7
Chapter

THERMODYNAMICS

A SINGLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

1. The standard state of a substance is the
(a) pure form at 1 bar
(b) most stable form at 25ºC and 1 bar
(c) most stable form at 0ºC
(d) pure gaseous form at 25ºC

2. An ideal gas occupying a volume of 2 dm^3 at a pressure of 5 bar undergoes isothermal and irreversible expansion against external pressure of 1 bar. The final volume of the system and the work involved in the process is :
(a) $10 dm^3$, 1000 J
(b) $10 dm^3$, –1000 J
(c) $8 dm^3$, –800 J
(d) $10 dm^3$, –800 J

3. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95K) $\rightarrow$ (4.0 atm, 5.0L, 245 K) with a change in internal energy $\Delta U = 30.0$ L atm. The change in enthalpy of the process in L atm is
(a) 40.0
(b) 42.3
(c) 44.0
(d) not defined, because it is not constant.

4. Work out the heat change (cal) when 40 g of He gas at 27ºC undergoes isothermal and reversible compression from initial pressure of 1 atm to 10 atm ($R = 2$ cal K^{-1} mol^{-1}).
(a) 13.818 k cal
(b) –13.818 k cal
(c) 55.272 k cal
(d) –55.272 k cal

5. If an ideal gas does the work of expansion solely at the cost of its internal energy, the process is
(a) reversible
(b) irrerversible
(c) isothermal
(d) adiabatic

6. In order to maintain constant temperature of a system involving an ideal gas, heat has to be removed. Then what is true?
(a) The gas is being compressed
(b) The gas is undergoing expansion
(c) The gas is performing the work
(d) There is neither expansion nor contraction of the gas

7. When 1.8 g of steam at the normal boiling point of water is converted into water at the same temperature, enthalpy and entropy changes respectively will be (ΔH_{vap}(for water) = 40.8 kJ mol^{-1})
(a) 4.08 kJ, 10.93 JK^{-1}
(b) –4.08 kJ, –40.8 JK^{-1}
(c) –4.08 kJ, –10.93 JK^{-1}
(d) 4.08 kJ, 40.8 JK^{-1}

8. During adiabatic expansion of 1 mole of a gas, the change in internal energy is –100 J. The work done in the process is
(a) –100 J
(b) 100 J
(c) 200 J
(d) zero

9. For which of the following changes, $\Delta H \neq \Delta U$
(a) $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$
(b) $H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$
(c) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$
(d) $CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$

10. The enthalpy of combustion of 2 moles of benzene at 27ºC differs from the value determined by bomb calorimeter by
(a) 7.483 kJ
(b) –7.483 kJ
(c) 2.494 kJ
(d) –2.494 kJ

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ

11. The bond energy of H_2 is 435 kJ mol^{-1}. It implies that

(a) 435 kJ energy is needed to dissociate 1 molecule of H_2 gas into gaseous H-atoms.

(b) 435 kJ energy is needed to dissociate 6.02×10^{23} molecules of H_2 gas into atoms of hydrogen.

(c) 435 kJ energy is required to dissociate 3.01×10^{23} molecules of H_2 gas into 6.02×10^{23} atoms of hydrogen

(d) None of these

12. At 25°C and 1 bar which one of the following has a non-zero ΔH_f^o ?

(a) $Br_{2(\ell)}$ (b) $C_{(\text{graphite})}$

(c) $I_{2(s)}$ (d) $O_{3(g)}$

13. 1 mole of H_2SO_4 is mixed with excess of NaOH in a dilute solution. The enthalpy change is nearly equal to

(a) 57.3 kJ (b) 114.6 kJ

(c) –114.6 kJ (d) –57.3 kJ

14. Which of the reaction defines ΔH_f^o of the product

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

(b) $\frac{1}{2}H_{2(g)} + \frac{1}{2}F_{2(g)} \longrightarrow HF_{(\ell)}$

(c) $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

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

15. For which of the following reactions does the enthalpy change represent the enthalpy of formation of AgCl ?

(a) $Ag^+_{(aq)} + Cl^-_{(aq)} \longrightarrow AgCl_{(s)}$

(b) $Ag_{(s)} + AuCl_{(s)} \longrightarrow Au_{(s)} + AgCl_{(s)}$

(c) $Ag_{(s)} + \frac{1}{2}Cl_{2(g)} \longrightarrow AgCl_{(s)}$

(d) $2Ag_{(s)} + Cl_{2(g)} \longrightarrow 2AgCl_{(s)}$

16. Enthalpy change for the reaction $H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(\ell)}$ is –57.3 kJ mol^{-1}. If 1 L of 0.5 M HNO_3 is mixed with 2L of 0.1 M KOH, the enthalpy change would be

(a) –28.65 kJ (b) 28.65 kJ

(c) –11.46 kJ (d) 11.46 kJ

17. When 1 mole of oxalic acid is treated with excess of NaOH in dilute aqueous solution, 106 kJ of heat is liberated. Predict the enthalpy of ionization of the acid.

