Chapter Thermodynamics

Topic-1: Thermodynamics

1 MCQs with One Correct Answer

1. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in JK^{-1} is (1 L atm = 101.3 J) **[Adv. 2016]**

(a) 5.763 (b) 1.013
(c) –1.013 (d) –5.763

2. A mono-atomic ideal gas undergoes a process in which the ratio of P to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas **[2006 - 3M; –1]**

(a) $\frac{3R}{2}$ (b) $2R$ (c) 0 (d) $\frac{5R}{2}$

3. When one mole of monoatomic ideal gas at T K undergoes adiabatic change under a constant external pressure of 1 atm, volume changes from 1 litre to 2 litre. The final temperature in Kelvin would be **[2005S]**

(a) $\frac{T}{2^{(2/3)}}$ (b) $T+\frac{2}{3}\times0.0821$

(c) T (d) $T-\frac{2}{3}\times0.0821$

4. Two moles of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litres at 300 K. The enthalpy change (in kJ) for the process is **[2004S]**

(a) 11.4 kJ (b) – 11.4 kJ (c) 0 kJ (d) 4.8 kJ

5. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) → (4.0 atm, 5.0 L, 245 K) with a change in internal energy, ΔU = 30.0 L atm. The change in enthalpy (ΔH) of the process in L atm is **[2002S]**

(a) 40.0
(b) 42.3
(c) 44.0
(d) not defined, because pressure is not constant

6. Which one of the following statements is false? **[2001S]**

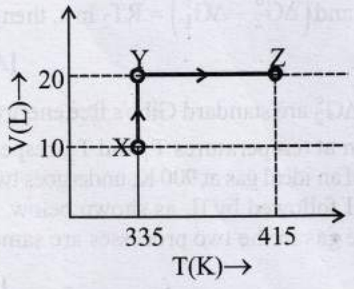
(a) Work is a state function.
(b) Temperature is a state function.
(c) Change in the state is completely defined when the initial and final states are specified.
(d) Work appears at the boundary of the system.

7. In thermodynamics, a process is called reversible when **[2001S]**

(a) surroundings and system change into each other.
(b) there is no boundary between system and surroundings.
(c) the surroundings are always in equilibrium with the system.
(d) the system changes into the surroundings spontaneously.

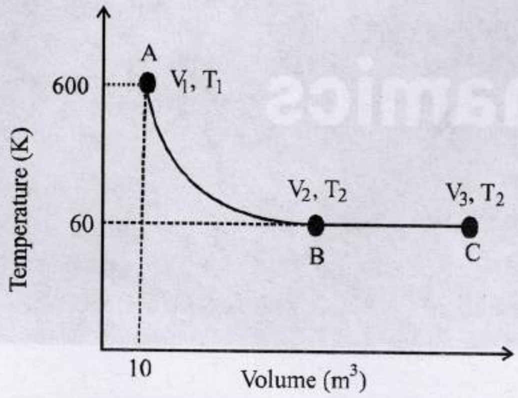
2 Integer Value Answer

8. Consider the following volume–temperature (V–T) diagram for the expansion of 5 moles of an ideal monoatomic gas.



Considering only P-V work is involved, the total change in enthalpy (in Joule) for the transformation of state in the sequence **X→Y→Z** is ______. **[Adv. 2024]**
[Use the given data: Molar heat capacity of the gas for the given temperature range, $C_{V,m}$ = 12 $J K^{-1} mol^{-1}$ and gas constant, R = 8.3 $J K^{-1} mol^{-1}$].

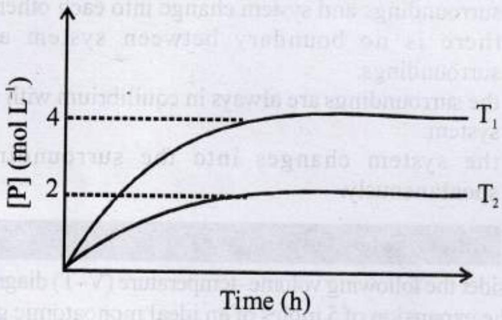
9. One mole of an ideal monoatomic gas undergoes two reversible processes (A → B and B → C) as shown in the given figure: **[Adv. 2023]**



A → B is an adiabatic process. If the total heat absorbed in the entire process (A → B and B → C) is $RT_2 \ln 10$, the value of $2 \log V_3$ is ______.

[Use, molar heat capacity of the gas at constant pressure, $C_{p,m} = \frac{5}{2}R$]

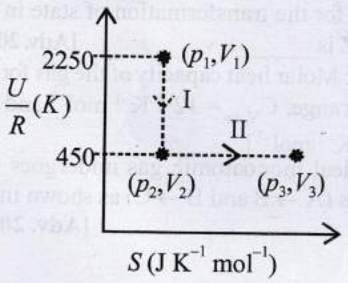
10. In a one–litre flask, 6 moles of A undergoes the reaction $A(g) \rightleftharpoons P(g)$. The progress of product formation at two temperatures (in Kelvin), T_1 and T_2, is shown in the figure:



If $T_1 = 2T_2$ and $\left(\Delta G_2^\circ - \Delta G_1^\circ\right) = RT_2 \ln x$, then the value of x is ______. **[Adv. 2023]**

[ΔG_1° and ΔG_2° are standard Gibb's free energy change for the reaction at temperatures T_1 and T_2, respectively.]

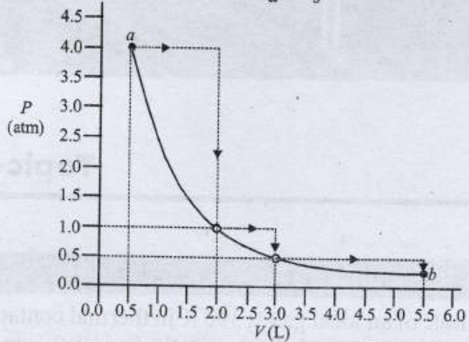
11. One mole of an ideal gas at 900 K, undergoes two reversible processes, I followed by II, as shown below. If the work done by the gas in the two processes are same, the value of $\ln \frac{V_3}{V_2}$ is ______. **[Adv. 2021]**



(U: internal energy, S: entropy, p: pressure, V: volume, R: gas constant)

(Given: molar heat capacity at constant volume, $C_{V,m}$ of the gas is $\frac{5}{2}R$)

12. 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]**

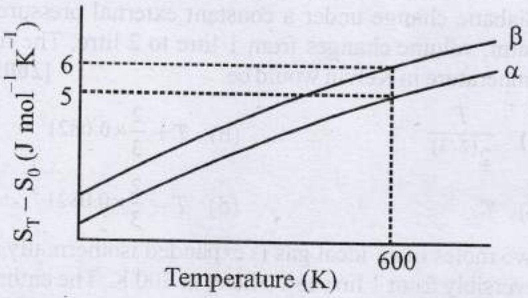


13. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1}, the numerical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

3 Numeric/New Stem Based Questions

Qusetion Stem for Question no. 14 & 15

The entropy versus temperature plot for phases α and β at 1 bar pressure is given. S_T and S_0 are entropies of the phases at temperatures T and 0 K, respectively.



The transition temperature for α to β phase change is 600 K and $C_{p,\beta} - C_{p,\alpha} = 1$ J mol^{-1} K^{-1}. Assume $(C_{p,\beta} - C_{p,\alpha})$ is independent of temperature in the range of 200 to 700 K. $C_{p,\alpha}$ and $C_{p,\beta}$ are heat capacities of α and β phases, respectively.

14. The value of entropy change, $S_\beta - S_\alpha$ (in J mol^{-1} K^{-1}), at 300 K is ______. **[Adv. 2023]**

[Use: $\ln 2 = 0.69$

Given: $S_\beta - S_\alpha = 0$ at 0 K]

15. The value of enthalpy change, $H_\beta - H_\alpha$ (in J mol^{-1}), at 300 K is ______. **[Adv. 2023]**

16. The value of standard enthalpy, ΔH^ϕ (in kJ mol^{-1}) for the given reaction is ______. **[Adv. 2021]**

17. The value of ΔS^{ϕ} (in $J K^{-1} mol^{-1}$) for the given reaction, at 1000 K is________. **[Adv. 2021]**

18. Tin is obtained from cassiterite by reduction with coke. Use the data given below to determine the minimum temperature (in K) at which the reduction of cassiterite by coke would take place. **[Adv. 2020]**

At 298 K: $\Delta_f H^0(SnO_2(s)) = -581.0 \text{ kJ mol}^{-1}$,

$\Delta_f H^0(CO_2(g)) = -394.0 \text{ kJ mol}^{-1}$,

$S^0(SnO_2(s)) = 56.0 \text{ J K}^{-1} \text{ mol}^{-1}$,

$S^0(Sn(s)) = 52.0 \text{ J K}^{-1} \text{ mol}^{-1}$,

$S^0(C(s)) = 6.0 \text{ J K}^{-1} \text{ mol}^{-1}$,

$S^0(CO_2(g)) = 210.0 \text{ J K}^{-1} \text{ mol}^{-1}$.

Assume that the enthalpies and the entropies are temperature independent.

