CHAPTER 6 Thermodynamics

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. A system is said to be .... if it can neither exchange matter nor energy with the surroundings. *(1993 - 1 Mark)*
2. The heat content of the products is more than that of the reactants in an .... reaction. *(1993 - 1 Mark)*
3. Enthalpy is an .... property. *(1997 - 1 Mark)*

B True / False

1. First law of thermodynamics is not adequate in predicting the direction of a process. *(1982 - 1 Mark)*
2. Heat capacity of a diatomic gas is higher than that of a monoatomic gas. *(1985 - ½ Mark)*

C MCQs with One Correct Answer

1. The difference between heats of reaction at constant pressure and constant volume for the reaction : $2\,C_6H_6(l) + 15O_{2(g)} \rightarrow 12CO_2(g) + 6H_2O(l)$ at 25°C in kJ is *(1991 - 1 Mark)*

   (a) –7.43 (b) +3.72
   (c) –3.72 (d) +7.43

2. 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) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

3. 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

4. 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.

5. 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.

6. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0L, 95(K) → (4.0 atm, 5.0 L, 245K) with a change in internal energy, $\Delta U = 30.0\ L\,atm$. 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

7. Which of the reaction defines ΔH_f° ? *(2003S)*

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

8. Two moles of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre 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

9. 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

10. The direct conversion of A to B is difficult, hence it is carried out by the following shown path :

$$\begin{tikzcd}
C \arrow[r] & D \arrow[d] \\
A \arrow[u] & B
\end{tikzcd}$$

Given $\Delta S_{(A\rightarrow C)} = 50\ e.u.$, $\Delta S_{(C\rightarrow D)} = 30\ e.u.$, $\Delta S_{(B\rightarrow D)} = 20\ e.u.$, where e.u. is the entropy unit, then $\Delta S_{(A\rightarrow B)}$ is *(2006 - 3M, –1)*

   (a) +60 e.u. (b) +100 e.u.
   (c) –60 e.u. (d) –100 e.u.

11. 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

12. 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) $\Delta G = -ve, \Delta S = +ve$

13. 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) $CH_4(g)$

14. 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 *(JEE Advanced 2013-I)*

(a) +2900 kJ (b) –2900 kJ
(c) –16.11 kJ (d) +16.11 kJ

15. For the process *(JEE Adv. 2014)*

$H_2O(l) \rightarrow H_2O(g)$

at $T = 100°C$ and 1 atmosphere pressure, the correct choice is

(a) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} > 0$
(b) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} < 0$
(c) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} > 0$
(d) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} < 0$

16. 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) *(JEE Adv. 2016)*

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

D MCQs with One or More Than One Correct

1. Identify the intensive quantities from the following: *(1993 - 1 Mark)*

(a) Enthalpy (b) Temperature
(c) Volume (d) Refractive Index

2. 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

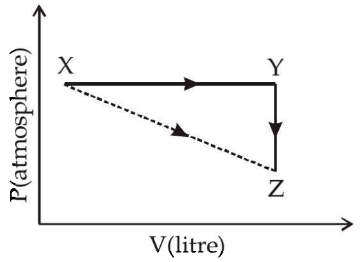
3. Among the following the state function(s) is (are) *(2009)*

(a) Internal energy
(b) Irreversible expansion work
(c) Reversible expansion work
(d) Molar enthalpy

4. Among the following, the intensive property is (properties are) *(2010)*

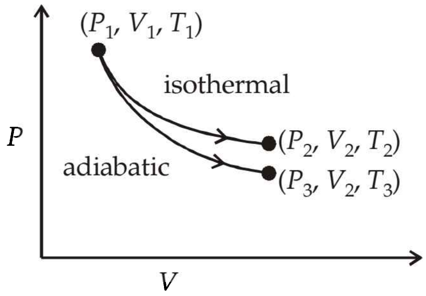
(a) molar conductivity (b) electromotive force
(c) resistance (d) heat capacity

5. 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) $\Delta S_{x\rightarrow z} = \Delta S_{x\rightarrow y} + \Delta S_{y\rightarrow z}$
(b) $w_{x\rightarrow z} = w_{x\rightarrow y} + w_{y\rightarrow z}$
(c) $w_{x\rightarrow y\rightarrow z} = w_{x\rightarrow y}$
(d) $\Delta S_{x\rightarrow y\rightarrow z} = \Delta S_{x\rightarrow y}$

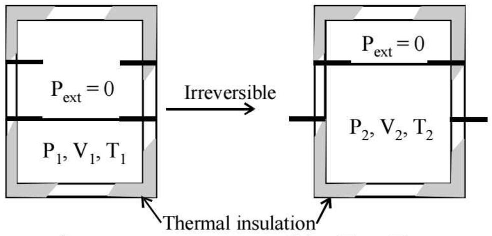
6. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct ?



(2012 - II)

(a) $T_1 = T_2$
(b) $T_3 > T_1$
(c) $w_{\text{isothermal}} > w_{\text{adiabatic}}$
(d) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

7. 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, *(JEE Adv. 2014)*



(a) $q = 0$ (b) $T_2 = T_1$
(c) $P_2V_2 = P_1V_1$ (d) $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

E Subjective Problems

1. The enthalpy for the following reaction ($\Delta H°$) 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.

2. The molar heats of combustion of $C_2H_2(g)$, C(graphite) and $H_2(g)$ are 310.62 kcal, 94.05 kcal and 68.32 kcal, respectively. Calculate the standard heat of formation of $C_2H_2(g)$. ***(1983 - 2 Marks)***

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

4. Given the following standard heats of reactions :
   (i) heat of formation of water = –68.3 kcal;
   (ii) heat of combustion of acetylene = –310.6 kcal;
   (iii) heat of combustion of eth ylene = –337.2 kcal;
   Calculate the heat of reaction for the hydrogenation of acetylene at constant volume (25°C). ***(1984 - 4 Marks)***

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

6. The standard molar heats of formation of ethane, carbon dioxide and liquid water are –21.1, –94.1 and –68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane. ***(1986 - 2 Marks)***

7. An intimate mixture of ferric oxide, Fe_2O_3, and aluminium, Al, is used in solid fuel rockets. Calculate the fuel value per gram and fuel value per cc of the mixture. Heats of formation and densities are as follows : ***(1988 - 2 Marks)***
   $H_f(Al_2O_3) = 399$ kcal/mole;
   $H_f(Fe_2O_3) = 199$ kcal/mole;
   Density of $Fe_2O_3 = 5.2$ g/cc;
   Density of Al = 2.7 g/cc.

