)(g)} + E_{\frac{1}{2}O_2(g)} \right) \end{bmatrix}$$

= - [(3 * 415 + 356 + 463) - (715 + 4 218 + 249)] kJ mol⁻¹ = - 228 kJ mol⁻¹(viii) C(s) + 2H₂(g) + 1/2 O₂(g) → CH₃OH(g), ΔH = - 228 kJ mol⁻¹(ix)j CH₃OH(g) → CH₃OH(J), ΔH = - 38 kJ mol⁻¹On adding, above two thermochemical equationC(s) + 2H₂(g) + 1/2 O₂(g) → CH₃OH(II), ΔH_f = - 266 kJ mol⁻¹

Hence standard heat of formation of CH₃OH (I) (Δ H_f) = - 226 kJ mol⁻¹

<u>Sol 19.</u>

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

Total hydration energy of AI³⁺ & 3CI⁻ ions of AICI₃ ($\Delta H_{hydration}$)

= (Hydration energy of AI^{3+} + 3 * Hydration energy of CI^{-})

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

NOTE : This amount of energy is more than that required for the ionization of AI into AI³⁺

(Ionisation energy of AI to $AI^{3+} = 5137 \text{ kJ mol}^{-1}$). Due to this reason, AICI₃ becomes ionic in aqueous solution. In aqueous solution it exists in ionic form as below $AICI_3 + 6H_2O \rightarrow [AI(H_2O)_6]^{3+} + 3CI^{-1}$



AICI₃ + aq. \rightarrow AICI_{3(aq.)}; Δ H = / Δ H = Energy released during hydration - Energy used during ionization = - 4665 - 3 * 381 + 5137 = - 671 kJ/mol Thus formation of ions will take place.

Sol 20.

20.
$$\begin{array}{c} CH_2 \\ H_2C & -CH_{2(g)} \end{array} \rightarrow CH_3CH = CH_{2(g)}; \end{array}$$

 $\begin{array}{lll} \Delta H = & -33.0 \ \text{kJ} & \dots(i) \\ C + O_2 \rightarrow CO_2(\text{g}); \ \Delta H = & -393.5 \ \text{kJ} & \dots(ii) \\ H_2 + & 1/2O_2 \rightarrow H_2O_{(l)}; \ \Delta H = & -285.8 \ \text{kJ} & \dots(iii) \\ 3C + & 3H_2 \rightarrow CH_3 \rightarrow CH_3 - CH = CH_{2(\text{g})}; \ \Delta H = & 20.42 \ \text{kJ} & \dots(iv) \\ \text{The required reaction is} \end{array}$

$$H_2C \xrightarrow{CH_2} CH_2 + \frac{9}{2}O_2 \xrightarrow{3CO_2 + 3H_2O;} \Delta H = ?$$

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

$$3C+3H_2 \rightarrow H_2C \xrightarrow{CH_2} CH_2; \Delta H = 53.42 \text{ kJ} \dots (v)$$

$$[3*(ii)+3*(iii)] - (v) \text{ yields}]$$

$$H_2C \longrightarrow CH_2 + (9/2)O_2 \rightarrow 3CO_2 + 3H_2O;$$

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

<u>Sol 21.</u>

Given $S_{(s)} + 3F_{2(g)} \rightarrow SF_{6(g)}$; $\Delta H = -1100 \text{ kJ}$ (i)

 $S_{(s)} \rightarrow S_{(g)}; \Delta H = 275 \text{ kJ} \qquad ...(ii)$

 $1/2 \ F_{2(g)} \to F_{(g)}; \Delta H = 80 \ kJ$...(iii) To get $SF_{6(g)} \to S_{(g)} + 6F_{(g)}$ we can proceed as (ii) + 6 * (iii) - (i) $\therefore SF_{6(g)} \to S_{(g)} + 6F_{(g)}; \Delta H = 1855 \ kJ$ Thus average bond energy for S-F bond = 1855/6 = 309.16 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, $T_2 = 188.5 \text{ K}$ No. of moles of argon gas, N = PV/RT = 1 * 1.25/0.082 * 300 = 0.05now we know that $\Delta H = nC_P\Delta T = 0.05 * 20.8(188.5 - 300) = -$ **115.41 joules** [:: $C_P = C_v + R = 12.48 + 3.314 = 20.8$]

<u>Sol 23.</u>

For following reaction $CO_{(g)} + 1/2 O_{2(g)} \rightarrow CO_{2(g)}$ ΔG° can be calculated as follows : $\Delta G^{\circ} = \Delta G_{p}^{\circ} - \Delta G^{\circ}_{R} = [\Delta G^{\circ}CO_{2} - (\Delta G^{\circ}CO + 1/2 \Delta G^{\circ}O_{2})]$ $= -394.4 - (-137.2 + 1/2 * 0) = -257.2 \text{ kJ mol}^{-1}$ 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 possible, so the reaction is every harming and a