19. For the reaction, $2CO + O_2 \longrightarrow 2CO_2$; $\Delta H = -560$kJ. 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]**

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. $C_{V,m}$ for argon is 12.48 $JK^{-1} mol^{-1}$. **[2000 - 4 Marks]**

21. An athlete is given 100 g 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]**

4 Fill in the Blanks

22. Enthalpy is an .... property. **[1997 - 1 Mark]**

23. A system is said to be .... if it can neither exchange matter nor energy with the surroundings. **[1993 - 1 Mark]**

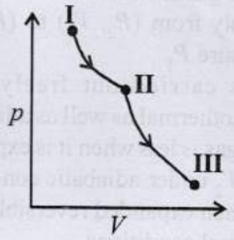
5 True / False

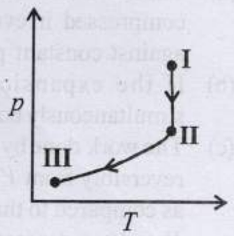
24. Heat capacity of a diatomic gas is higher than that of a monoatomic gas. **[1985 - ½ Mark]**

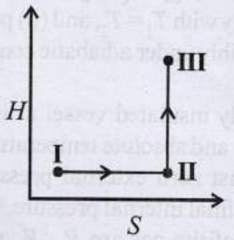
25. First law of thermodynamics is not adequate in predicting the direction of a process. **[1982 - 1 Mark]**

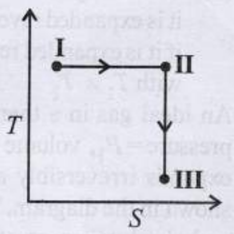
6 MCQs with One or More than One Correct Answer

26. An ideal gas undergoes a reversible isothermal expansion from state I to state II followed by a reversible adiabatic expansion from state II to state III. The correct plot(s) representing the changes from state I to state III is (are) (p : pressure, V : volume, T : temperature, H : enthalpy, S : entropy) **[Adv. 2021]**

(a)


(b)


(c)


(d)


27. In thermodynamics, the $P-V$ work done is given by

$$w = -\int dV\, P_{ext}.$$

For a system undergoing a particular process, the work done is,

$$w = -\int dV \left(\frac{RT}{V-b} - \frac{a}{V^2} \right).$$

This equation is applicable to a **[Adv. 2020]**

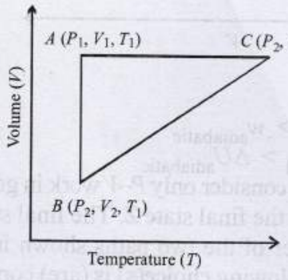
(a) system that satisfies the van der Waals equation of state.

(b) process that is reversible and isothermal.

(c) process that is reversible and adiabatic.

(d) process that is irreversible and at constant pressure.

28. A reversible cyclic process for an ideal gas is shown below. Here, P, V, and T are pressure, volume and temperature, respectively. The thermodynamic parameters q, w, H and U are heat, work, enthalpy and internal energy, respectively. **[Adv. 2018]**



The correct option(s) is (are)

(a) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = P_2(V_2 - V_1)$

(b) $w_{BC} = P_2(V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$

(c) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{AC} = \Delta U_{BC}$

(d) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

29. An ideal gas is expanded from (P_1, V_1, T_1) to (P_2, V_2, T_2) under different conditions. The correct statement(s) among the following is (are) **[Adv. 2017]**

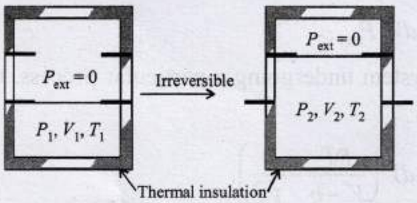
(a) The work done on the gas is maximum when it is compressed irreversibly from (P_2, V_2) to (P_1, V_1) against constant pressure P_1

(b) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic

(c) The work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions

(d) The change in internal energy of the gas is (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$

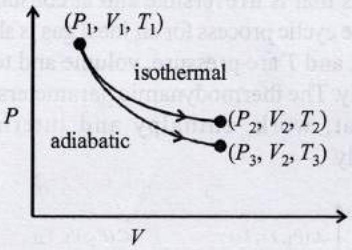
30. An ideal gas in a thermally insulated vessel at internal pressure $= P_1$, volume $= V_1$ and absolute temperature $= T_1$ expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are P_2, V_2 and T_2, respectively. For this expansion, **[Adv. 2014]**



(a) $q = 0$ (b) $T_2 = T_1$

(c) $P_2V_2 = P_1V_1$ (d) $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

31. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct ? **[2012 - II]**



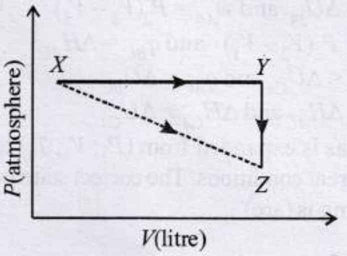
(a) $T_1 = T_2$

(b) $T_3 > T_1$

(c) $w_{isothermal} > w_{adiabatic}$

(d) $\Delta U_{isothermal} > \Delta U_{adiabatic}$

32. For an ideal gas, consider only $P–V$ work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct? [Take ΔS as change in entropy and w as work done]. **[2012]**



(a) $\Delta S_{X \to Z} = \Delta S_{X \to Y} + \Delta S_{Y \to Z}$

(b) $w_{X \to Z} = w_{X \to Y} + w_{Y \to Z}$

(c) $w_{X \to Y \to Z} = w_{X \to Y}$

(d) $\Delta S_{X \to Y \to Z} = \Delta S_{X \to Y}$

33. Among the following, the intensive property is (properties are) **[2010]**

(a) molar conductivity (b) electromotive force

(c) resistance (d) heat capacity

34. Among the following the state function(s) is (are) **[2009]**

(a) Internal energy

(b) Irreversible expansion work

(c) Reversible expansion work

(d) Molar enthalpy

35. Identify the intensive quantities from the following: **[1993 - 1 Mark]**

(a) Enthalpy (b) Temperature

(c) Volume (d) Refractive Index

7 Match the Following

36. Match the thermodynamic processes given under Column-I with the expressions given under Column-II. **[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 in an isolated container	(r) $\Delta S_{sys} < 0$
(D) Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm	(s) $\Delta U = 0$
	(t) $\Delta G = 0$

8 Comprehension/Passage Based Questions

Passage-I

The amount of energy required to break a bond is same as the amount of energy released when the same bond is formed. In gaseous state, the energy required for *homolytic cleavage* of a bond is called Bond Dissociation Energy (BDE) or Bond Strength. BDE is affected by *s*-character of the bond and the stability of the radicals formed. Shorter bonds are typically stronger bonds. BDEs for some bonds are given below :

$H_3C-H(g) \longrightarrow H_3C^{\bullet}(g) + H^{\bullet}(g) \quad \Delta H^{\circ} = 105 \text{ kcal mol}^{-1}$

$Cl-Cl(g) \longrightarrow Cl^{\bullet}(g) + Cl^{\bullet}(g) \quad \Delta H^{\circ} = 58 \text{ kcal mol}^{-1}$

$H_3C-Cl(g) \longrightarrow H_3C^{\bullet}(g) + Cl^{\bullet}(g) \quad \Delta H^{\circ} = 85 \text{ kcal mol}^{-1}$

$H-Cl(g) \longrightarrow H^{\bullet}(g) + Cl^{\bullet}(g) \quad \Delta H^{\circ} = 103 \text{ kcal mol}^{-1}$

37. Correct match of the C–H bonds (shown in bold) in Column J with their BDE in Column K is

Column J Molecule	Column K BDE (kcal mol^{-1})
(P) $H-CH(CH_3)_2$	(i) 132
(Q) $H-CH_2Ph$	(ii) 110
(R) $H-CH=CH_2$	(iii) 95
(S) $H-C\equiv CH$	(iv) 88

[Adv. 2021]

(a) P – iii, Q – iv, R – ii, S – i
(b) P – i, Q – ii, R – iii, S – iv
(c) P – iii, Q – ii, R – i, S – iv
(d) P – ii, Q – i, R – iv, S – iii

38. For the following reaction

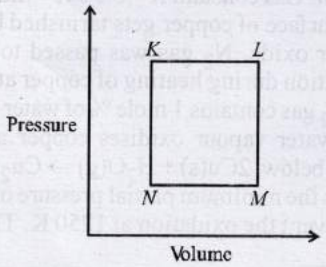
$$CH_4(g) + Cl_2(g) \xrightarrow{\text{light}} CH_3Cl(g) + HCl\,(g)$$

the correct statement is **[Adv. 2021]**

(a) Initiation step is exothermic with $\Delta H^o = -58$ kcal mol^{-1}
(b) Propagation step involving $^{\bullet}CH_3$ formation is exothermic with $\Delta H^o = -2$ kcal mol^{-1}.
(c) Propagation step involving CH_3Cl formation is endothermic with $\Delta H^o = +27$ kcal mol^{-1}.
(d) The reaction is exothermic with $\Delta H^o = -25$ kcal mol^{-1}.

Passage-II

A fixed mass '*m*' of a gas is subjected to transformation of states from *K* to *L* to *M* to *N* and back to *K* as shown in the figure **[Adv. 2013]**



39. The succeeding operations that enable this transformation of states are
(a) Heating, cooling, heating, cooling
(b) Cooling, heating, cooling, heating
(c) Heating, cooling, cooling, heating
(d) Cooling, heating, heating, cooling

40. The pair of isochoric processes among the transformation of states is
(a) *K* to *L* and *L* to *M*
(b) *L* to *M* and *N* to *K*
(c) *L* to *M* and *M* to *N*
(d) *M* to *N* and *N* to *K*

9 Assertion and Reason Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

(a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -1.
(b) If both Statement-1 and Statement-2 are correct, but Statement-2 is not the correct explanation of the Statement-1.
(c) If Statement -1 is correct but Statement -2 is incorrect.
(d) If Statement -1 is incorrect but Statement -2 is correct.