(a) 4.3 kJ mol^{-1} (b) –4.3 k J mol^{-1}

(c) –8.6 kJ mol^{-1} (d) 8.6 kJ mol^{-1}

18. Standard enthalpy of combustion of CH_4 is – 890 kJ mol^{-1} and standard enthalpy of vaporisation of water is 40.5 kJ mol^{-1}. Calculate the enthalpy change for the reaction :

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$$

(a) –890 kJ mol^{-1} (b) –809 kJ mol^{-1}

(c) 809 kJ mol^{-1} (d) –971 kJ mol^{-1}

19. Temperature of 5 moles of a gas is decreased by 2 K at constant pressure. Indicate the correct statement.

(a) work done by the gas = 5 R

(b) work done by the gas = 10 R

(c) work done over the gas = 10R

(d) work done = 0

20. If bond energies are denoted by ε, the enthalpy of the reaction : $CH \equiv CH_{(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)}$, is

(a) $\varepsilon_{C\equiv C} + 2\varepsilon_{H-H} - \varepsilon_{C-C} - 4\varepsilon_{C-H}$

(b) $\varepsilon_{C\equiv C} + 2\varepsilon_{H-H} - \varepsilon_{C-C} - 6\varepsilon_{C-H}$

(c) $\varepsilon_{C\equiv C} - 2\varepsilon_{H-H} - \varepsilon_{C-C} - 4\varepsilon_{C-H}$

(d) $\varepsilon_{C\equiv C} + 2\varepsilon_{H-H} - \varepsilon_{C=C} - 4\varepsilon_{C-H}$

21. Enthalpy of combustion of carbon, hydrogen and C_3H_8 are x_1, x_2 and x_3 mol^{-1} respectively. Estimate the enthalpy of formation of C_3H_8

(a) $x_3 – x_1 – x_2$ (b) $x_3 – 3x_1 – 4x_2$

(c) $3x_1 + 4x_2 – x_3$ (d) $x_1 + x_2 – x_3$

22. The enthalpy of atomisation of CH_4 and C_2H_6 are 360 and 620 k cal mol^{-1} respectively. The C–C bond energy is expected to be

(a) 210 k cal mol^{-1} (b) 130 k cal mol^{-1}

(c) 180 k cal mol^{-1} (d) 80 k cal mol^{-1}

MARK YOUR RESPONSE	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ
	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ
	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ			

23. Enthalpy of combustion of CH_4, C_2H_6 and C_3H_8 are – 210.8, – 368.4 and – 526.2 k cal mol^{-1} respectively. Enthalpy of combustion of hexane can be predicted as

(a) – 840 k cal mol^{-1} (b) – 684 k cal mol^{-1}
(c) – 1000 k cal mol^{-1} (d) none of these

24. The lattice energy of solid NaCl is 180 k cal mol^{-1} and enthalpy of solution is 1 k cal mol^{-1}. If the hydration energies of Na^+ and Cl^- ions are in the ratio 3 : 2, what is the enthalpy of hydration of sodium ion ?

(a) 71.6 k cal mol^{-1} (b) – 71.6 k cal mol^{-1}
(c) 107.4 k cal mol^{-1} (d) – 107.4 k cal mol^{-1}

25. If bond enthalpies of N ≡ N, H –H and N –H bonds are x_1, x_2 and x_3 respectively, ΔH_f^o for NH_3 will be

(a) $x_1 + 3x_2 - 6x_3$ (b) $½x_1 + 3/2x_2 - 3x_3$
(c) $3x_3 - ½x_1 - 3/2x_2$ (d) $6x_3 - x_1 - 3x_2$

26. If enthalpy of vaporisation of graphite and benzene are x_1 and x_2 mol^{-1} respectively and various bond energies are symbolized by ε, ΔH_f^o for benzene is given by

(a) $6x_1 + 3\varepsilon_{H-H} - 3\varepsilon_{C=C} - 3\varepsilon_{C-C} - 6\varepsilon_{C-H} \quad x_2$

(b) $6x_1 + 3\varepsilon_{H-H} - 3\varepsilon_{C-C} - 3\varepsilon_{C=C} - 6\varepsilon_{C-H} - x_2$