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

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

10. 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)***
    $\Delta H^\circ_{combustion}$(ethane) = –372.0
    $\Delta H^\circ_{combustion}$(propane) = –530.0
    $\Delta H^\circ_{C(s) \rightarrow C(g)}$ = 172.0
    Bond energy of H–H = 104.0
    ΔH°_f of $H_2O(l)$ = –68.0
    ΔH°_f of $CO_2(g)$ = –94.0

11. A gas mixture of 3.67 litres of ethylene and methane on complete combustion at 25°C produces 6.11 litres of CO_2. Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are –1423 and –891 kJ mol^{-1} at 25°C. ***(1991 - 5 Marks)***

12. Determine the enthalpy change of the reaction.
    $C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$, at 25°, using the given heat of combustion values under standard conditions:

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

    The standard heat of formation of $C_3H_8(g)$ is –103.8 kJ/mol. ***(1992 - 3 Marks)***

13. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and 6x litre/hour of O_2) is to be readjusted for butane, C_4H_{10}. In order to get the same calorific output, what should be the rate of supply of butane and oxygen ? Assume that losses due to incomplete combustion, etc, are the same for both the fuels and the gases behave ideally. ***(1993 - 3 Marks)***
    Heats of combustion :
    $$CH_4 = 809\ \text{kJ/mol};\ C_4H_{10} = 2878\ \text{kJ/mol}$$

14. The polymerisation of ethylene to linear polyethylene is represented by the reaction ***(1994 - 2 Marks)***
    $$nCH_2{=}CH_2 \longrightarrow \left[CH_2 - CH_2 \right]_n$$
    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.

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

16. Compute the heat of formation of liquid methyl alcohol in kilojoules per mole, using the following data. Heat of vaporization of liquid methyl alcohol = 38 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states; H, 218 kJ/mol; C, 715 kJ/mol; O, 249kJ / mol.
    Average bond energies :
    C – H = 415kJ/mol, C – O = 365 kJ/mol, O – H = 463 kJ/mol ***(1997 - 5 Marks)***

17. Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution. (Ionisation energy for Al = 5137 kJ mol^{-1}; $\Delta H_{hydration}$ for Al^{3+} = –4665 kJ mol^{-1}; $\Delta H_{hydration}$ for Cl^- = – 381 kJ mol^{-1}.) ***(1997 - 2 Marks)***

18. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of $CO_2(g)$, $H_2O(l)$ and propene(g) are – 393.5, – 285.8 and 20.42 kJ mol^{-1} respectively. The enthalpy of isomerisation of cyclopropane to propene is – 33.0 kJ mol^{-1}. ***(1998 - 5 Marks)***

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

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

22. 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.

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

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

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

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

23. When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1, 2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate 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)***

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

25. C_v value of He is always 3R/2 but C_v value of H_2 is 3R/2 at low temperature and 5R/2 at moderate temperature and more than 5R/2 at higher temperature explain in two to three lines. ***(2003 - 2 Marks)***

26. An insulated container contains 1 mol of a liquid, molar volume 100 ml, at 1 bar. When liquid is steeply pressed to 100 bar, volume decreases to 99 ml. Find. ΔH and ΔU for the process. ***(2004 - 2 Marks)***

27. 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 : $\Delta G_f^\circ(N_2O_4) = 100 kJ;\ \Delta G_f^\circ(NO_2) = 50\ kJ$

(i) Find ΔG of the reaction at 298 K.
(ii) Find the direction of the reaction

28. 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)***

F Match The Following

DIRECTION (Q. 1 & 2): *Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example :*

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

	p	q	r	s	t
A	●	○	○	●	●
B	○	●	●	○	○
C	●	●	○	○	○
D	○	○	○	●	○

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

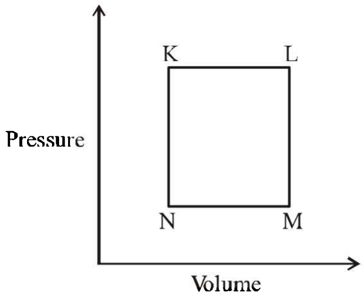
Column-I	**Column-II**
(A) $CO_2(s) \rightarrow CO_2(g)$	(p) phase transition
(B) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	(q) allotropic change
(C) $2H^\bullet \rightarrow H_2(g)$	(r) ΔH is positive
(D) $P_{(white,\ solid)} \rightarrow P_{(red,\ solid)}$	(s) ΔS is positive
	(t) ΔS is negative

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

	Column-I		**Column-II**
(A)	Freezing of water at 273 K and 1 atm	(p)	$q = 0$
(B)	Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(q)	$w = 0$
(C)	Mixing of equal volumes of two ideal gases at constant temperature and pressure 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)	$\Delta G = 0$

G Comprehension Based Questions

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



(JEE Adv. 2013)

1. 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
2. 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

H Assertion & Reason Type Questions

1. 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)*

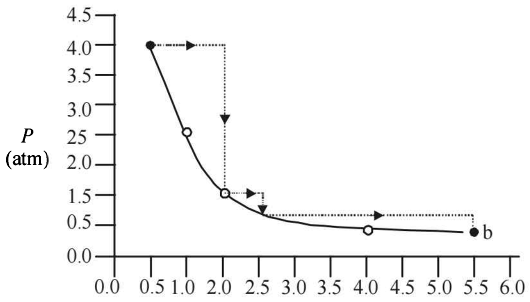
   (a) If both assertion and reason are CORRECT, and reason is the CORRECT explanation of the assertion.
   (b) If both assertion and reason are CORRECT, but reason is NOT the CORRECT explanation of the assertion.
   (c) If assertion is CORRECT, but reason is INCORRECT.
   (d) If assertion is INCORRECT, but reason is CORRECT.
2. **Statement - 1 :** There is a natural asymmetry between converting work to heat and converting heat to work.and

   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)*

   (a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
   (b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
   (c) Statement-1 is True, Statement-2 is False
   (d) Statement-1 is False, Statement-2 is True

I Integer Value Correct Type

1. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1}, the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is *(2009 - 6M)*
2. One mole of an ideal gas is taken from *a* to *b* along two paths denoted by the solid and the dashed lines as shown in the graphs below. If the work done along the solid line path w_s and that along the dotted line path is w_d, then the integer closest to the ratio w_d / w_s is : *(2010)*



Section-B JEE Main / AIEEE

1. If an endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point, then
   (a) ΔH is –ve, ΔS is +ve **[2002]**
   (b) ΔH and ΔS both are +ve
   (c) ΔH and ΔS both are –ve
   (d) ΔH is +ve, ΔS is -ve

2. A heat engine abosrbs heat Q_1 at temperature T_1 and heat Q_2 at temperature T_2. Work done by the engine is J $(Q_1 + Q_2)$. This data **[2002]**
   (a) violates 1st law of thermodynamics
   (b) violates 1st law of thermodynamics if Q_1 is –ve
   (c) violates 1st law of thermodynamics of Q_2 is –ve
   (d) does not violate 1st law of thermodynamics.

3. For the reactions, **[2002]**
   $2C + O_2 \rightarrow 2CO_2$; $\Delta H = -393$ J
   $2Zn + O_2 \rightarrow 2ZnO$; $\Delta H = -412$ J
   (a) carbon can oxidise Zn
   (b) oxidation of carbon is not feasible
   (c) oxidation of Zn is not feasible
   (d) Zn can oxidise carbon.