41. **Statement - 1 :** There is a natural asymmetry between converting work to heat and converting heat to work.
Statement - 2 : No process is possible in which the sole result is the absorption of heat form a reservoir and its complete conversion into work. **[2008S]**

42. Read the following statement and explanation and answer as per the options given below :
Assertion : The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.
Reason : The volume occupied by the molecules of an ideal gas is zero. **[2000S]**

10 Subjective Problems

43. 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 process. **[2004 - 2 Marks]**

44. 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]**

45. Two moles of a perfect gas undergo the following processes: **[2002 - 5 Marks]**
(a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L);
(b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L);
(c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L).
  (i) Sketch with labels each of the processes on the same *P*-*V* diagram.
  (ii) Calculate the total work (*W*) and the total heat change (*q*) involved in the above processes.
  (iii) What will be the values of ΔU, ΔH and ΔS for the overall process?

46. "The heat energy *q*, absorbed by a gas is ΔH", is true at what condition(s). **[1984 - 1 Mark]**

Topic-2: Thermochemistry

1 MCQs with One Correct Answer

1. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at $T = 298$ K are
$\Delta_f G^0$ [C(graphite)] = 0 kJ mol^{-1}
$\Delta_f G^0$ [C(diamond)] = 2.9 kJ mol^{-1}
The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by 2×10^{-6} m^3 mol^{-1}. If C(graphite) is converted to C(diamond) isothermally at $T = 298$ K, the pressure at which C(graphite) is in equilibrium with C(diamond), is
[Useful information : 1 J = 1 kg m^{2}s^{-2}; 1 Pa = 1 kg m^{-1} s^{-2}; 1 bar = 10^5 Pa] **[Adv. 2017]**
(a) 14501 bar (b) 58001 bar
(c) 1450 bar (d) 29001 bar

2. For the process **[Adv. 2014]**
$H_2O(l) \rightarrow H_2O(g)$
at $T = 100°C$ and 1 atmosphere pressure, the correct choice is
(a) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} > 0$
(b) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} < 0$
(c) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} > 0$
(d) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} < 0$

3. The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose(s) at 25 °C are –400 kJ/mol, –300 kJ/mol and –1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25 °C is **[Adv. 2013-I]**
(a) +2900 kJ (b) –2900 kJ
(c) –16.11 kJ (d) +16.11 kJ

4. The species which by definition has **ZERO** standard molar enthalpy of formation at 298 K is **[2010]**
(a) Br_2 (g) (b) Cl_2 (g)
(c) H_2O (g) (d) CH_4 (g)

5. For the process $H_2O(l)$ (1 bar, 373 K) $\rightarrow H_2O(g)$ (1 bar, 373 K), the correct set of thermodynamic parameters is **[2007]**
(a) $\Delta G = 0, \Delta S = +ve$ (b) $\Delta G = 0, \Delta S = -ve$
(c) $\Delta G = +ve, \Delta S = 0$ (d) $\Delta G = -ve, \Delta S = +ve$

6. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is
(Given : $\Delta_r H^\circ_{298K} = -54.07$ kJ mol^{-1}, $\Delta_r S^\circ_{298K} = 10$ JK^{-1} mol^{-1} and $R = 8.314$ JK^{-1} mol^{-1}; $2.303 \times 8.314 \times 298 = 5705$) **[2007]**
(a) 5 (b) 10 (c) 95 (d) 100

7. The enthalpy of vapourization of liquid is 30 kJ mol^{-1} and entropy of vapourization is 75 J mol^{-1} K. The boiling point of the liquid at 1 atm is **[2004S]**
(a) 250 K (b) 400 K (c) 450 K (d) 600 K

8. Which of the reaction defines ΔH°_f? **[2003S]**
(a) $C(\text{diamond}) + O_2(g) \longrightarrow CO_2(g)$
(b) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \longrightarrow HF(g)$
(c) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
(d) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$

9. The ΔH_f^0 for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are –393.5, –110.5 and –241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction
$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ is **[2000S]**
(a) 524.1 (b) 41.2 (c) –262.5 (d) –41.2

10. For which change $\Delta H \neq \Delta E$: **[1995S]**
(a) $H_2(g) + I_2(g) \rightarrow 2HI(g)$
(b) $HCl + NaOH \rightarrow NaCl$
(c) $C(s) + O_2(g) \rightarrow CO_2(g)$
(d) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

11. The difference between heats of reaction at constant pressure and constant volume for the reaction :
$2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$ at 25 °C in kJ is **[1991 - 1 Mark]**
(a) –7.43 (b) +3.72 (c) –3.72 (d) +7.43

3 Numeric / New Stem Based Questions

12. 2 mol of Hg(g) is combusted in a fixed volume bomb calorimeter with excess of O_2 at 298 K and 1 atm into HgO(s). During the reaction, temperature increases from 298.0 K to 312.8 K. If heat capacity of the bomb calorimeter and enthalpy of formation of Hg(g) are 20.00 kJ K^{-1} and 61.32 kJ mol^{-1} at 298 K, respectively, the calculated standard molar enthalpy of formation of HgO(s) at 298 K is X kJ mol^{-1}. The value of |X| is ________.
[Given: Gas constant R = 8.3 J K^{-1} mol^{-1}] **[Adv. 2022]**

13. The surface of copper gets tarnished by the formation of copper oxide. N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below: $2Cu(s) + H_2O(g) \rightarrow Cu_2O(s) + H_2(g)$
p_{H2} is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln(p_{H2})$ is ______.
(Given: total pressure = 1 bar, R (universal gas constant) = 8 J K^{-1} mol^{-1}, ln (10) = 2.3. Cu (s) and Cu_2O (s) are mutually immiscible.
At 1250 K : $2\,Cu(s) + \frac{1}{2}O_2(g) \rightarrow Cu_2O(s)$; $\Delta G^\circ = -78{,}000$ J mol^{-1}
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$; $\Delta G^\circ = -1{,}78{,}000$ J mol^{-1};
(G is the Gibbs energy) **[Adv. 2018]**

14. Diborane is a potential rocket fuel which undergoes combustion according to the reaction. **[2000 - 2 Marks]**
$B_2H_6(g) + 3\,O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$
From the following data, calculate the enthalpy change for the combustion of diborane.
$2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s)$ $\Delta H = -1273$ kJ mol^{-1}
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$ $\Delta H = -286$ kJ mol^{-1}
$H_2O(l) \longrightarrow H_2O(g)$ $\Delta H = 44$ kJ mol^{-1}
$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g)$ $\Delta H = 36$ kJ mol^{-1}

15. 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]**

16. 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]**

17. 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, 249 kJ / mol. Average bond energies :
C – H = 415 kJ/mol, C – O = 365 kJ/mol, O – H = 463 kJ/mol **[1997 - 5 Marks]**

18. 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]**

19. The polymerisation of ethylene to linear polyethylene is represented by the reaction **[1994 - 2 Marks]**

$$nCH_2 = CH_2 \longrightarrow \lbrack CH_2 - CH_2 \rbrack_n$$

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.

20. Determine the enthalpy change of the reaction.
$C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$, at 25 °C, 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 $C_3H_8(g)$ is – 103.8 kJ/mol. **[1992 - 3 Marks]**

21. 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]**

22. 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]**

23. 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.

24. 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]**

25. 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]**

26. 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 ethylene = – 337.2 kcal;
Calculate the heat of reaction for the hydrogenation of acetylene at constant volume (25 °C). **[1984 - 4 Marks]**

27. 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]**

28. 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.

4 Fill in the Blanks

29. When Fe(s) is dissolved in aqueous hydrochloric acid in a closed vessel, the work done is .... **[1997 - 1 Mark]**

30. The heat content of the products is more than that of the reactants in an .... reaction. **[1993 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

31. Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation **[Adv. 2019]**

(a) $\frac{1}{8}S_8(s) + O_2(g) \rightarrow SO_2(g)$
(b) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
(c) $\frac{3}{2}O_2(g) \rightarrow O_3(g)$
(d) $2C(g) + 3H_2(g) \rightarrow C_2H_6(g)$

32. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant *K* in terms of change in entropy is described by **[Adv. 2017]**

(a) With increase in temperature, the value of *K* for exothermic reaction decreases because the entropy change of the system is positive
(b) With increase in temperature, the value of *K* for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases
(c) With increase in temperature, the value of *K* for endothermic reaction increases because the entropy change of the system is negative
(d) With increase in temperature, the value of *K* for exothermic reaction decreases because favourable change in entropy of the surroundings decreases

33. The following is (are) endothermic reaction(s): **[1999 - 3 Marks]**

(a) Combustion of methane
(b) Decomposition of water
(c) Dehydrogenation of ethane to ethylene
(d) Conversion of graphite to diamond

7 Match the Following

34. Match the transformations in **column I** with appropriate options in **column II** **[2011]**

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

10 Subjective Problems

35. In the following equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ **[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 : $\Delta G_f^\circ(N_2O_4) = 100\text{kJ}; \ \Delta G_f^\circ(NO_2) = 50 \text{ kJ}$

(i) Find ΔG of the reaction at 298 K.