(c) $6x_1 + 3\varepsilon_{C-C} + 3\varepsilon_{C=C} + 6\varepsilon_{C-H} - 3\varepsilon_{H-H} - x_2$

(d) $6x_1 + 3\varepsilon_{C-C} + 3\varepsilon_{C=C} + 6\varepsilon_{C-H} - 3\varepsilon_{H-H} \quad x_2$

27. 90 g of water at 0°C is frozen at constant pressure. If enthalpy of fusion of ice is 6.0 k J mol^{-1}, the entropy change in the process is

(a) 109.93 J k^{-1} (b) –109.93 Jk^{-1}
(c) 21.97 J k^{-1} (d) none of these

28. The enthalpy of neutralization of NH_4OH and CH_3COOH is – 10.5 k cal mol^{-1} and enthalpy of neutralization of CH_3COOH with strong base is – 12.5 k cal mol^{-1}. The enthalpy of ionization of NH_4OH will be

(a) 4.0 k cal mol^{-1} (b) 3.0 k cal mol^{-1}
(c) 2.0 k cal mol^{-1} (d) 3.2 k cal mol^{-1}

29. The enthalpy change for a given reaction at 298 K is – x J mol^{-1}. For the reaction to be spontaneous at 298 K, the entropy change at that temperature

(a) can be negative, but numerically greater than $\frac{x}{298}$ Jk^{-1}

(b) can be negative, but numerically smaller than $\frac{x}{298}$ Jk^{-1}.

(c) can not be negative

(d) can not be positive

30. The bond enthalpies of H_2, X_2 and HX are in the ratio of 2 : 1 : 2. If enthalpy of formation of HX is – 50 k J mol^{-1}, the bond enthalpy of X_2 is

(a) 100 kJ mol^{-1} (b) 200 k J mol^{-1}
(c) 300 k J mol^{-1} (d) 400 k J mol^{-1}

31. Calculate enthalpy change for the change $8S_{(g)} \longrightarrow S_{8(g)}$, given that

$H_2S_{2(g)} \longrightarrow 2H_{(g)} + 2S_{(g)}, \Delta H \quad 239.0 \text{ k cal mol}^{-1}$;

$H_2S_{(g)} \longrightarrow 2H_{(g)} + S_{(g)}, \Delta H \quad 175.0 \text{ k cal mol}^{-1}$

(a) + 512.0 k cal (b) – 512.0 k cal
(c) 508.0 k cal (d) – 508.0 k cal

32. The enthalpy change for the hydration,

$CuSO_{4(s)} \quad 5H_2O_{(g)} \longrightarrow CuSO_4.5H_2O_{(s)}$

is – 71.50 k cal mol^{-1}. If enthalpy of vaporisation of water is 10.5 k cal mol^{-1} at 25° C, what would be enthalpy change for the hydration,

$CuSO_{4(s)} \quad 5H_2O_{(\ell)} \longrightarrow CuSO_4.5H_2O_{(s)}$

(a) 61.0 k cal mol^{-1} (b) – 61.0 k cal mol^{-1}
(c) 19.0 k cal mol^{-1} (d) – 19.0 k cal mol^{-1}

33. If x_1, x_2 and x_3 are enthalpies of H–H, O=O and O–H bonds repectively, and x_4 is the enthalpy of vaporisation of water, estimate the standard enthalpy of combustion of hydrogen:

(a) $x_1 \quad \frac{x_2}{2} - 2x_3 \quad x_4$ (b) $x_1 \quad \frac{x_2}{2} - 2x_3 - x_4$

(c) $x_1 \quad \frac{x_2}{2} - x_3 \quad x_4$ (d) $2x_3 - x_1 - \frac{x_2}{2} - x_4$

34. Which of the following processes takes place with decrease of entropy?

(a) Solid → gas
(b) sugar + water → solution
(c) $NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$
(d) $A_{(g)} + B_{(g)} \rightarrow$ mixture

MARK YOUR RESPONSE	23. ⓐⓑⓒⓓ	24. ⓐⓑⓒⓓ	25. ⓐⓑⓒⓓ	26. ⓐⓑⓒⓓ	27. ⓐⓑⓒⓓ
	28. ⓐⓑⓒⓓ	29. ⓐⓑⓒⓓ	30. ⓐⓑⓒⓓ	31. ⓐⓑⓒⓓ	32. ⓐⓑⓒⓓ
	33. ⓐⓑⓒⓓ	34. ⓐⓑⓒⓓ			