4. The heat required to raise the temperature of body by 1 K is called **[2002]**
   (a) specific heat (b) thermal capacity
   (c) water equivalent (d) none of these.

5. The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy ? **[2003]**
   (a) > 40 kJ (b) < 40 kJ
   (c) Zero (d) 40 kJ

6. If at 298 K the bond energies of C — H, C — C, C = C and H — H bonds are respectively 414, 347, 615 and 435 kJ mol^{-1}, the value of enthalpy change for the reaction
   $H_2C = CH_2(g) + H_2(g) \rightarrow H_3C — CH_3(g)$ at 298 K will be **[2003]**
   (a) – 250 kJ (b) + 125 kJ
   (c) – 125 kJ (d) + 250 kJ

7. In an irreversible process taking place at constant T and P and in which only pressure-volume work is being done, the change in Gibbs free energy (dG) and change in entropy (dS), satisfy the criteria **[2003]**
   (a) $(dS)_{V,E} > 0, (dG)_{T,P} < 0$ (b) $(dS)_{V,E} = 0, (dG)_{T,P} = 0$
   (c) $(dS)_{V,E} = 0, (dG)_{T,P} > 0$ (d) $(dS)_{V,E} < 0, (dG)_{T,P} < 0$

8. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_c is **[2003]**
   (a) $-\Delta G = RT \ln K_c$ (b) $\Delta G^o = RT \ln K_c$
   (c) $-\Delta G^o = RT \ln K_c$ (d) $\Delta G = RT \ln K_c$

9. The enthalpy change for a reaction does **not** depend upon **[2003]**
   (a) use of different reactants for the same product
   (b) the nature of intermediate reaction steps
   (c) the differences in initial or final temperatures of involved substances
   (d) the physical states of reactants and products

10. An ideal gas expands in volume from 1×10^{-3} to 1×10^{-2} m^3 at 300 K against a constant pressure of 1×10^5 Nm^{-2}. The work done is **[2004]**
    (a) 270 kJ (b) – 900 kJ
    (c) – 900 (d) 900 kJ

11. The enthalpies of combustion of carbon and carbon monoxide are – 393.5 and – 283 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide per mole is
    (a) – 676.5 kJ (b) 676.5 kJ **[2004]**
    (c) 110.5 kJ (d) – 110.5 kJ

12. Consider an endothermic reaction X → Y with the activation energies E_b and E_f for the backward and forward reactions, respectively. In general **[2005]**
    (a) there is no definite relation between E_b and E_f
    (b) $E_b = E_f$
    (c) $E_b > E_f$
    (d) $E_b < E_f$

13. Consider the reaction : $N_2 + 3H_2 \rightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔU are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ? **[2005]**
    (a) $\Delta H > \Delta U$ (b) $\Delta H < \Delta U$
    (c) $\Delta H = \Delta U$ (d) $\Delta H = 0$

14. If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and ΔH_f for the formation of XY is – 200 kJ mole^{-1}. The bond dissociation energy of X_2 will be **[2005]**
    (a) 400 kJ mol^{-1} (b) 300 kJ mol^{-1}
    (c) 200 kJ mol^{-1} (d) 100 kJ mol^{-1}

15. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct? **[2006]**

(a) $(T_f)_{rev} = (T_f)_{irrev}$

(b) $T_f = T_i$ for both reversible and irreversible processes

(c) $(T_f)_{irrev} > (T_f)_{rev}$

(d) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process

16. The standard enthalpy of formation ($\Delta_f H^o$) at 298 K for methane, $CH_4(g)$ is -74.8 kJ mol^{-1}. The additional information required to determine the average energy for C – H bond formation would be **[2006]**

(a) the first four ionization energies of carbon and electron gain enthalpy of hydrogen

(b) the dissociation energy of hydrogen molecule, H_2

(c) the dissociation energy of H_2 and enthalpy of sublimation of carbon

(d) latent heat of vapourization of methane

17. The enthalpy changes for the following processes are listed below : **[2006]**

$Cl_2(g) \rightarrow 2Cl(g)$, 242.3 kJ mol^{-1}

$I_2(g) \rightarrow 2I(g)$, 151.0 kJ mol^{-1}

$ICl(g) \rightarrow I(g) + Cl(g)$, 211.3 kJ mol^{-1}

$I_2(s) \rightarrow I_2(g)$, 62.76 kJ mol^{-1}

Given that the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation for ICl(g) is : **[2006]**

(a) +16.8 kJ mol^{-1} (b) +244.8 kJ mol^{-1}

(c) –14.6 kJ mol^{-1} (d) –16.8 kJ mol^{-1}

18. $(\Delta H - \Delta U)$ for the formation of carbon monoxide (CO) from its elements at 298 K is **[2006]**

($R = 8.314$ J K^{-1} mol^{-1})

(a) –2477.57 J mol^{-1} (b) 2477.57 J mol^{-1}

(c) –1238.78 J mol^{-1} (d) 1238.78 J mol^{-1}

19. In conversion of lime-stone to lime,

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ the values of $\Delta H°$ and $\Delta S°$ are + 179.1 kJ mol^{-1} and 160.2 J/K respectively at 298 K and 1 bar. Assuming that $\Delta H°$ and $\Delta S°$ do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is **[2007]**

(a) 1118 K (b) 1008 K

(c) 1200 K (d) 845 K.

20. Assuming that water vapour is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vapourised at 1 bar pressure and 100°C, (given : molar enthalpy of vapourisation of water at 1 bar and 373 K = 41 kJ mol^{-1} and R = 8.3 J mol^{-1} K^{-1}) will be **[2007]**

(a) 41.00 kJ mol^{-1} (b) 4.100 kJ mol^{-1}

(c) 3.7904 kJ mol^{-1} (d) 37.904 kJ mol^{-1}

21. Identify the correct statement regarding a spontaneous process: **[2007]**

(a) Lowering of energy in the process is the only criterion for spontaneity.

(b) For a spontaneous process in an isolated system, the change in entropy is positive.

(c) Endothermic processes are never spontaneous.

(d) Exothermic processes are always spontaneous.

22. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below:

$$\frac{1}{2}Cl_2(g) \xrightarrow{\frac{1}{2}\Delta_{diss}H^{\ominus}} Cl(g) \xrightarrow{\Delta_{eg}H^{\ominus}} Cl^-(g)$$

$$\xrightarrow{\Delta_{Hyd}H^{\ominus}} Cl^-(aq)$$

(using the data,

$\Delta_{diss} H^{\ominus}_{Cl_2} = 240$ kJ mol^{-1}, $\Delta_{eg} H^{\ominus}_{Cl} = -349$ kJ mol^{-1},

$\Delta_{hyd} H^{\ominus}_{Cl^-} = -381$ kJ mol^{-1}), will be **[2008]**

(a) + 152 kJ mol^{-1} (b) – 610 kJ mol^{-1}

(c) – 850 kJ mol^{-1} (d) + 120 kJ mol^{-1}

23. Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 J K^{-1} mol^{-1}, respectively. For the reaction,

$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightarrow XY_3, \Delta H = -30\text{kJ}$, to be at equilibrium, the temperature will be **[2008]**

(a) 1250 K (b) 500 K

(c) 750 K (d) 1000 K

24. On the basis of the following thermochemical data : ($\Delta_f G° H^+_{(aq)} = 0$) **[2009]**

$H_2O(l) \rightarrow H^+(aq) + OH^-(aq); \Delta H = 57.32\text{kJ}$

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell);\ \Delta H = -286.20\text{kJ}$

The value of enthalpy of formation of OH^- ion at 25° C is:

(a) –228.88 kJ (b) +228.88 kJ

(c) –343.52 kJ (d) –22.88 kJ

25. The standard enthalpy of formation of NH_3 is – 46.0 kJ mol^{-1}. If the enthalpy of formation of H_2 from its atoms is – 436 kJ mol^{-1} and that of N_2 is – 712 kJ mol^{-1}, the average bond enthalpy of N – H bond in NH_3 is **[2010]**

(a) – 964 kJ mol^{-1} (b) + 352 kJ mol^{-1}

(c) + 1056 kJ mol^{-1} (d) – 1102 kJ mol^{-1}

26. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when **[2010]**

(a) $T_e > T$ (b) $T > T_e$

(c) T_e is 5 times T (d) $T = T_e$

27. The entropy change involved in the isothermal reversible expansion of 2 mole of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27°C is: **[2011]**

(a) 38.3 $J\ mol^{-1}\ K^{-1}$ (b) 35.8 $J\ mol^{-1}\ K^{-1}$
(b) 32.3 $J\ mol^{-1}\ K^{-1}$ (d) 42.3 $J\ mol^{-1}\ K^{-1}$

28. The incorrect expression among the following is : **[2012]**

(a) $\dfrac{\Delta G_{system}}{\Delta S_{total}} = -T$

(b) In isothermal process, $w_{reversible} = -nRT\ \ell n \dfrac{V_f}{V_i}$

(c) $\ln K = \dfrac{\Delta H^\circ - T\Delta S^\circ}{RT}$ (d) $K = e^{-\Delta G^\circ / RT}$

29. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be: **[JEE M 2013]**
(R = 8.314 J/mol K) (ln 7.5 = 2.01)

(a) q = + 208 J, w = − 208 J (b) q = − 208 J, w = − 208 J
(c) q = − 208 J, w = + 208 J (d) q = + 208 J, w = + 208 J

30. For complete combustion of ethanol,

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l),$$

the amount of heat produced as measured in bomb calorimeter, is 1364.47 $kJ\ mol^{-1}$ at 25°C. Assuming ideality the enthalpy of combustion, Δ_cH, for the reaction will be: ($R = 8.314\ kJ\ mol^{-1}$) **[JEE M 2014]**

(a) −1366.95 $kJ\ mol^{-1}$ (b) −1361.95 $kJ\ mol^{-1}$
(c) −1460.95 $kJ\ mol^{-1}$ (d) −1350.50 $kJ\ mol^{-1}$

31. The heats of combustion of carbon and carbon monoxide are –393.5 and –283.5 $kJ\ mol^{-1}$, respectively. The heat of formation (in kJ) of carbon monoxide per mole is : **[JEE M 2016]**

(a) –676.5 (b) – 110.5
(c) 110.5 (d) 676.5

6 Thermodynamics

Section-A : JEE Advanced/ IIT-JEE

A **1.** isolated **2.** endotherimic **3.** extensive

B **1.** T **2.** F

C **1.** (a) **2.** (d) **3.** (b) **4.** (c) **5.** (a) **6.** (c) **7.** (b) **8.** (c)
9. (b) **10.** (a) **11.** (b) **12.** (a) **13.** (b) **14.** (c) **15.** (b) **16.** (c)

D **1.** (b, d) **2.** (b, c, d) **3.** (a,d) **4.** (a, b) **5.** (a, c) **6.** (a, c, d) **7.** (a, b, c)

E **1.** 101.19 kcal **2.** 54.20 kcal **4.** 41.104 kcal
5. – 22 kcal **6.** – 372.0 kcal/mole of ethane **7.** 3.94 kcal/cc **8.** 319.1 g
9. – 121 kJ/mole **10.** 82 kcal, 99 kcal **11.** 50.90 kJ **12.** – 55.7 kJ/mole
13. 0.2803 *x l* /hr, 5.461 *x l*/hr **14.** – 72. kJ/mole **15.** – 152 kJ/mole
16. – 266 kJ/mole **17.** ionic **18.** –2091.32 kJ **19.** 309.16 kJ
20. – 115.41 joules **22.** – 2035 kJ/mole
23. + 15.992 kJ/mole, +12.312 kJ/mole –3.688 kJ/mole, B > C > A
24. (ii) – 6.13 L atm, 620.7 J, (iii) 0, 0, 0 **26.** 9900 bar mL, 100 bar mL
27. (i) – 56.0304 L atm ; (ii) forward **28.** 557 kJ mol^{-1}

F **1.** A - p, r, s; B - r, s; C -t; D - p, q, t
2. A - r, t; B - p, q, s; C -p, q, s; D - p, q, s, t

G **1.** (c) **2.** (b)

H **1.** (b) **2.** (a)

I **1.** 9 **2.** 2

Section-B : JEE Main/ AIEEE

1. (b) **2.** (a) **3.** (d) **4.** (b) **5.** (c) **6.** (c) **7.** (a)
8. (c) **9.** (b) **10.** (c) **11.** (d) **12.** (d) **13.** (b) **14.** (N)
15. (c) **16.** (c) **17.** (a) **18.** (d) **19.** (a) **20.** (d) **21.** (b)
22. (b) **23.** (c) **24.** (a) **25.** (b) **26.** (b) **27.** (a) **28.** (c)
29. (a) **30.** (a) **31.** (b)

Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. **isolated**
2. **endothermic**
3. **extensive** (because its value does not depend on quantity of substance)

B. True/False

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

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

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

C. MCQs with One Correct Answer

1. **(a)** **TIPS/Formulae :**

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 $= 12 - 15 = -3$

$\Delta H - \Delta E = -3 \times 8.314 \times 298\,J = -7.43$ kJ.

2. (d) **TIPS/Formulae :**

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

3. (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

$\Delta H_f H_2O_{2(g)} = -241.8$ kJ/mol

$$\therefore\ \Delta H = [\Delta H_f CO_{(g)} + \Delta H_f H_2O_{(g)}] - [\Delta H_f CO_{2(g)} + \Delta H_f H_{2(g)}]$$

$$= [-110.5 + (-241.8)] - (-393.5 + 0) \quad \left[\because \Delta H_f (H_2)_g = 0\right]$$

$= 41.2$ kJ mol^{-1}

4. (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.