(ii) Find the direction of the reaction

36. 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 ΔG° 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]**

37. 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 $-0.094 \text{ kJ mol}^{-1}\text{ K}^{-1}$. The standard Gibbs free energies of formation for CO_2 and CO are -394.4 and $-137.2 \text{ kJ mol}^{-1}$, respectively. **[2000 - 3 Marks]**

38. 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}; $\Delta H_{\text{hydration}}$ for $Al^{3+} = -4665 \text{ kJ mol}^{-1}$; $\Delta H_{\text{hydration}}$ for $Cl^- = -381 \text{ kJ mol}^{-1}$.) **[1997 - 2 Marks]**

39. 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 6*x* 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.

Heats of combustion :

$$CH_4 = 809 \text{ kJ/mol}; \ C_4H_{10} = 2878 \text{ kJ/mol}$$

[1993 - 3 Marks]

40. Using the data (all values are in kcal mol^{-1} at 25 °C) given below, calculate the bond energy of C–C and C–H bonds. **[1990 - 5 Marks]**

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

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

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

Bond energy of H–H = 104.0

ΔH°_f of $H_2O(l) = -68.0$

ΔH°_f of $CO_2(g) = -94.0$

Answer Key

Topic-1 : Thermodynamics

1. (c) **2.** (b) **3.** (a) **4.** (c) **5.** (c) **6.** (a) **7.** (c) **8.** (8120) **9.** (7) **10.** (8)
11. (10) **12.** (2) **13.** (9) **14.** (0.31) **15.** (300) **16.** (166.28) **17.** (141.34) **18.** (935.00) **19.** (557) **20.** (115.87)
21. (319.1) **22.** (extensive) **23.** (isolated) **24.** (True) **25.** (True) **26.** (a,b,d) **27.** (a,b,c) **28.** (b,c)
29. (a,b,c) **30.** (a,b,c) **31.** (a,c,d) **32.** (a,c) **33.** (a,b) **34.** (a,d) **35.** (b,d)
36. (A- (r, t); B -(p, q, s); C -(p, q, s); D- (p, q, s, t)) **37.** (a) **38.** (d) **39.** (c) **40.** (b) **41.** (a) **42.** (b)

Topic-2 : Thermochemistry

1. (a) **2.** (b) **3.** (c) **4.** (b) **5.** (a) **6.** (b) **7.** (b) **8.** (b) **9.** (b)
10. (d) **11.** (a) **12.** (90.39) **13.** (–14.6) **14.** (–2035) **15.** (309.16) **16.** (–2091.32)
17. (–266) **18.** (–152) **19.** (–72) **20.** (–55.7) **21.** (50.90) **22.** (–121) **23.** (3.94)
24. (–372.0) **25.** (–22) **26.** (41.104) **27.** (54.20) **28.** (101.19) **29.** (zero)
30. (endothermic) **31.** (a,c) **32.** (b,d) **33.** (b,c,d) **34.** (A – p, r, s ; B – r, s ; C – t ; D – p, q, t)

Hints & Solutions

Topic-1: Thermodynamics

1. **(c)** From 1st law of thermodynamics
$q_{sys} = \Delta U - w = 0 - [-P_{ext}.\Delta V]$
$= 3.0\text{ atm} \times (2.0\text{ L} - 1.0\text{ L}) = 3.0\text{ L-atm}$

$$\therefore \Delta S_{surr} = \frac{(q_{rev})_{surr}}{T} = -\frac{q_{sys}}{T}$$

$$= -\frac{3.0 \times 101.3\text{ J}}{300\text{ K}} = -1.013\text{ J/K}$$

2. **(b)** In general, the molar heat capacity for any process is given by

$$C = C_v + \frac{R}{1-\gamma}, \text{ when } PV^\gamma = \text{constant}$$

Here $\frac{P}{V} = 1$, *i.e.* $PV^{-1} = \text{constant} \Rightarrow \gamma = -1$

For monoatomic gas, $C_v = \frac{3}{2}R$

$$\therefore C = \frac{3}{2}R + \frac{R}{1-(-1)} = \frac{3}{2}R + \frac{R}{2} = \frac{4R}{2} = 2R.$$

3. **(a)** $TV^{\gamma-1} = \text{Constant}$ $\quad$ ($\because$ change is adiabatic)

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

For monoatomic gas $\gamma = \frac{5}{3}$

$$\therefore T_1V_1^{2/3} = T_2V_2^{2/3} \Rightarrow T(1)^{2/3} = T_2(2)^{2/3}$$

$$T_2 = \frac{T}{2^{(2/3)}}$$

4. **(c)** $\Delta H = nC_p\Delta T$ solution; since $\Delta T = 0$ so, $\Delta H = 0$
5. **(c)**
$\Delta H = \Delta U + P_2V_2 - P_1V_1$ $\quad$ Given, $\Delta U = 30.0\text{ L atm}$
$P_1 = 2.0\text{ atm}, V_1 = 3.0\text{ L}, T_1 = 95\text{ K}$
$P_2 = 4.0\text{ atm}, V_2 = 5.0\text{ L}, T_2 = 245\text{ K}$
$\Delta H = \Delta U + P_2V_2 - P_1V_1$
$= 30 + (4 \times 5) - (2 \times 3) = 30 + 20 - 6 = 44\text{ L atm}.$
6. **(a)** Work is not a state function because it depends upon the path followed.
7. **(c)** In a reversible process, the driving and the opposite forces are nearly equal, hence the system and the surroundings always remain in equilibrium with each other.
8. **(8120)** X → Y is an isothermal process an ideal gas:
$\Delta H = 0, \Delta U = 0$
Y → Z is an isochoric process
$\Rightarrow \Delta V = 0$
$\therefore W = 0$
$\Delta U = nC_{v.m}(T_2 - T_1)$
$= 5 \times 12(415 - 335)$
$= 4800\text{ J}$
$\Delta H = \Delta U + \Delta(PV)$
$= \Delta U + nR\Delta T$
$= 4800 + 5 \times 8.3 \times (415 - 335)$
$= 8120\text{ J}$

9. **(7)** For A → B (Reversible adiabatic)

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

$$\Rightarrow 600(V_1)^{2/3} = 60(V_2)^{2/3} \quad \left(\because \gamma = \frac{5}{3}\right)$$

$$\Rightarrow 10 = \left(\frac{V_2}{10}\right)^{2/3}$$

$V_{total} = E_{AB} + q_{BC}$
$= 0 + q_{BC} = q_{BC}$
$q_{BC} = RT_2 \ln 10$

$$\Rightarrow q_{BC} = 60\text{ R} \ln 10 = 60\text{ R} \ln \frac{V_3}{V_2}$$

[$\because$ B → C is reversible isothermal]

$$\Rightarrow 60\text{ R} \ln 10 = 60\text{ R} \ln \left(\frac{V_3}{10^{5/2}}\right)$$

$$\Rightarrow \log 10 = \log V_3 - \frac{5}{2}$$

$$\Rightarrow \log V_3 = \frac{7}{2} \Rightarrow 2 \log V_3 = 7$$

10. **(8)** At T_1 K: $\quad A(g) \rightleftharpoons P(g)$
$t = 0$ $\quad 6$
At eq, T_1K $\quad 6 - x \quad x = 4$ (from plot)
At eq, T_2K $\quad 6 - y \quad y = 2$ (from plot)

$$\Rightarrow \text{At } T_1\text{ K}: K_{P_1} = \frac{4}{2} = 2$$

$$\Rightarrow \text{At } T_2\text{ K}: K_{P_2} = \frac{2}{4} = \frac{1}{2}$$

$$\text{Now, } \Delta G_2^\circ = -RT_2 \ln K_{P_2} = -RT_2 \ln \frac{1}{2} = RT_2 \ln 2$$

$$\Delta G_1^\circ = -RT_1 \ln K_{P_1} = RT_1 \ln 2$$

Given : $\Delta G_2^\circ - \Delta G_1^\circ = RT_2 \ln 2 + RT_1 \ln 2$
$= RT_2 \ln 2 + 2RT_2 \ln 2$
$= 3RT_2 \ln 2 = RT_2 \ln x \; (T_1 = 2T_2)$
$\Rightarrow x = 2^3 = 8$

11. **(10)**

Process (I) ⇒ (Adiabatic reversible)

$$\frac{\Delta U}{R} = 450 - 2250$$

$\Delta U = -1800R$

$W_I = \Delta U = -1800\,R$

Process (II) ⇒ (Reversible isothermal process)

$T_1 = 900\,K$

Calculation of T_2 after reversible adiabatic process

$\Delta U = nC_v dT$

$$\Rightarrow -1800\,R = 1 \times \frac{5}{2} R (T_2 - 900)$$

$$T_2 = 180\,K$$

$$W_{II} = -nRT_2 \ln \frac{V_3}{V_2} = W_I$$

$$\Rightarrow -1 \times R \times 180 \ln \frac{V_3}{V_2} = -1800R$$

$$\Rightarrow \ln \frac{V_3}{V_2} = 10$$

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

$$w_d = -\frac{33}{4} \text{ L atm}$$

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

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

$$\frac{w_d}{w_s} = \frac{-\frac{33}{4}}{-4.8} = 1.72 \simeq 2.0$$

13. **(9)** Energy released by combustion of 3.5 g gas

$= 2.5 \times (298.45 - 298)$ kJ

Energy released by 1 mole of gas

$$= \frac{2.5 \times 0.45}{3.5/28} = 9 \text{ kJmol}^{-1}$$

14. **(0.31)**

$\alpha \rightarrow \beta$ and $S^0_{\beta(600)} - S^0_{\alpha(600)} = 6 - 5 = 1$ (from graph)

$$S^0_{\alpha(600)} - S^0_{\alpha(300)} + C_{P(\alpha)} \ln \frac{600}{300}$$

$$S^0_{\beta(600)} = S^0_{\beta(300)} + C_{P(\beta)} \ln \frac{600}{300}$$

$$S^0_{\beta(600)} - S^0_{\alpha(600)} = S^0_{\beta(300)} - S^0_{\alpha(300)} + C_{P(\beta)} - C_{P(\alpha)} \ln 2$$

$$6 - 5 = S^0_{\beta(300)} - S^0_{\alpha(300)} + [1 \times \ln 2]$$

$$1 = S^0_{\beta(300)} - S^0_{\alpha(300)} + 0.69$$

So $S^0_{\beta(300)} - S^0_{\alpha(300)} = 0.31 \text{ J mol}^{-1} \text{ K}^{-1}$