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

<u>Sol 24.</u>

The chemical reaction for combustion of diborane is $B_2H_6(g) \ 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g), \Delta H = ?$ For this the enthalpy change can be calculated in the following way. $\Delta H = [\Delta H_{B_2O_3(s)} + 3\Delta H_{H_2O(g)}] - \Delta H_{B_2O_6(g)};$ $(::\Delta H_f^{\circ} \text{ of } O_2 = 0)$ $\Delta H_{H_2O(g)}$ can be obtained by adding $3\Delta H_{H_2O(\ell)}$ and $\Delta H_{H_2O(g)}$, 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.**

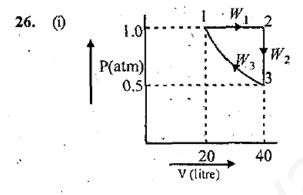
 $\Delta G^{\circ} = -2.303 \text{RT} \log [\text{Product}]/[\text{Reactant}]$ Calculation of ΔG values : Thus for the equilibrium $B \rightleftharpoons A$ $\Delta G_1^{\circ} = (-2.303 * 8.314 * 448) \log 1.3/95.2$ Or $\Delta G_1^{\circ} = \mathbf{15.992} \text{ kJ mole}^{-1}$ Similarly for the equilibrium $B \rightleftharpoons C$ $\Delta G_2^{\circ} = (-2.303 * 8.314 * 448) \log 3.5/95.2$ 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 $B \rightleftharpoons A$, $\Delta G_1^{\circ} = + 15.992 \text{ kJ mole}^{-1}$ $B \rightleftharpoons C$, $\Delta G_2^{\circ} = + 12.312 \text{ kJ mole}^{-1}$



B \rightleftharpoons C, ΔG_3° = - 3.688 kJ mole⁻¹ Thus, the correct order of stability, **B** > C > A **NOTE :** Mechanism of isomerisation

$$\begin{array}{c} H_{3}C - CH_{2} - CH_{2} - C \equiv C - H \xrightarrow{OH} CH_{3} - CH_{2} - CH_{2} - CH \xrightarrow{O} CH \xrightarrow{O} CH_{3} - CH_{2} - CH \xrightarrow{O} CH \xrightarrow{O}$$

Sol 26.



(ii) Total work (W) = $W_1 + W_2 + W_{3=} = -P\Delta V + 0 + 2.303nRT \log V_2/V_1$ = -1 * 20 + 2.303 * 2 * 0.082 * 121.95 log 2 = -20 + 13.87 = -6.13 L atm

$$\begin{bmatrix} PV = nRT \\ T = \frac{PV}{nR} = \frac{5*40}{2*0.082} \end{bmatrix} = 121.95k$$

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 value in a given state of a system.

<u>Sol 27.</u>

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.

<u>Sol 28.</u>

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, $q = 0 / \Delta U = w$ $\Delta U = q + W$ $= q - P(V_2 - V_1)$ 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 * 99) - (1 * 100)]= 100 + (9900 - 100) = 9900 bar mL

<u>Sol 29.</u>

(i) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ Initially $P_{N_2O_4} = P_{NO_2} = 10$ Reaction quotient $= \frac{(P_{NO_2})^2}{P_{N_2O_4}} = 100/10 = 10$ $\Delta G^\circ = 2\Delta G^0_{f(NO_2)} - \Delta G^\circ_{f(N_2O_4)} = 100 - 100 = 0$ $\Delta G = \Delta G^\circ - 2.303 \text{ RT log Kp}$ $= 0 - 2.303 * 298 \log 10$

= - 56.0304 L atm

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

<u>Sol 30.</u>

$$\begin{split} \Delta H &= \Delta U + \Delta (PV) = \Delta U + V \, \Delta P \qquad (\because \Delta V = 0) \\ \text{or } \Delta U &= \Delta H - V \, \Delta P = -560 - [1(40 - 70) * 0.1] \\ &= -560 + 3 = -557 \text{ kJ mol}^{-1} \\ \text{So the magnitude is 557 kJ mol}^{-1} \\ &\because \Delta G^\circ = -2.303 \text{RT} \log K_p \text{ at equilibrium } \Delta G^\circ = 0 \\ &\therefore -2.303 \text{RT} \log K_p = 0 \\ \text{Log } K_p = 0 \text{ or } K_p = 1 \end{split}$$