5. (a) Work is not a state function because it depends upon the path followed.

6. (c) **TIPS/Formulae :**

$\Delta H = \Delta U + P_2V_2 - P_1V_1$ Given, $\Delta U = 30.0$ L atm

$P_1 = 2.0$ atm, $V_1 = 3.0$ L, $T_1 = 95$ K

$P_2 = 4.0$ atm, $V_2 = 5.0$ L, $T_2 = 245$ K

$\Delta H = \Delta U + P_2V_2 - P_1V_1$

$= 30 + (4 \times 5) - (2 \times 3) = 30 + 20 - 6 = 44$ L atm.

7. (b) **TIPS/Formulae :**

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).

8. (c) $\Delta H = nC_p\Delta T$ solution; since $\Delta T = 0$ so, $\Delta H = 0$

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

10. (a) $\Delta S_{(A \to B)} = \Delta S_{(A \to C)} + \Delta S_{(C \to D)} - \Delta S_{(B \to D)}$

$= 50 + 30 - 20 = 60$ e.u.

11. (b) $A \rightleftharpoons B$

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

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

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

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

12. (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, $\Delta G = 0$.

13. (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.

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

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

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

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

For one gram of glucose, enthalpy of combustion

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

15. (b) Given conditions are boiling conditions for water due to which

$\Delta S_{total} = 0$

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

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

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

$\Delta S_{surroundings} < 0$

16. (c) From 1st law of thermodynamics

$q_{sys} = \Delta U - w = 0 - [-P_{ext} \cdot \Delta V]$

$= 3.0\,\text{atm} \times (2.0\,L - 1.0\,L) = 3.0$ L-atm

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

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

D. MCQs with One or More Than One Correct

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

2. **(b, c, d)** All combustion reactions are exothermic in nature.
3. **(a,d)** Internal energy and molar enthalpy are state functions. Work (reversible or irreversible) is a path function.
4. **(a, b)** Mass independent properties (molar conductivity and electromotive force) are intensive properties. Resistance and heat capacity are mass dependent, hence extensive properties.
5. **(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].
6. **(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.
7. **(a, b, c)** Since the vessel is thermally insulated, $q = 0$

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

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

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

E. Subjective Problems

1. The required reaction in terms of dissociation energy is

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

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.

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

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

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

$$OH(g) \to O(g) + H(g); \qquad \Delta H = -101.19 \text{ kcal (adding)}$$

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**.

2. The required equation is :

$2C_{(s)} + H_{2(g)} \to C_2H_2; \quad \Delta H = ?$

Write the thermochemical equations for the given data

(i) $C_2H_{2\,(g)} + \frac{5}{2}O_{2(g)} \to 2CO_{2(g)} + H_2O_{(\ell)}; \quad \Delta H = -310.62$ kcal

(ii) $C_{(s)} + O_{2(g)} \to CO_{2(g)}; \quad \Delta H = -94.05$ kcal

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

For getting the above required reaction, we will have to

NOTE :

(a) Bring C_2H_2 in the product that can be done by reversing the equation (i) to give equation (iv).

(b) Multiply equation (ii) by 2 to get 2C atoms in the reactants and thus equation (v) is obtained.

(c) Keep equation (iii) as such.

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

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

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

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

On adding, $2C + H_2 \to C_2H_2; \ \Delta H = 54.20$ kcal

Hence the standard heat of formation of $C_2H_2(g)$

= **54.20 kcal**

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

4. The given data can be written as follows

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

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

$\Delta H = -310.6$ kcal

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

The required thermochemical equation is

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

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

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

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

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

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

5.

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

$\therefore$ ΔH of the reaction $= (104 + 58) - 2(103)$

$= 162 - 206 = - 44$ kcal

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

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

6. The required chemical reaction.

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

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

(*ii*) $H_2(g) + ½O_2(g) \longrightarrow H_2O(g);$ $\Delta H = -68.3$ kcal

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

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

$\Delta H = 4\Delta H_{CO_2} + 6\Delta H_{H_2O} - (2\Delta H_{C_2H_6} + 7\Delta H_{O_2})$

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

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

$=$ **–372.0 kcal/mole of ethane**

7. $Fe_2O_3 \quad + \quad 2Al \quad \rightarrow 2Fe + Al_2O_3$

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

Heat of reaction $= 399 - 199 = 200$ kcal [Al & Fe are in their standard states]

Total weight of reactants $= 160 + 54 = 214$ g

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

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

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

Total volume $= 20 + 30.77 = 50.77$ cc

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

8. 100 g of glucose = 1560 kJ

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

Energy left unutilised in body $= 1560 - 780 = 780$ kJ

Energy to be given out $= 1560 - 780 = 780$ kJ

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

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

9. The required reaction is

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

Cyclohexene Cyclohexane

The given facts can be written as :

$H_2(g) + ½O_2(g) \rightarrow H_2O, \quad \Delta H_2 = -241$ kJ/mol ...(2)

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

$C_6H_{12}(g) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O, \ \Delta H_4 = -3920$ kJ/mol ...(4)

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

$C_6H_{10}(g) + H_2(g) \rightarrow C_6H_{12}(g)$

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

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

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

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

10. 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**

11. Combustion of C_2H_4 and CH_4 takes place as follows :

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

1 vol. 2 vol.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

1 vol. 1 vol.

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 $CH_4 = x\,l$ and
Vol. of CO_2 produced by $(3.67 - x)\,l$ of $C_2H_4 = 2\,(3.67 - x)\,l$
$\therefore$ 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 $= 3.67 - 1.23 = 2.44\,l$

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

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

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

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

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

Heat evolved due to combustion of $0.335\,l$ of CH_4

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

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

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

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

12. From the given data, we can write :

(*i*) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O;$ $\Delta H_1 = -285.8$ kJ/mol
(*ii*) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O;$ $\Delta H_2 = -890$ kJ mol
(*iii*) $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O;$ $\Delta H_3 = -1560$ kJ/mol
(*iv*) $C(s) + O_2 \rightarrow CO_2;$ $\Delta H_4 = -393.5$ kJ/mol
(*v*) $3C(s) + 4H_2 \rightarrow C_3H_8(g);$ $\Delta H_5 = -103.8$ kJ/mol

The required reaction is $C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g),\ \Delta H = ?$

It can be obtained by the following calculations.