15. **(300)** As the phase transition temperature is 600 K

So at 600 K ; $\Delta G^\circ_{rxn} = 0$

So $\Delta H^\circ_{\text{reaction (600)}} = T\,\Delta S^\circ_{\text{reaction (600)}}$

$\Delta H^\circ_{(600)} = 600 \times 1 = 600$ Joule/mole

So, $\Delta H_{600} - \Delta H_{300} = \Delta C_P (T_2 - T_1)$

$= 1 \times 300 = 300 \text{ J mol}^{-1}$

$\Rightarrow \Delta H_{300} = \Delta H_{600} - 300 = 600 - 300 = 300 \text{ J mol}^{-1}$

16. **(166.28)** Slope $= \frac{dy}{dx} = \frac{d(\ln K)}{d(10^4/T)}$

$$\Rightarrow \frac{-\Delta H^\phi}{10^4 R} = \frac{-7-(-3)}{12-10}$$

$$\Rightarrow \Delta H^\phi = 2 \times 10^4 \times R = 2 \times 10^4 \times 8.314 \text{ J/mol}$$

$$= 166.28 \text{ kJ/mol}$$

17. **(141.34)** Form the plot when, $\frac{10^4}{T} = 10$ $[T = 1000\,K]$

$$\ln\left(\frac{p_z}{1}\right) = -3$$

$$\Delta G^\circ = -RT \ln K \Rightarrow \Delta H^\phi - T\Delta S^\phi = -RT \ln \frac{P_z}{p^\phi}$$

Substituting in following equation :

$$\ln\left(\frac{p_z}{1}\right) = -\frac{\Delta H^\ominus}{RT} + \frac{\Delta S^\ominus}{R}$$

We get, $-3 = -\frac{2 \times 10^4 \times R}{R \times 1000} + \frac{\Delta S^\ominus}{R}$

$$\Rightarrow \Delta S^\ominus = 17R \Rightarrow \Delta S^\ominus = 17 \times 8.314 \text{ J/K-mol}$$

$$\Rightarrow \Delta S^\ominus = 141.34 \text{ J/K-mol}$$

18. **(935.00)** $SnO_2(s) + C(s) \longrightarrow Sn(s) + CO_2(g)$

$\Delta_r H^o = [-394] - [-581] = 187 \text{ kJ/mole} = 187 \times 10^3 \text{ J/mol}$

$\Delta_r S^o = [52 + 210] - [56 + 6] = 200 \text{ JK}^{-1} \text{ mol}^{-1}$

$$T = \frac{\Delta_r H^o}{\Delta_r S^o} = \frac{187 \times 10^3}{200} = 935\,K$$

19. **(557)**

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

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

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

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

20. **(115.87)** $C_p - C_v = R$

$\Rightarrow C_p = 12.48 + 8.31 = 20.794 \text{ J mol}^{-1} \text{ K}^{-1}$

$$\gamma = \frac{C_p}{C_v} = \frac{20.794}{12.48} = 1.67$$

For a reversible adiabatic process,

$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

$$\Rightarrow T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1} \Rightarrow T_2 = 300\left(\frac{1.25}{2.50}\right)^{1.67-1}$$

$\Rightarrow T_2 = 188.55$ K

Number of moles of gas,

$$n = \frac{PV_1}{RT_1} \Rightarrow n = \frac{1 \times 1.25}{0.0821 \times 300} = 0.05$$

Enthalpy change at constant pressure,

$$\Delta H = n \cdot C_p \cdot \Delta T$$
$$= 0.05 \times 20.794 \times (300 - 188.55)$$
$$= 115.87 \text{ Joule.}$$

21. **(319.1)**

100 g of glucose = 1560 kJ

Energy utilised in body $= \frac{50}{100} \times 1560 = 780$ 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 = 18 g water]

Hence, amount water to be perspired to avoid storage of energy $= \frac{18}{44} \times 780 = \mathbf{319.1\ g}$

22. **extensive** (because its value depends on quantity of substance)

23. **isolated**

24. **True;**

Heat capacity	**Monoatomic**	**Diatomic**
C_v	$3R/2$	$5R/2$
C_p	$5R/2$	$7R/2$

Thus, the heat capacity of diatomic gas is higher than that of a monoatomic gas.

25. **True;** It only tells that if the heat gained by one end would be exactly equal to heat lost by the other. It does not predict the direction.

26. **(a, b, d)** From state I to II (Reversible isothermal expansion):

$T \to$ constant, $\Delta V \to$ +ve, $\Delta S \to$ +ve, $\Delta H \to 0$

$\Delta P \to$ –ve

From state II to III (Reversible adiabatic expansion):

$q \to 0$, $\Delta V \to$ +ve, $\Delta S \to$ constant

$\Delta H \to$ –ve, $\Delta P \to$ –ve, $\Delta T \to$ –ve

$\therefore$ Plots (a), (b), (d) are correct while (c) is wrong as from state II to III, H is decreasing.

27. **(a, b, c)**

P-V work done is applicable for reversible isobaric as well as isothermal and adiabatic process.

$$w = -\int P_{ext} \cdot dV$$

For van der Waals equation,

$$P_{ext} = P = \left(\frac{RT}{v-b} - \frac{a}{v^2}\right)$$

$$w = -\int dv\left(\frac{RT}{v-b} - \frac{a}{v^2}\right) \quad \text{..... (i)}$$

Equation (i) is not applicable to irreversible process. Therefore work done is calculated assuming pressure is constant throughout the process.

28. **(b, c)**

A– C $\Rightarrow$ isochoric process

A– B $\Rightarrow$ isothermal process

B– C $\Rightarrow$ isobaric process

(a) $q_{AC} = \Delta U_{AC} = nC_{V,m}(T_2 - T_1) = \Delta U_{BC}$

$W_{AB} = -nRT_1 \ln\left(\frac{V_2}{V_1}\right)$ (pressure is not constant)

(b) $W_{BC} = -P_2(V_1 - V_2) = P_2(V_2 - V_1)$

$q_{BC} = \Delta H_{BC} = nC_{P,m}(T_2 - T_1) = \Delta H_{AC}$

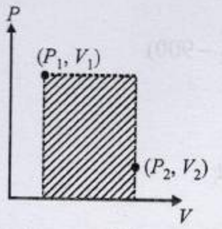
(c) $\Delta H_{CA} = nC_{P,m}(T_1 - T_2)$

(d) $\Delta U_{CA} = nC_{V,m}(T_1 - T_2)$

$\Delta H_{CA} < \Delta U_{CA}$ since both are negative $(T_1 < T_2)$ and $C_{p,m} > C_{V,m}$

29. **(a, b, c)**

(a)



During irreversible compression, maximum work is done on the gas (corresponding to shaded area) when $P_1 = P_2$

(d) When $T_1 = T_2 \Rightarrow \Delta U = nC_V \Delta T = 0$

In reversible adiabatic expansion, $T_2 < T_1$.

$\therefore$ ΔT = –ve and also ΔU = –ve

(b) In free expansion, $P_{ext} = 0$, $\therefore W = 0$

From Ist law of thermodynamics,

$\Delta U = q + W$

$\therefore \Delta U = q$

If expansion is carried out isothermally, $\Delta U = 0$

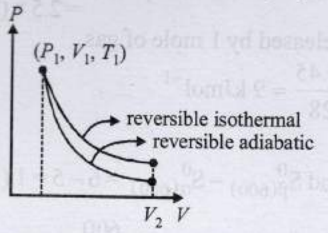
Hence $q = 0$

$\therefore$ It is adiabatic process.

If carried out adiabatically ($q = 0$), $\therefore \Delta U = 0$

$\therefore$ It is an isothermal process.

(c) During adiabatic expansion, the final temperature is less than the initial temperature. Therefore, the final volume in adiabatic expansion will also be less than the final volume in isothermal expansion. This can be graphically shown as:



The magnitude of work done by the gas is equal to the area under the curve. As seen from the figure, the area under curve in reversible isothermal is more. Hence, the magnitude of work done is lesser in adiabatic reversible expansion as compared to the corresponding work in isothermal expansion.

30. **(a, b, c)** Since the vessel is thermally insulated, $q = 0$

Further since, $P_{ext} = 0$, so $w = 0$, hence $\Delta U = 0$

Therefore, $\Delta T = 0$, $T_2 = T_1$, and $P_2V_2 = P_1V_1$

However, the process is adiabatic irreversible, so we can't apply $P_2V_2^{\gamma} = P_1V_1^{\gamma}$.

31. **(a, c, d)** $T_1 = T_2$ because process is isothermal.

Work done in adiabatic process is less than in isothermal process because area covered by isothermal curve is more than the area covered by the adiabatic curve.

In adiabatic process expansion occurs by using internal energy.

hence, it decreases while in isothermal process temperature remains constant, that's why no change in internal energy.