35. Entropy of mixing of ideal gases in terms of mole fractions X_i is given by

(a) $-nR\sum X_i \ell_n X_I$ (b) $-R\Sigma\Sigma X_i \ell_n X_i$

(c) $R\Sigma\Sigma_i \ell_n X_i$ (d) $-nRT\Sigma R_i \ell_n X_i$

36. If H is considered as the function of P and T, then which of the following relations is /are correct?

(a) $dH = \left(\frac{dH}{dT}\right)_P dT + \left(\frac{dH}{dP}\right)_T dP$

(b) $dH = C_p dT + \left(\frac{dH}{dP}\right)_T dP$

(c) $\left(\frac{dH}{dP}\right)_T = -V$

(d) all

37. Which of the following is not the function of the path?

(a) q (b) w

(c) $q \times w$ (d) $q + w$

38. Which of the following has highest calorific value ?

(a) CH_4 (b) C_2H_6

(c) CH_3OH (d) H_2

39. Which of the following thermodynamic condition at constant pressure and temperature is necessary for the spontaneity of a process?

(a) $d(U–TS+PV)>0$ (b) $d(U–TS+PV)<0$

(c) $d(U–TS+PV)=0$ (d) $d(U+TS+PV)<0$

40. If the ratio of molar heat capacities of a gas at constant pressure and constant volume i.e., $\frac{C_P}{C_v} = \gamma$, the respective values of C_P and C_v are

(a) $\frac{R}{\gamma-1}, \frac{\gamma R}{\gamma-1}$ (b) $\frac{\gamma R}{\gamma-1}, \frac{R}{\gamma-1}$

(c) $\frac{\gamma-1}{\gamma R}, \frac{\gamma-1}{R}$ (d) $\frac{\gamma-1}{R}, \frac{\gamma-1}{\gamma R}$

41. Electrical energy produced in a galvanic cell is equal to

(a) decrease in work function

(b) increase in entropy

(c) decrease in free energy

(d) decrease in enthalpy

42. 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. The average S–F bond enthalpy in SF_6 is

(a) 57.5 kJ mol^{-1} (b) 309.16 k J mol^{-1}

(c) –309.16 k J mol^{-1} (d) 269.17 k J mol^{-1}

43. A gas absorbs 200 J heat and undergoes simultaneous expansion against a constant external pressure of 10^5 Pa. The volume changes from 4L to 5L. The change in internal energy is

(a) 300 J (b) 100 J

(c) –300 J (d) – 100 J

44. Polymerisation of ethene to poly-ethene is represented by the equation

$$n(CH_2 = CH_2) \longrightarrow (-CH_2 - CH_2-)_n$$

Given that average enthalpies of C = C and C – C bonds at 298 K are 590 and 331 k J mol^{-1} respectively, predict the enthalpy change when 56 g of ethene changes to polyethylene.

(a) 72 kJ (b) – 72 kJ

(c) 144 kJ (d) – 144 kJ

45. When 1 mole of crystalline NaCl is obtained from sodium and chlorine gas, 410 kJ of heat is released. The heat of sublimation of Na metal is 108 kJ mol^{-1} and Cl – Cl bond enthalpy is 242 kJ mol^{-1}. If the ionisation energy of Na is 493.0 kJ mol^{-1} and the electron affinity of chlorine is 368 kJ mol^{-1}, the lattice energy of NaCl is

(a) 764 kJ mol^{-1} (b) – 764 kJ mol^{-1}

(c) 885 kJ mol^{-1} (d) – 885 kJ mol^{-1}

46. ΔH_f^o of water is – 285.8 kJ mol^{-1}. If enthalpy of neutralization of monoacid strong base is –57.3 kJ mol^{-1}, ΔH_f^o of OH$^-$ ion will be

(a) –228.5 kJ mol^{-1} (b) 228.5 kJ mol^{-1}

(c) 114.25 kJ mol^{-1} (d) – 114.25 kJ mol^{-1}

47. If all the reactants and the products in a reaction are in their standard states of unit activity, then which is true of the following ?