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

In other words, $\Delta H = 3\Delta H_4 - \Delta H_5 + 5\Delta H_1 - \Delta H_2 - \Delta H_3$
$\therefore \Delta H = 3(-393.5) - (-103.8) + 5(-285.8) + 890 + 1560$
$= -2609.5 + 2553.8 =$ **-55.7 kJ/mol**

13. Combustion of CH_4 and C_4H_{10} takes place as follows
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O,\ \Delta H = -809$ kJ mol^{-1}
$C_4H_{10} + 13/2O_2 \rightarrow 4CO_2 + 5H_2O,\ \Delta H = -2878$ kJ mol^{-1}
In order to get the same calorific output due to C_4H_{10},

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

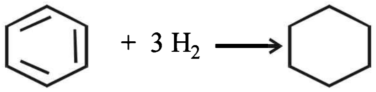
Rate of supply of oxygen $= 0.2803\,x \times \dfrac{13}{2} \times 3 =$ **$5.481\,x\ l$/hr**

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

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

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**

15. 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 $= 3 \times -119 = -357$ kJ mol^{-1}

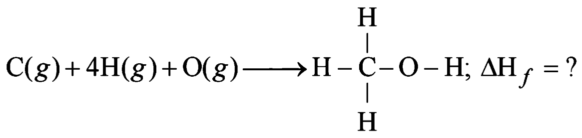


Actual enthalpy of the reaction can be evaluated as follows.

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

$$\therefore \text{Resonance energy} = \Delta H_{\text{Exp}} - \Delta H_{\text{cal}}$$
$$= -357 - (-205) = \mathbf{-152 kJ\ mol^{-1}}$$

16. The required thermochemical equation is



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

$$\Delta H_f = \left[\Delta H_{C(s)\rightarrow C(g)} + 2\Delta H_{H-H} + \frac{1}{2}\Delta H_{O=O}\right]$$
$$- \left[3\Delta H_{C-H} + \Delta H_{C-O} + \Delta H_{O-H} + \Delta H_{\text{vap.}CH_3OH}\right]$$
$$= [715 + 2 \times 436 + 249] - [3 \times 415 + 356 + 463 + 38]$$
$$= \mathbf{-266\ kJ\ mol^{-1}}$$

17. **TIPS/Formulae :**

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

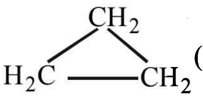
Total hydration energy of Al^{3+} & $3Cl^-$ ions of $AlCl_3$ ($\Delta H_{\text{hydration}}$)
= (Hydration energy of Al^{3+} + 3 × Hydration energy of Cl^-)
$= [-4665 + 3\,(-381)]$kJ mole^{-1} $= -5808$ kJ mole^{-1}

NOTE : This amount of energy is more than that required for the ionisation of Al into Al^{3+} (Ionisation energy of Al to $Al^{3+} = 5137$ kJ mol^{-1}). Due to this reason, $AlCl_3$ becomes ionic in aqueous solution. In aqueous solution it exists in ionic form as below

$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$
$AlCl_3 + aq. \rightarrow AlCl_{3(aq.)};\ \Delta H = ?$

ΔH = Energy released during hydration
– Energy used during ionisation
$= -4665 - 3 \times 381 + 5137 = -671$ kJ/mol

Thus formation of ions will take place.

18.  $(g) \rightarrow CH_3CH=CH_2(g)$;

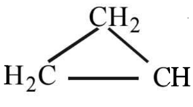
$\Delta H = -33.0\ kJ$ ...(i)

$C + O_2 \rightarrow CO_2(g); \Delta H = -393.5 kJ$ ...(ii)

$H_2 + 1/2 O_2 \rightarrow H_2O_{(l)}; \Delta H = -285.8\ kJ$ ...(iii)

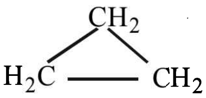
$3C + 3H_2 \rightarrow CH_3{-}CH=CH_{2(g)}; \Delta H = 20.42\ kJ$ ...(iv)

The required reaction is

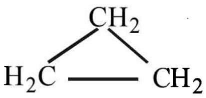
 $+ \frac{9}{2}O_2 \longrightarrow 3CO_2 + 3H_2O; \quad \Delta H = ?$

To calculate the value of ΔH follow the following steps.

(iv) – (i) yields

$3C + 3H_2 \rightarrow$  $; \Delta H = 53.42\ kJ$ ...(v)

[3 × (ii) + 3 × (iii)] – (v) yields]

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

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

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

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

$1/2\ F_{2(g)} \rightarrow F_{(g)}; \Delta H = 80\ kJ$ .....(iii)

To get $SF_{6(g)} \rightarrow S_{(g)} + 6F_{(g)}$ we can proceed as

(ii) + 6 × (iii) - (i)

$\therefore SF_{6(g)} \rightarrow S_{(g)} + 6F_{(g)}; \Delta H = 1855\ kJ$

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

20. **TIPS/Formulae :** For adiabatic expansion, we have

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

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

No. of moles of argon gas, $n = \frac{PV}{RT} = \frac{1 \times 1.25}{0.082 \times 300} = 0.05$

Now we know that

$\Delta H = nC_p\Delta T = 0.05 \times 20.8(188.5 - 300) = \mathbf{-115.41\ Joules}$

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

21. For following reaction

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

ΔG° can be calculated as follows :

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

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

Since,

$\Delta G° = \Delta H° - T\Delta S^0$ or $-257.2 = \Delta H - 300(0.094)$

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

Since,

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

22. The chemical reaction for combustion of diborane is

$$B_2H_6\,(g) + 3O_2\,(g) \longrightarrow B_2O_3\,(s) + 3H_2O\,(g), \Delta H = ?$$

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

$\Delta H = [\Delta H_{B_2O_3(s)} + 3\Delta H_{H_2O(g)}] - \Delta H_{B_2H_6(g)};$

$(\because \Delta H_f^\circ \text{ of } O_2 = 0)$

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

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

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

23. **TIPS/Formulae :**

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

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

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

Similarly for equilibrium, $A \rightleftharpoons C$

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

Hence, we have that

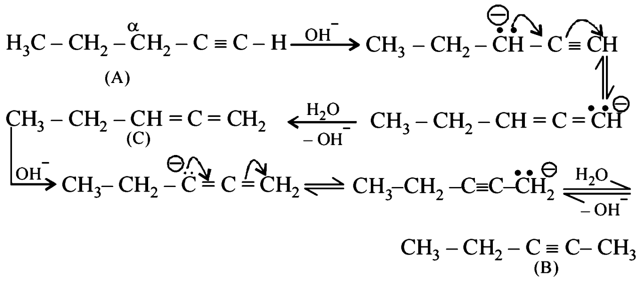
$B \rightleftharpoons A, \quad \Delta G_1^\circ = +15.992\ kJ\ mole^{-1}$

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

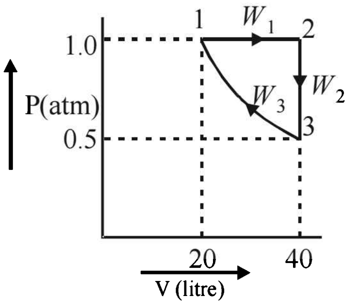
$A \rightleftharpoons C, \quad \Delta G_3^\circ = -3.688\ kJ\ mole^{-1}$

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

NOTE : Mechanism of isomerisation



24. (i)



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

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

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

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

$$\begin{bmatrix} PV = nRT \\ T = \dfrac{PV}{nR} = \dfrac{.5 \times 40}{2 \times 0.082} \end{bmatrix} = 121.95\,\text{K}$$

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

$\Delta U = q + W = 0$, so $q = -W = -(-6.13)\,\text{L.atm} = \mathbf{620.7\ J}$

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 $\mathbf{\Delta S = 0}$. Similarly $\mathbf{\Delta H = 0}$ and $\mathbf{\Delta U = 0}$ for the same reason i.e. U and H are also state functions having definite values in a given state of a system.