32. **(a, c)** $\Delta S_{X\to Z} = \Delta S_{X\to Y} + \Delta S_{Y\to Z}$ [Entropy is a state function, hence additive]

$w_{X\to Y\to Z} = w_{X\to Y}$ [Work done in $Y \to Z$ is zero because it is an isochoric process].

33. **(a, b)** Mass independent properties (molar conductivity and electromotive force) are intensive properties. Resistance and heat capacity are mass dependent, hence extensive properties.

34. **(a, d)** Internal energy and molar enthalpy are state functions. Work (reversible or irreversible) is a path function.

35. **(b, d)** Properties independent of mass are intensive properties. Hence, (b) and (d) which are independent of mass are the obvious choices.

36. **A-(r, t); B-(p, q, s); C-(p, q, s); D-(p, q, s, t)**

(A) → r, t

$H_2O(l) \rightleftharpoons H_2O(s)$

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 $q_p = C_p dT$ $(\because dT = 0)$

$\Rightarrow q = 0$

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

(C) → p, q, s

Mixing of two ideal gases at constant temperature

Hence, $\Delta T = 0$

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

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.

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

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

37. **(a)** Stability of free radical $\propto \dfrac{1}{\text{Bond energy}}$

(P) 

2° free radical

(Q) $Ph-CH_2-H \longrightarrow Ph-\dot{C}H_2 + H^\bullet$

Most stable due to resonance

(R) $CH_2=CH-H \longrightarrow CH_2=\dot{C}H + H^\bullet$

Less stable

(S) $CH\equiv C-H \longrightarrow CH\equiv\dot{C} + H^\bullet$

More % s-Character decreases stability of free radical

Q require least BDE and S required maximum BDE.

So, order of BDE is Q < P < R < S.

38. **(d)**

$$CH_4 \longrightarrow {}^\bullet CH_3 + H^\bullet \qquad \Delta H = 105 \text{ kcal/mol}$$

$$Cl_2 \longrightarrow Cl^\bullet + Cl^\bullet \qquad \Delta H = 58 \text{ kcal/mol}$$

$$Cl^\bullet + {}^\bullet CH_3 \longrightarrow CH_3-Cl \qquad \Delta H = -85 \text{ kcal/mol}$$

$$Cl^\bullet + H^\bullet \longrightarrow HCl \qquad \Delta H = -103 \text{ kcal/mol}$$

$$\overline{CH_4 + Cl_2 \longrightarrow CH_3-Cl + HCl \qquad \Delta H = -25 \text{ kcal/mol}}$$

Initiation step is endothermic, hence option (a) is wrong.

Propagation step involving ${}^\bullet CH_3$ formation is endothermic, hence option (b) is wrong.

Propagation step involving CH_3Cl formation is exothermic, hence option (c) is wrong.

So, overall raction is exothermic with $\Delta H^o = -25$kcal/mol, hence option (d) is correct.

39. **(c)** $K \to L \Rightarrow V$ increasing at constant P

Hence, T increases (Heating).

$L \to M \Rightarrow P$ decreasing at constant V

Hence, T decreases (Cooling),

$M \to N \Rightarrow V$ decreasing at constant P

Hence, T decreases (Cooling),

$N \to K \Rightarrow P$ increasing at constant V

Hence, T increases (Heating).

40. **(b)** L to M and N to K, both are having constant volume, therefore, these processes are isochoric.

41. **(a)** Statement 1 is true because it is not possible to convert whole of heat to work. For such a conversion, we need an efficiency of 100% but so far, we have not been able to get such a machine (carnot engine).

Statement 2 is true because it is not possible to convert the whole of heat absorbed from a reservoir into work. Some of the heat is always given to the sink.

Also, statement 2 is correct explanation for statement 1.

Thus, the correct choice is option (a).

42. **(b)** **Assertion :** For isothermal expansion,

$\Delta T = 0 \Rightarrow \Delta U = 0$

For an ideal gas, work done against vacuum is zero, *i.e.* $W = 0$

Now, $\Delta Q = \Delta U + W \Rightarrow \Delta Q = 0$

Thus, assertion is correct.

Reason : By kinetic theory of ideal gases, the volume occupied by the molecules of an ideal gas is zero.

Thus, reason is correct, but it is not the correct explanation of the assertion.

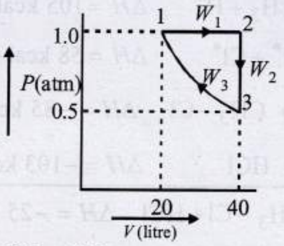
43. For adiabatic process, $W = P(V_2 - V_1)$

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

$$\Delta U = q + W = q - P(V_2 - V_1)$$
$$= 0 - 100(99 - 100) = \mathbf{100\ bar\ mL}$$
$$\Delta H = \Delta U + \Delta(PV) = \Delta U + (P_2V_2 - P_1V_1)$$
$$= 100 + [(100 \times 99) - (1 \times 100)]$$
$$= 100 + (9900 - 100) = \mathbf{9900\ bar\ mL}$$

44. 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 translational motion. Contribution from vibrational motion is not appreciable at low temperature but increases from 0 to R on raising temperature.

45. (i)



(ii) $PV = nRT$

$$T = \frac{PV}{nR} = \frac{0.5\times 40}{2\times 0.082} = 121.95\text{ K}$$

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

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

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

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

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 $= \mathbf{620.7\ J}$

In a cyclic proces, sheat absorbed is completely converted into work.

(iii) Entropy is a state function and since the system has returned to its initial state, so $\mathbf{\Delta S = 0}$. Similarly $\mathbf{\Delta H = 0}$ and $\mathbf{\Delta U = 0}$ for the same reason.

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

Topic-2: Thermochemistry

1. **(a)** C(graphite) → C(diamond) (Isothermally)

$\Delta_r G^\circ = \Delta G^\circ(\text{diamond}) - \Delta G^\circ(\text{graphite})$

$= 2.9 - 0 = 2.9\text{ kJ mol}^{-1}$

Gibbs free energy is the maximum useful work, then

$-\Delta G^\circ = w_{max} = \Delta PV$

$-2.9\times 10^3 = -\Delta P\times 2\times 10^{-6}$

$$\Delta P = \frac{2.9\times 10^3}{2\times 10^{-6}} = 1.45\times 10^9\text{ Pa} = 1.45\times 10^9\times 10^{-5}\text{ bar}$$

$= 1.45\times 10^4\text{ bar} = 14500\text{ bar}$

$P = \Delta P + P_0 = 14500 + 1 = 14501$ bar

2. **(b)** Given conditions are boiling conditions for water due to which system is in equilibrium.

$H_2O(l) \rightleftharpoons H_2O(g)$

$\Delta S_{total} = 0$

$\Delta S_{system} + \Delta S_{surroundings} = 0$

$\Delta S_{system} = -\Delta S_{surroundings}$

For process, $\Delta S_{system} > 0$

$\Delta S_{surroundings} < 0$

3. **(c)** The standard enthalpy of the combustion of glucose can be calculated by the eqn.

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

$\Delta H_C = 6\times \Delta H_f(CO_2) + 6\times \Delta H_f(H_2O) - \Delta H_f(C_6H_{12}O_6)$

$\Delta H^\circ = 6(-400) + 6(-300) - (-1300) = -2900$ kJ/mol

For one gram of glucose, enthalpy of combustion

$$\Delta H^\circ = -\frac{2900}{180} = -16.11\text{ kJ/g}$$

4. **(b)** The species in its elemental form has zero standard molar enthalpy of formation at 298 K. At 298K, Cl_2 is gas while Br_2 is liquid.

5. **(a)** Since, liquid is passing into gaseous phase so entropy will increase and at 373 K during the phase transformation, it remains at equilibrium. So, $\Delta G = 0$.

6. **(b)** $A \rightleftharpoons B$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, $\Delta G^\circ = -2.303\,RT\log_{10}K$

$-2.303\,RT\log_{10}K = \Delta H^\circ - T\Delta S^\circ$

$\Rightarrow\ 2.303\,RT\log_{10}K = T\Delta S^\circ - \Delta H^\circ$

$$\log_{10}K = \frac{T\Delta S^\circ - \Delta H^\circ}{2.303RT} = \frac{298\times 10 + 54.07\times 1000}{2.303\times 8.314\times 298} = 10$$

7. **(b)** $\Delta S = \frac{\Delta Q_{rev.}}{T}$; $75 = \frac{30\times 10^3}{T}$ $\therefore T = 400$ K

8. **(b)** ΔH_f° is the enthalpy change when 1 mole of the substance is formed from its elements in their standard states. In (a) carbon is present in diamond however, standard state of carbon is graphite. Again, in (d) CO (g) is involved so it can't be the right option. Further in (c) 2 moles of NH_3 are generated. Hence, the correct option is (b).