(a) $\Delta G^o = 0$ (b) $\Delta G = 0$

(c) $\Delta G = \Delta G^o$ (d) $\Delta H^o - T\Delta S^o = 0$

MARK YOUR RESPONSE	35. ⓐⓑⓒⓓ	36. ⓐⓑⓒⓓ	37. ⓐⓑⓒⓓ	38. ⓐⓑⓒⓓ	39. ⓐⓑⓒⓓ
	40. ⓐⓑⓒⓓ	41. ⓐⓑⓒⓓ	42. ⓐⓑⓒⓓ	43. ⓐⓑⓒⓓ	44. ⓐⓑⓒⓓ
	45. ⓐⓑⓒⓓ	46. ⓐⓑⓒⓓ	47. ⓐⓑⓒⓓ		

48. Given that $S^o_{H_2} = 131\,JK^{-1}mol^{-1}$, $S^o_{Cl_2} = 223\,JK^{-1}mol^{-1}$ and $S^o_{HCl} = 187\,JK^{-1}mol^{-1}$. The standard entropy change in the formation of 1 mole of $HCl_{(g)}$ from $H_{2(g)}$ and $Cl_{2(g)}$ will be

(a) $20\,JK^{-1}$ (b) $10\,JK^{-1}$

(c) $187\,JK^{-1}$ (d) $374\,JK^{-1}$

49. The enthalpy of neutralization of a weak acid in 1*M* solution with a strong base is $-56.1\,kJ\,mol^{-1}$. If enthalpy of ionization of the acid is $1.5\,kJ\,mol^{-1}$ and enthalpy of neutralization of the strong acid with a strong base is $-57.3\,kJ\,equiv^{-1}$, what is the % ionization of the weak acid in molar solution (assume the acid to be monobasic)?

(a) 10 (b) 15

(c) 20 (d) 25

50. ΔH_f^o of NF_3 is $-113\,kJ\,mol^{-1}$ and N–F bond energy is $273.0\,kJ\,mol^{-1}$. If $N \equiv N$ and F–F bond energies are in the ratio 6 : 1, their magnitudes will be :

(a) $950.0\,kJ\,mol^{-1}$, $158.3\,kJ\,mol^{-1}$

(b) $840\,kJ\,mol^{-1}$, $140\,kJ\,mol^{-1}$

(c) $941.3\,kJ\,mol^{-1}$, $156.9\,kJ\,mol^{-1}$

(d) $780.0\,kJ\,mol^{-1}$, $130.0\,kJ\,mol^{-1}$

51. In which of the following equations, the enthalpy change will represent ΔH_f^o of $N_2H_{4(\ell)}$ with sign reversed?

(a) $N_{2(g)} + 2H_{2(g)} \rightarrow N_2H_{4(g)}$

(b) $2N_{(g)} + 4H_{(g)} \rightarrow N_2H_{4(\ell)}$

(c) $N_2H_{4(\ell)} \rightarrow 2N_{(g)} + 4H_{(g)}$

(d) $N_2H_{4(\ell)} \rightarrow N_{2(g)} + 2H_{2(g)}$

52. Equal volumes of equimolar solutions of HNO_3 and H_2SO_4 are neutralized by dilute KOH solution and *x* and *y* are the respective enthalpy changes. Which of the following is true ?

(a) $x = y$ (b) $x = 2y$

(c) $2x = y$ (d) none of these

53. 9 g of water is vaporised under reversible conditions at its boiling point of 100ºC and at an external constant pressure of 1 atm. If enthalpy of vaporisation of water is $41.5\,kJ\,mol^{-1}$, which of the following thermodynamic changes will be zero ?

(a) ΔU (b) ΔH

(c) ΔS (d) ΔG

54. 250 ml of 0.1 *M* HCl and 250 ml of 0.1 *M* KOH, both being at the same temperature, are mixed thoroughly and the temperature rise is found to be ΔT_1. If the experiment is repeated using 500 ml each of the two solutions and ΔT_2 is the temperature rise, then which is true ?

(a) $\Delta T_2 > 2\Delta T_1$ (b) $\Delta T_1 = 2\Delta T_2$

(c) $\Delta T_1 = \Delta T_2$ (d) none of these

55. Enthalpy of vaporisation of water is $40.5\,kJ\,mol^{-1}$. If average bond energy of O–H bond in H_2O is $456\,kJ\,mol^{-1}$, which of the following represents ΔH_f^o of water ?

(a) $-912\,kJ\,mol^{-1}$ (b) $-952.5\,kJ\,mol^{-1}$

(c) $-871.5\,kJ\,mol^{-1}$ (d) none of these

56. Heat produced when 100 ml of 0.2 *M* H_2SO_4 is mixed with 500 ml of 0.1*M* NaOH is *x* kJ. Enthalpy of neutralisation of H_2SO_4 is :