25. 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. 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.

26. **TIPS/Formulae :** For adiabatic process, $W = P(V_2 - V_1)$

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

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

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

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

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

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

27. (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 & will lie in the right direction, (forward).

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

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}.

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

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

F. Match the Following

1. **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) It is phase transition.

White and red P are allotropes.

Red P is more stable than white.

So ΔH is –ve.

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

(A) → r, t

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

It is at equilibrium at 273 K and 1 atm

So ΔS_{sys} is negative

As it is equilibrium process so $\Delta G = 0$

(B) $\rightarrow$ 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) $\rightarrow$ 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) $\rightarrow$ p, q, s, t

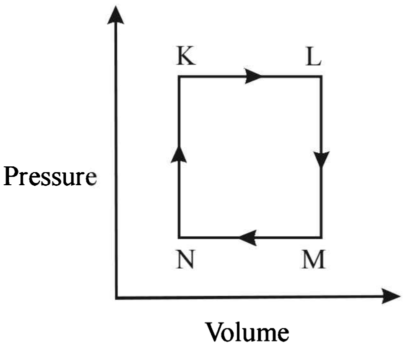
Reversible heating and cooling of gas follows same path also initial and final position is same.

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

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

G. Comprehension Based Questions

1. (c)



K $\rightarrow$ L $\Rightarrow$ V increasing at constant P

Hence T increases (Heating)

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

Hence T decreases (Cooling)

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

Hence T decreases (Cooling)

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

Hence T increases (Heating)

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

H. Assertion & Reason Type Questions

1. **(b)** By first law of thermodynamics $dq = dE + dW$. Under isothermal condition for ideal gas $dW = 0$ as volume occupied by the molecules of ideal gas is zero. Also $(dE)_T = 0$ as for ideal gas there is no change in internal energy at constant T due to no force of attraction between the molecules. $\therefore dq = 0 + 0 = 0$.

2. **(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).

I. Interger Value Correct Type

1. Energy released by combustion of 3.5 g gas

$$= 2.5 \times (298.45 - 298)\,\text{kJ}$$

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

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

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

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

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

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

Section-B JEE Main/ AIEEE

1. **(b)** **TIPS/Formulae :**

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

Since $\Delta G = \Delta H - T\Delta S$ for an endothermic reaction,

$\Delta H = +ve$ and at low temperature $\Delta S = +ve$

Hence $\Delta G = (+)\Delta H - T(+)\Delta S$

and if $T\Delta S < \Delta H$ (at low temp)

$\Delta G = +ve$ (non spontaneous)

But at high temperature, reaction becomes spontaneous i.e. $\Delta G = -ve$.

because at higher temperature $T\Delta S > \Delta H$.

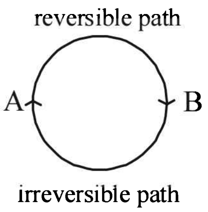
2. **(a)** According to first law of thermodynamics energy can neither be created nor destroyed although it can be converted from one form to another.

NOTE : Carnot cycle is based upon this principle but during the conversion of heat into work some mechanical energy is always converted to other form of energy hence this data violates 1st law of thermodynamics.

3. **(d)** ΔH negative shows that the reaction is spontaneous. Higher negative value for Zn shows that the reaction is more feasible.

4. **(b)** The heat required to raise the temperature of body by 1K is called thermal capacity or heat capacity.

5. **(c)** For a cyclic process the net change in the internal energy is zero because the change in internal energy does not depend on the path.



6. **(c)** $CH_2 = CH_2(g) + H_2(g) \rightarrow CH_3\text{-}CH_3$

Enthalpy change = Bond energy of reactants – Bond energy of products.

$$\Delta H = 1(C{=}C) + 4(C{-}H) + 1(H{-}H) - 1(C{-}C) - 6(C{-}H)$$
$$= 1(C{=}C) + 1(H{-}H) - 1(C{-}C) - 2(C{-}H)$$
$$= 615 + 435 - 347 - 2 \times 414 = 1050 - 1175 = -125\ \text{kJ}.$$

7. **(a)** For spontaneous reaction, dS > 0 and dG should be negative i.e. < 0.

8. **(c)** $\Delta G^\circ = -RT\ln K_c$ or $-\Delta G^\circ = RT\ln K_c$

9. **(b)** Enthalpy change for a reaction does not depend upon the nature of intermediate reaction steps.

10. **(c)** $w = -P\Delta V = -10^{-5}(1\times10^{-2} - 1\times10^{-3}) = -900J$

11. **(d)** (i) $C + O_2 \rightleftharpoons CO_2, \Delta H = -393.5\ \text{kJmol}^{-1}$

(ii) $CO + \frac{1}{2}O_2 \rightleftharpoons CO_2,$

$\Delta H = -283.0\ \text{kJmol}^{-1}$

Operating (i) - (ii), we have

$$C + \frac{1}{2}O_2 \rightarrow CO \quad \Delta H = -110.5\ \text{kJmol}^{-1}$$

12. **(d)** Enthalpy of reaction $(\Delta H) = E_{a_{(f)}} - E_{a_{(b)}}$

for an endothermic reaction $\Delta H = +ve$ hence for ΔH to be negative

$$E_{a_{(b)}} < E_{a_{(f)}}$$

13. **(b)** $\Delta H = \Delta U + \Delta nRT$ for $N_2 + 3H_2 \longrightarrow 2NH_3$

$\Delta n_g = 2 - 4 = -2$

$\therefore \Delta H = \Delta U - 2RT$ or $\Delta U = \Delta H + 2RT$ $\therefore \Delta U > \Delta H$

14. **(N)** $X_2 + Y_2 \longrightarrow 2XY, \Delta H = 2(-200).$

Let *x* be the bond dissociation energy of X_2. Then

$\Delta H = -400 = \xi_{x-x} + \xi_{y-y} - 2\xi_{x-y} = x + 0.5x - 2x = -0.5x$

or $x = \frac{400}{0.5} = 800\ \text{kJ mol}^{-1}$

(In the question paper, this option was not mentioned. So the answer has been marked 'N')

15. **(c)** **NOTE :** In a reversible process the work done is greater than in irreversible process. Hence the heat absorbed in reversible process would be greater than in the latter case. So

$$T_f(\text{rev.}) < T_f(\text{irr.})$$

16. **(c)** The standard enthalpy of formation of CH_4 is given by the equation :

$$C(s) + 2H_2(g) \longrightarrow CH_4(g)$$

Hence, dissociation energy of hydrogen and enthalpy of sublimation of carbon is required.