9. **(b)** $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$, $\Delta H = ?$

$\Delta H = \sum \Delta H_f\text{ (Product)} - \sum \Delta H_f\text{ (reactant)}$

Given, $\Delta H_f CO_2(g) = -393.5$ kJ/mol

$\Delta H_f CO(g) = -110.5$ kJ/mol

$\Delta H_f H_2O(g) = -241.8$ kJ/mol

$\therefore\ \Delta H = [\Delta H_f CO(g) + \Delta H_f H_2O(g)]$

$- [\Delta H_f CO_2(g) + \Delta H_f H_2(g)]$

$= [-110.5 + (-241.8)] - [-393.5 + 0]$

$[\because \Delta H_f(H_2)(g) = 0]$

$= 41.2\text{ kJ mol}^{-1}$

10. **(d)** $\Delta H = \Delta E + \Delta nRT$ For $\Delta H \neq \Delta E, \Delta n \neq 0$

Where Δn = no. of moles of gaseous products – no. of moles of gaseous reactants

(a) $\Delta n = 2 - 2 = 0$

(b) $\Delta n = 0$ ($\because$ they are either in solid or liquid state)

(c) $\Delta n = 1 - 1 = 0$ ($\because$ C is in solid state)

(d) $\Delta n = 2 - 4 = -2$

$\therefore$ (d) is correct answer

11. **(a)** Heat capacity at constant volume $(q_v) = \Delta E$

Heat capacity of constant pressure $(q_p) = \Delta H$

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

Δn = no. of moles of gaseous products
– no. of moles of gaseous reactants
$= 12 - 15 = -3$
$\Delta H - \Delta E = -3 \times 8.314 \times 298\,\text{J} = -7.43\,\text{kJ}$.

12. **(90.39)** $2Hg(g) + O_2(g) \rightarrow 2HgO(s)$
$\Delta_r H^\circ = 2\Delta_f H^\circ(HgO, s) - 2\Delta_f H^\circ(Hg, g) - \Delta_f H^\circ(O_2, g)$
$= 2\Delta_f H^\circ(HgO, s) - 2\Delta_f H^\circ(Hg, g)$ ... (i)
$[\because \Delta_f H^\circ(O_2, g) = 0]$

Now, $\Delta_r H^\circ$ is the heat evolved by bomb calorimeter due to the occurrence of the reaction at constant volume.
$\therefore -(Q_v)_r = \Delta_r U$
$\therefore \Delta_r H = \Delta_r U + \Delta n_g RT = -C\Delta T + \Delta n_g RT$
[where C – the heat capacity of calorimeter = 20 kJ/K at 298 K]
$= -[20(312.8 - 298)] - 3\,RT$
$= -296 - 3 \times 8.3 \times 10^{-3} \times 298\,\text{kJ} = -303.42\,\text{kJ}$
Hence, from eq. (i)
$-303.42 = 2\Delta_f H^\circ(HgO, s) - 2 \times 61.32$
or, $2\Delta_f H^\circ(HgO, s) = -180.78\,\text{kJ}$
$\therefore$ Standard Molar Enthalpy of formation of HgO
$$= \frac{-180.78}{2} = -90.39\,\text{kJ}$$
$\Rightarrow |X| = 90.39$

13. **(– 14.6)**

(i) $2Cu(s) + \frac{1}{2}O_2(g) \longrightarrow Cu_2O(s) : \Delta G^\circ = -78\ \text{kJ/mol}$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g),\ \Delta G^\circ = -178\ \text{kJ/mol}$

(i) – (ii) then

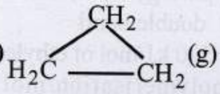
$2Cu(s) + H_2O(g) \longrightarrow Cu_2O(s) + H_2(g)$
$\Delta G^\circ = -78 + 178 = 100\,\text{kJ/mol} = 10^5\,\text{J/mol}$
Now for the above reaction
$$\Delta G = \Delta G^\circ + RT\ln\left(\frac{P_{H_2}}{P_{H_2O}}\right)$$
To prevent the above reaction: $\Delta G \geq 0$
$$\Delta G^\circ + RT\ln\left(\frac{P_{H_2}}{P_{H_2O}}\right) \geq 0$$
$$\Rightarrow\quad 10^5 + 8 \times 1250\ln\left(\frac{P_{H_2}}{P_{H_2O}}\right) \geq 0$$
$\ln P_{H_2} \geq -10 + \ln P_{H_2O}$
Now, $P_{H_2O} = X_{H_2O} \times P_{\text{total}} = 0.01 \times 1 = 10^{-2}$
$\Rightarrow\quad \ln P_{H_2} \geq -10 - 2\ln 10$
$\Rightarrow\quad \ln P_{H_2} \geq -14.6$ (Given $\ln 10 = 2.3$)
$\therefore$ Minimum $\ln P_{H_2} = -14.6$

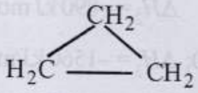
14. **(–2035)**
The chemical reaction for combustion of diborane is
$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g),\ \Delta H = ?$
For this the enthalpy change can be calculated in the following way.

$\Delta_c H = [\Delta_f H_{B_2O_3(s)} + 3\Delta_f H_{H_2O(g)}] - \Delta_f H_{B_2H_6(g)}$;
$(\because \Delta_f H_{O_2} = 2)$

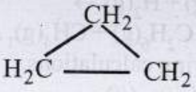
$\Delta_f H_{H_2O(g)}$ can be obtained by adding $\Delta_r H_{H_2O(l)}$ and $\Delta_r H_{H_2O(g)}$, *i.e.* $-286 + 44 = -242\,\text{kJ mol}^{-1}$
$\Delta H = [-1273 + 3 \times (-242)] - 36\,\text{kJ mol}^{-1} = -1273 - 726 - 36$
$= \mathbf{-2035\ kJ\ mol^{-1}}$

15. **(309.16)**
Given $S(s) + 3F_2(g) \rightarrow SF_6(g);\ \Delta H = -1100\,\text{kJ}$ .....(i)
$S(s) \rightarrow S(g);\ \Delta H = 275\,\text{kJ}$ .....(ii)
$1/2\,F_2(g) \rightarrow F(g);\ \Delta H = 80\,\text{kJ}$ .....(iii)
To get $SF_6(g) \rightarrow S(g) + 6F(g)$ we can proceed as
(ii) + 6 × (iii) - (i)
$\therefore SF_6(g) \rightarrow S(g) + 6F(g);\ \Delta H = 1855\,\text{kJ}$
Thus, average bond energy for S-F bond
$$= \frac{1855}{6} = \mathbf{309.16kJ}$$

16. **(–2091.32)**  $(g) \rightarrow CH_3CH = CH_2(g);$
$\Delta H = -33.0\,\text{kJ}$ ...(i)
$C(s) + O_2(g) \rightarrow CO_2(g);\ \Delta H = -393.5\text{kJ}$ ...(ii)
$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l);\ \Delta H = -285.8\,\text{kJ}$ ...(iii)
$3C(s) + 3H_2(g) \rightarrow CH_3{-}CH = CH_2(g);\ \Delta H = 20.42\,\text{kJ}$ ...(iv)
The required reaction is

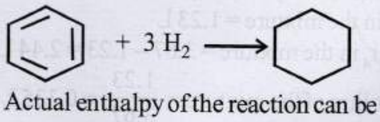
 $+ \frac{9}{2}O_2 \longrightarrow 3CO_2 + 3H_2O;\ \Delta H = ?$

To calculate the value of ΔH follow the following steps.
(i) + 3 × (ii) + 3 × (iii)] – (iv) :

 $+ (9/2)O_2 \rightarrow 3CO_2 + 3H_2O;$
$\Delta H = \mathbf{-2091.32\ kJ}$

17. **(–266)** The required thermochemical equation is
$C(g) + 4H(g) + O(g) \longrightarrow CH_3OH(l);\ \Delta H_f = ?$
$$\Delta H_f = \left[\Delta H_{C(s)\rightarrow C(g)} + 2\Delta H_{H-H} + \frac{1}{2}\Delta H_{O=O}\right]$$
$$-\left[3\Delta H_{C-H} + \Delta H_{C-O} + \Delta H_{O-H} + \Delta H_{\text{vap.}CH_3OH}\right]$$
$= [715 + 2 \times 436 + 249] - [3 \times 415 + 356 + 463 + 38]$
$= \mathbf{-266\ kJ\ mol^{-1}}$

18. **(–152)** 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 $= 3 \times (-119) = -357\,\text{kJ mol}^{-1}$



Actual enthalpy of the reaction can be evaluated as follows.

$$\Delta H_{(\text{Reaction})} = \Delta H_f^\circ(\text{Product}) - \Delta H_f^\circ(\text{Reactants})$$
$$= -156 - (49 + 0) = -205\,\text{kJ mol}^{-1}$$

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

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

19. **(–72)** $n\text{CH}_2 = \text{CH}_2 \rightarrow (\text{CH}_2 - \text{CH}_2)_n$

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.

$$\text{+}\!(\text{CH}_2 - \text{CH}_2)\!\text{+}\!\text{+}(\text{CH}_2 - \text{CH}_2)\text{+}\text{+}(\text{CH}_2 - \text{CH}_2)\text{+}\text{+}(\text{CH}_2 - \text{CH}_2)\text{+}$$

e.g. Number of single bonds formed by 4 moles of ethylene = 8

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

$= 2 \times 331 = 662$ kJ/mol of ethylene

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

$= 590$ kJ/mol of ethylene

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

20. **(–55.7)** From the given data, we can write :

(*i*) $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}; \quad \Delta H_1 = -285.8$ kJ/mol

(*ii*) $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}; \quad \Delta H_2 = -890$ kJ mol

(*iii*) $\text{C}_2\text{H}_6 + \frac{7}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}; \ \Delta H_3 = -1560$ kJ/mol

(*iv*) $\text{C(s)} + \text{O}_2 \rightarrow \text{CO}_2; \quad \Delta H_4 = -393.5$ kJ/mol

(*v*) $3\text{C(s)} + 4\text{H}_2 \rightarrow \text{C}_3\text{H}_8\text{(g)}; \quad \Delta H_5 = -103.8$ kJ/mol