(a) $-50\,x$ kJ (b) $-25\,x$ kJ

(c) $+25\,x$ kJ (d) $-20\,x$ kJ

57. Compounds with higher positive enthalpy of formation are less stable because :

(a) It is difficult to synthesize them

(b) Energy rich state leads to instability

(c) Elevated temperature is required to synthesize them

(d) Molecules of such compounds are distorted

58. The favourable condition for a process to be spontaneous is :

(a) $T\Delta S > \Delta H$, $\Delta H = +\text{ive}$, $\Delta S = -\text{ive}$

(b) $T\Delta S > \Delta H$, $\Delta H = +\text{ive}$, $\Delta S = +\text{ive}$

(c) $T\Delta S = \Delta H$, $\Delta H = -\text{ive}$, $\Delta S = -\text{ive}$

(d) $T\Delta S = \Delta H$, $\Delta H = +\text{ive}$, $\Delta S = +\text{ive}$

MARK YOUR RESPONSE	48. ⓐⓑⓒⓓ	49. ⓐⓑⓒⓓ	50. ⓐⓑⓒⓓ	51. ⓐⓑⓒⓓ	52. ⓐⓑⓒⓓ
	53. ⓐⓑⓒⓓ	54. ⓐⓑⓒⓓ	55. ⓐⓑⓒⓓ	56. ⓐⓑⓒⓓ	57. ⓐⓑⓒⓓ
	58. ⓐⓑⓒⓓ				

59. When 110 g of manganese (At. mass = 55) dissolves in dilute HNO_3 at 27°C under atmospheric pressure, the work done in the process is :

(a) $2494.2\,J$ (b) $-2494.2\,J$
(c) $-4988.4\,J$ (d) $4988.4\,J$

60. Enthalpy of formation of gaseous H_2O at 298 K is – 241.8 $kJ\ mol^{-1}$. Calculate its value at the standard boiling point of water. Given the following value of molar heat capacities (C_p) at constant pressure (assume them to be temperature independent).

$$C_p(H_2O_{(g)}) = 33.58\,JK^{-1}mol^{-1};$$

$$C_p(H_2) = 28.98\,JK^{-1}mol^{-1};$$

$$C_p(O_2) = 29.36\,JK^{-1}mol^{-1}$$

(a) $-241.05\ kJmol^{-1}$ (b) $-242.55\ kJmol^{-1}$
(c) $-991.8\ kJmol^{-1}$ (d) $242.55\ kJmol^{-1}$

61. The difference between the heat change at constant pressure and that at constant volume for the combustion of 46g of ethanol at 27°C is

(a) $-4.59\,kJ$ (b) $+4.59\,kJ$
(c) $+2.49\,kJ$ (d) $-2.49\,kJ$

62. The dissolution of KCl in water is endothermic yet it dissolves in water spontaneously. Which one of the following best explains this behaviour ?

(a) Endothermic processes are energetically favoured.
(b) The electrostatic bonds between the ions are not too strong.
(c) Energy changes have nothing to do with the dissolution processes.
(d) The entropy driving force causes the dissolution.

63. The heat of sublimation of iodine is 24 cal g^{-1} at 50°C. If specific heat of solid iodine and its vapour are 0.055 and $0.031\,cal\,g^{-1}$ respectively, the heat of sublimation of iodine at 100°C is

(a) $22.8\ cal\ g^{-1}$ (b) $25.2\ calg^{-1}$
(c) $-22.8\ cal\ g^{-1}$ (d) $-25.2\ cal\ g^{-1}$

64. When 0.1 mole of anhydrous $CuSO_4$ is dissolved in water, the heat evolved is 1.451 kcal. If 0.1 mole of $CuSO_4.5H_2O$ is dissolved in water, the heat absorbed is 0.264 kcal. The molar heat of hydration of $CuSO_4$ is

(a) 11.87 kcal (b) – 11.87 kcal
(c) 17.15 kcal (d) – 17.15 kcal

65. In an adiabatic irreversible expansion of an ideal gas against a constant external pressure P_2, the $P - V$ work is given by

(a) $-W_{irr} = nR\left(T_2 - \frac{T_1P_2}{P_1}\right)$

(b) $-W_{irr} = nR\left(T_2 + \frac{T_1P_2}{P_1}\right)$

(c) $-W_{irr} = nRT_1\left(1 - \frac{P_2}{P_1}\right)$

(d) $-W_{irr} = nRT_2\left(1 - \frac{P_2}{P_1}\right)$

66. Temperature of 2 moles of an ideal gas is raised by 1°C at a constant pressure. The enthalpy change for the process is

(a) $3R$ (b) $4R$
(c) $5R$ (d) $7R$

67. A monobasic acid is dissociated in 0.1 M solution. When 200ml of the acid solution is neutralized by 0.1 M NaOH, heat evolved is 244 cal. If the heat of neutralization of a strong acid with a strong base is – 13.7 kcal, the molar heat of dissociation of the acid is

(a) $2.20\ k\,cal\,mol^{-1}$ (b) $1.50\ k\,cal\,mol^{-1}$
(c) $-1.50\ k\,cal\,mol^{-1}$ (d) $2.0\ k\,cal\,mol^{-1}$

68. Heat of neutralization of a strong acid HA and a weaker acid HB with KOH are – 13.7 and – 12.7 $k\,cal\,mol^{-1}$. When 1 mole of KOH was added to a mixture containing 1 mole each of HA and HB, the heat change was – 13.5 kcal. In what ratio is the base distributed between HA and HB.