17. **(a)** $I_2(s) + Cl_2(g) \longrightarrow 2ICl(g)$

$$\Delta A = [\Delta I_2(s) \rightarrow I_2(g) + \Delta H_{I-I} + \Delta H_{Cl-Cl}] - 2[\Delta H_{I-Cl}]$$
$$= 151.0 + 242.3 + 62.76 - 2 \times 211.3 = 33.46$$

$$\Delta H_f^\circ(ICl) = \frac{33.46}{2} = 16.73\ \text{kJ / mol}$$

18. **(d)** For the reaction, $C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO$

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

$$\Delta n = 1 - \frac{1}{2} = \frac{1}{2};\ \Delta H - \Delta U = \frac{1}{2} \times 8.314 \times 298$$
$$= 1238.78\ \text{J mol}^{-1}$$

19. **(a)** $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

For a spontaneous reaction $\Delta G^\circ < 0$

or $\Delta H^\circ - T\Delta S^\circ < 0 \Rightarrow T > \frac{\Delta H^\circ}{\Delta S^\circ}$

$$\Rightarrow T > \frac{179.3 \times 10^3}{160.2} > 1117.9K \approx 1118K$$

20. **(d)** Given $\Delta H = 41\ kJ\ mol^{-1} = 41000\ J\ mol^{-1}$

$T = 100°C = 273 + 100 = 373\ K, n = 1$

$\Delta U = \Delta H - \Delta nRT = 41000 - (2 \times 8.314 \times 373)$

$= 37898.88\ J\ mol^{-1} \simeq 37.9\ kJmol^{-1}$

21. **(b)** Spontaneity of reaction depends on tendency to acquire minimum energy state and maximum randomness. For a spontaneous process in an isolated system the change in entropy is positive.

22. **(b)** The energy involved in the conversion of

$\frac{1}{2}Cl_2(g)$ to Cl^{-1} (aq) is given by

$$\Delta H = \frac{1}{2}\Delta_{diss}H^{(-)}_{Cl_2} + \Delta_{eg}H^{(-)}_{Cl} + \Delta_{hyl}H^{(-)}_{Cl}$$

Substituting various values from given data, we get

$$\Delta H = \left(\frac{1}{2} \times 240\right) + (-349) + (-381)\,kJmol^{-1}$$

$$= (120 - 349 - 381)\ kJ\ mol^{-1} = -610\ kJ\ mol^{-1}$$

i.e., the correct answer is (b)

23. **(c)** For a reaction to be at equilibrium $\Delta G = 0$. Since $\Delta G = \Delta H - T\Delta S$ so at equilibrium $\Delta H - T\Delta S = 0$ or $\Delta H = T\Delta S$

For the reaction

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3;\quad \Delta H = -30kJ\ \text{(given)}$$

Calculating ΔS for the above reaction, we get

$$\Delta S = 50 - \left[\frac{1}{2} \times 60 + \frac{3}{2} \times 40\right] JK^{-1}$$

$$= 50 - (30 + 60)\ JK^{-1} = -40\ JK^{-1}$$

At equilibrium, $T\Delta S = \Delta H \quad [\because \Delta G = 0]$

$\therefore\ T \times (-40) = -30 \times 1000\ [\because 1kJ = 1000J]$

or $T = \frac{-30 \times 1000}{-40}$ or 750 K

24. **(a)** Given, for reaction

(i) $H_2O(\ell) \longrightarrow H^+(aq.) + OH^-(aq.);\ \Delta H_r = 57.32\ kJ$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell);\ \Delta H_r = -286.20\ kJ$

For reaction (i)

$\Delta H_r = \Delta H°_f(H^+ .aq) + \Delta H°_f(OH^- .aq) - \Delta H°_f(H_2O, \ell)$

$57.32 = 0 + \Delta H°_f(OH^-, aq) - \Delta H°_f(H_2O, \ell)$ ...(iii)

For reaction (ii)

$\Delta H_r = \Delta H°_f(H_2O, \ell) - \Delta H°_f(H_2, g) - \frac{1}{2}\Delta H°_f(O_2, g)$

$-286.20 = \Delta H°_f(H_2O, \ell)$

On replacing this value in equ. (iii) we have

$57.32 = \Delta H°_f(OH^-, aq) - (-286.20)$

$\Delta H°_f = -286.20 + 57.32 = -228.88\ kJ$

25. **(b)** $N_2 + 3H_2 \longrightarrow 2NH_3 \quad \Delta H = 2 \times -46.0\ kJ\ mol^{-1}$

Let x be the bond enthalpy of N – H bond then

[**Note :** Enthalpy of formation or bond formation enthalpy is given which is negative but the given reaction involves bond breaking hence values should be taken as positive.]

$\Delta H = \Sigma$ Bond energies of products

$- \Sigma$ Bond energies of reactants

$2 \times -46 = 712 + 3 \times (436) - 6x;\ -92 = 2020 - 6x$

$6x = 2020 + 92 \Rightarrow 6x = 2112 \Rightarrow x = +352\ kJ/mol$

26. **(b)** At equilibrium $\Delta G = 0$

Hence, $\Delta G = \Delta H - T_e\Delta S = 0$

$\therefore\ \Delta H = T_e\Delta S$ or $T_e = \frac{\Delta H}{\Delta S}$

For a spontaneous reaction

ΔG must be negative which is possible only if $\Delta H < T\Delta S$

or $T > \frac{\Delta H}{\Delta S};\ T_e < T$

27. **(a)** Entropy change for an isothermal reversible process is given by

$$\Delta S = nR\ln\frac{V_2}{V_1} = 2 \times 8.314 \times 2.303\log\frac{100}{10}$$

$$= 38.3\ J\ mol^{-1}\ K^{-1}$$

28. **(c)** $\Delta G° = \Delta H° - T\Delta S°;\ -RT\ \ell nK = \Delta H° - T\Delta S°$

$$\ell nK = -\frac{\Delta H° - T\Delta S°}{RT}$$

30. **(a)** $C_2H_5OH(\ell) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$

Bomb calorimeter gives ΔU of the reaction

Given, $\Delta U = -1364.47\ kJ\ mol^{-1}$

$\Delta n_g = -1$

$\Delta H = \Delta U + \Delta n_g RT$

$$= -1364.47 - \frac{1 \times 8.314 \times 298}{1000} = -1366.93\ kJ\ mol^{-1}$$

31. **(b)** Given

$C(s) + O_2(g) \rightarrow CO_2(g);\quad \Delta H = -393.5\ kJ\ mol^{-1}$ ...(i)

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g);\ \Delta H = -283.5\ kJ\ mol^{-1}$ ...(ii)

$\therefore$ Heat of formation of CO = eqn(i) – eqn(ii)

$= -393.5 - (-283.5) = -110\ kJ$