The required reaction is $\text{C}_3\text{H}_8\text{(g)} + \text{H}_2\text{(g)} \rightarrow \text{C}_2\text{H}_6\text{(g)} + \text{CH}_4\text{(g)}, \Delta H = ?$

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**

21. **(50.90)** Combustion of C_2H_4 and CH_4 takes place as follows:

$$\underset{\text{1 vol.}}{\text{C}_2\text{H}_4} + 3\text{O}_2 \rightarrow \underset{\text{2 vol.}}{2\text{CO}_2} + 2\text{H}_2\text{O}$$

$$\underset{\text{1 vol.}}{\text{CH}_4} + 2\text{O}_2 \rightarrow \underset{\text{1 vol.}}{\text{CO}_2} + 2\text{H}_2\text{O}$$

Let the vol. of CH_4 in mixture $= x$ L

$\therefore$ Vol. of C_2H_4 in the mixture $= (3.67 - x)$ L

Vol. of CO_2 produced by x L of $\text{CH}_4 = x$ L and

Vol. of CO_2 produced by $(3.67 - x)$ L of $\text{C}_2\text{H}_4 = 2\,(3.67 - x)$ L

$\therefore$ Total vol. of CO_2 produced $= x + 2\,(3.67 - x)$

or $6.11 = x + 2\,(3.67 - x)$ or $x = 1.23$ L

$\therefore$ 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

[$\because$ Volume at NTP = 22.4 L]

Heat evolved due to combustion of 0.335 L of CH_4

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

Similarly, heat evolved due to combustion of 0.665 L of

$\text{C}_2\text{H}_4 = -\frac{0.665 \times 1423}{24.45} = -38.70$ kJ

$\therefore$ Total heat evolved $= 12.20 + 38.70 =$ **50.90 kJ**

22. **(–121)** The required reaction is

$$\underset{\text{Cyclohexene}}{\text{C}_6\text{H}_{10}\text{(g)}} + \text{H}_2\text{(g)} \rightarrow \underset{\text{Cyclohexane}}{\text{C}_6\text{H}_{12}\text{(g)}}, \quad \Delta H_1 = ? \qquad ...(1)$$

The given facts can be written as :

$\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(l)}, \ \Delta H_2 = -241$ kJ/mol ...(2)

$\text{C}_6\text{H}_{10}\text{(g)} + \frac{17}{2}\text{O}_2\text{(g)} \rightarrow 6\text{CO}_2\text{(g)} + 5\text{H}_2\text{O}; \Delta H_3 = -3800$ kJ/mol ...(3)

$\text{C}_6\text{H}_{12}\text{(g)} + 9\text{O}_2\text{(g)} \rightarrow 6\text{CO}_2\text{(g)} + 6\text{H}_2\text{O}, \ \Delta H_4 = -3920$ 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).

$\text{C}_6\text{H}_{10}\text{(g)} + \text{H}_2\text{(g)} \rightarrow \text{C}_6\text{H}_{12}\text{(g)}$

$$\begin{aligned}\Delta H_1 &= (\Delta H_2 + \Delta H_3) - \Delta H_4\\ &= [-241 + (-3800)] - (-3920)\\ &= (-241 - 3800) - (-3920)\\ &= -4041 + 3920 = \mathbf{-121\ kJ/mole}\end{aligned}$$

23. **(3.94)**

$$\underset{2 \times 56 + 48 = 160}{\text{Fe}_2\text{O}_3} + \underset{2 \times 27 = 54}{2\text{Al}} \rightarrow 2\text{Fe} + \text{Al}_2\text{O}_3$$

Heat of reaction $= 399 - 199 = 200$ kcal [Al and 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 $\text{Fe}_2\text{O}_3 = \frac{160}{5.2} = 30.77$ cc

Total volume $= 20 + 30.77 = 50.77$ cc

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

24. **(–372.0)** The required chemical reaction.

$2\text{C}_2\text{H}_6 + 7\text{O}_2 \longrightarrow 4\text{CO}_2 + 6\text{H}_2\text{O}; \Delta H = x$

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*) $\text{C(s)} + \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)}; \Delta H = -94.1$ kcal

(*ii*) $\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{H}_2\text{O(g)}; \Delta H = -68.3$ kcal

(*iii*) $2\text{C(s)} + 3\text{H}_2\text{(g)} \longrightarrow \text{C}_2\text{H}_6\text{(g)}; \Delta H = -21.1$ kcal

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

$$\Delta H = 4\Delta H_{\text{CO}_2} + 6\Delta H_{\text{H}_2\text{O}} - (2\Delta H_{\text{C}_2\text{H}_6} + 7\Delta H_{\text{O}_2})$$

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

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

$=$ **-372.0 kcal/mole of ethane**

25. **(–22)**

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

Formation of hydrogen chloride can be represented as

$H-H + Cl-Cl \rightarrow 2H-Cl$

Thus, the reaction involves

Cleavage of one H – H bond, $\Delta H = 104$ kcal

Cleavage of one Cl – Cl bond, $\Delta H = 58$ kcal

Formation of two H – Cl bonds, $\Delta H = 2 \times (-103)$ 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

HCl gas $= -\frac{44}{2} =$ **-22 kcal**

26. **(41.104)** The given data can be written as follows

(i) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l); \quad \Delta H = -68.3$ 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) $C_2H_4(g) + 3O_2(g) \rightarrow 2H_2O(l) + 2CO_2(g);$

$\Delta H = -337.2$ kcal

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 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

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

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

$= -41.7 + 0.596 =$ **41.104 kcal**

27. **(54.20)** The required equation is :

$2C(s) + H_2(g) \rightarrow C_2H_2; \quad \Delta H = ?$

Write the thermochemical equations for the given data

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

$\Delta H = -310.62$ kcal

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

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

For getting the above required reaction, we will have to

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

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

28. **(101.19)**

The required reaction in terms of dissociation energy is

$OH(g) \rightarrow O(g) + H(g); \quad \Delta H = ?$

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.

$OH(g) \rightarrow \frac{1}{2}H_2(g) + \frac{1}{2}O_2(g); \ \Delta H = +10.06$ kcal

[Reversing eq (i)]

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

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

$OH(g) \rightarrow O(g) + H(g); \qquad \Delta H = -101.19$ 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**.

29. **zero;** In a closed vessel, $\Delta V = 0$

30. **endothermic**

31. **(a, c)** Enthalpy of formation is the enthalpy change for formation of 1 mole of substance from its elements present in the most stable natural form.

32. **(b,d)** $\Delta S_{surr} = \frac{\Delta H}{T_{surr}}$

For endothermic reaction, if T_{surr} increases, unfavourable change in entropy of the surroundings decreases.

For exothermic reaction, if T_{surr} increases, favourable change in entropy of the surroundings decreases.

33. **(b, c, d)** All combustion reactions are exothermic in nature.

(b) Decomposition reactions are endothermic in nature.

(c) $C_2H_6(g) \longrightarrow C_2H_4(g) + H_2(g)$

More stable compound is converting into less stable compound. Thus, reaction is endothermic.

(d) Graphite $\longrightarrow$ Diamond

More stable allotrope is converting into less stable allotrope. Thus, reaction is endothermic.

34. **A – p, r, s ; B – r, s ; C – t ; D – p, q, t**

(A) $CO_2(s) \rightarrow CO_2(g)$

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) $2H^\bullet \rightarrow H_2(g)$

Entropy decreases as number of gaseous particles decreases.

(D) The transition between different allotropes is considered as phase transtion.

White and red P are allotropes.

Due to polymeric nature of red P, its entropy is less than that of white P.

Red P is more stable than white.

So ΔH is –ve.

35. (i) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

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

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

$$\Delta G^\circ = 2\Delta G^\circ_{f(NO_2)} - \Delta G^\circ_{f(N_2O_4)} = 100 - 100 = 0$$

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

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

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

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

Calculation of ΔG values :

Thus for the equilibrium $B \rightleftharpoons A$

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

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

Similarly for the equilibrium $B \rightleftharpoons C$

$$\Delta G_2^\circ = (-2.303 \times 8.314 \times 448) \log \frac{3.5}{95.2}$$

or $\Delta G_2^\circ = \mathbf{12.312\ kJ\ mol^{-1}}$

Similarly for equilibrium, $A \rightleftharpoons C$

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

Hence, we have that

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

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

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

Thus, the correct order of stability, $\boldsymbol{B > C > A}$

37. For following reaction

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$$

ΔG° can be calculated as follows :

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

$$= -394.4 - (-137.2 + \frac{1}{2} \times 0) = -257.2\,\text{kJ mol}^{-1}$$

Since,

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

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

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

38. For ionisation $\Delta H_{\text{Hydration}} > \Delta H_{\text{ionisation}}$

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

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

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

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

$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

$AlCl_3 + aq. \rightarrow AlCl_3(aq.);\ \Delta H = ?$

ΔH = Energy released during hydration
– Energy used during ionisation

$= -4665 - 3 \times 381 + 5137 = -671\,\text{kJ/mol}$

Thus, formation of ions will take place.

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

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

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

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

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

$$\text{Rate of supply of oxygen} = 0.28\,x \times \frac{13}{2} \times 3 = \mathbf{5.481\,x\ L/hr}$$

40. 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)

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

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

$\therefore$ 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

$3C + 4H_2 \rightarrow C_3H_8;\ \Delta H_1 = -20$ k cal ...(10)

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

$x + 6y = 676$

$2x + 8y = 956$

$\therefore x = 82$ 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**