(a) 3 : 1 (b) 1 : 3
(c) 4 : 1 (d) 1 : 4

MARK YOUR RESPONSE	59.ⓐⓑⓒⓓ	60.ⓐⓑⓒⓓ	61.ⓐⓑⓒⓓ	62.ⓐⓑⓒⓓ	63.ⓐⓑⓒⓓ
	64.ⓐⓑⓒⓓ	65.ⓐⓑⓒⓓ	66.ⓐⓑⓒⓓ	67.ⓐⓑⓒⓓ	68.ⓐⓑⓒⓓ

69. Calculate the entropy change when 2.8 g of N_2 gas expands isothermally and reversibly from an initial volume of 1 L to final volume of 10 L at 27°C

(a) $19.15\ JK^{-1}$ (b) $1.915\ JK^{-1}$

(c) $0.83\ JK^{-1}$ (d) $8.31\ JK^{-1}$

70. Calculate the resonance energy for CO_2 from the following :

$\Delta H_{C=O} = 339\,\text{kJ mol}^{-1}$

$\Delta H_{O=O} = 498\ \text{kJ mol}^{-1}$

$\Delta H(C_{(s)} \rightarrow C_{(g)}) = 718\ \text{kJ mol}^{-1}$

$\Delta H_{\text{ combustion}}(\text{carbon}) = -393\ \text{kJ mol}^{-1}$

(a) $913\ \text{KJ mol}^{-1}$ (b) $-913\ \text{KJ mol}^{-1}$

(c) $145\ \text{KJ mol}^{-1}$ (d) $-145\ \text{KJ mol}^{-1}$

71. If ΔH and ΔE are the change in enthalpy and change in internal energy respectively for a gaseous reaction, then

(a) $\Delta H > \Delta E$, always

(b) $\Delta H < \Delta E$, only if $n_{\text{product}} > n_{\text{reactants}}$

(c) $\Delta H < \Delta E$, always

(d) $\Delta H < \Delta E$, only if $n_{\text{product}} < n_{\text{reactants}}$

72. The bond dissociation energies of CH_4 and C_2H_6 respectively are 360 and 620 k cal mol^{-1}. The C – C bond energy would be

(a) 260 k cal/mol (b) 180 k cal/mol

(c) 130 k cal/mol (d) 80 k cal/mol

73. One mole of an ideal gas $\left(C_v = \frac{3}{2}R\right)$ at 300 K is allowed to expand reversibly and adiabatically against a constant external pressure of 3.5 atmosphere from a volume of 10 litres to a volume of 20 litres

(a) – 1384 J (b) + 1384 J

(c) – 1483 J (d) none of these

74. The heat of formation of $CH_3OCH_3(g)$ is

(a) – 14.5 k cal (b) – 15.4 k cal

(c) + 14.5 k cal (d) + 15.4 k cal

[Given : $\varepsilon_{H-H} = 103\,\text{kcal}$, $\varepsilon_{C-H} = 87\,\text{kcal}$

$\varepsilon_{C-O} = 70\,\text{kcal}$, $\varepsilon_{O=O} = 177\,\text{kcal}$; Heat of vapourisation of 1 gram atom of carbon = 125 k cal.]

75. A solution of composition $CuCl_2 + 10H_2O$ diluted with x moles of water, the heat disengaged is given by

$$Q_v = \frac{2 \times 5023}{x + 21.24}$$

The heat of solution of $CuCl_2$ in 600 moles of water is 11080 cal. Heat of solution of anhydrous $CuCl_2$ is 10 moles of water is

(a) 5023 cal (b) 6230 cal

(c) 4850 cal (d) 11080 cal

MARK YOUR RESPONSE	69. ⓐⓑⓒⓓ	70. ⓐⓑⓒⓓ	71. ⓐⓑⓒⓓ	72. ⓐⓑⓒⓓ	73. ⓐⓑⓒⓓ
	74. ⓐⓑⓒⓓ	75. ⓐⓑⓒⓓ			

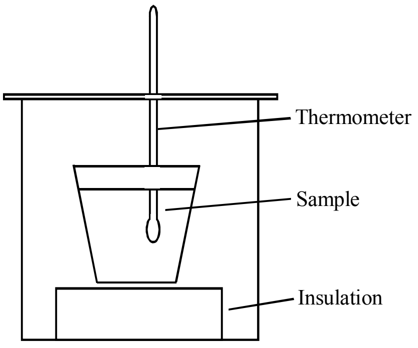
B

COMPREHENSION TYPE

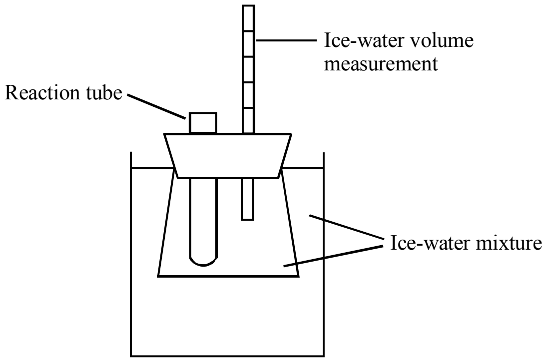
This section contains groups of questions. Each group is followed by some multiple choice questions based on a paragraph. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

PASSAGE-1

Chemist's seemingly insatiable need to measure heat has led to a broad spectrum of measurement methods. Beginning students are familiar with simple "coffee cup" style calorimeters that rely on the known specific heat of water to infer heat values from measurements of temperature change. A student uses the calorimeter shown in Figure - 1 below to determine the enthalpy of solution, $\Delta H_{\text{solution}}$, of KOH :



Coffee-cup Calorimeter
Figure 1



Ice Calorimeter
Figure 2

She finds that when a 5.6 g sample of solid KOH is added to 100 mL of water, the temperature in the solution rises from 24.0°C to 37.0°C.

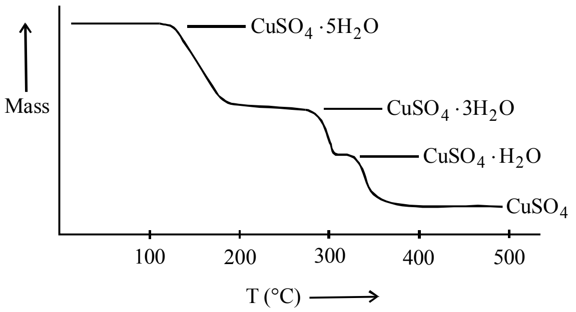
Another traditional style of calorimeter is the ice calorimeter, in which the heat released in an exothermic reaction is trapped in an ice-water mixture, causing ice to melt (Figure - 2). Each gram of ice that melts produces a gram of liquid having a somewhat greater density, with the result that the volume of the ice-water mixture contracts by 0.091 mL per gram of ice melted. Thus, a measurement of volume change, together with the knowledge that the specific heat of fusion of ice is 334 J/g, leads to a value for the heat liberated in a reaction.

A student employs this method to determine the enthalpy of combustion of methanol. He finds that when a sample of methanol weighing 0.300 g is burned in excess of oxygen in an ice calorimeter, according to the reaction,

$$2CH_3OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l)$$

the volume of ice and water surrounding the sample decreases by 1.82 mL.

Calorimetry has become quite sophisticated, and one of the methods available to analytical laboratories is thermal gravimetric analysis (TGA), a technique that measures the mass of a simple as heat is suplied at a constant rate. The result is a graph, as illustrated in Figure - 3 for hydrated copper (II) sulfate, $CuSO_4.5H_2O$.



TGA curve for $CuSO_4 \cdot 5H_2O$
Figure 3

Figure - 3 shows that as heat is added to the sample, mass is lost in distinct stages, each characterized by a loss of either one or two water molecules from an original molecule of hydrate.

1. If the specific heat of the solution of KOH in water is assumed to be 4.183 J g^{-1} K^{-1}, what is the approximate value of $\Delta H_{\text{solution}}$ for KOH? (Assume that the calorimeter is thermally insulated from its surroundings).
(a) – 57 kJ/mol (b) – 4.6 kJ/mol
(c) 57 kJ/mol (d) 4.6 kJ/mol

2. Which of the following changes in the KOH solubility experiment would be the LEAST likely to change the measured value of ΔT?
(a) Doubling the amount of water used
(b) Doubling the amount of KOH used
(c) Doubling the amount of water and doubling the amount of KOH used
(d) Substituting an equal mass of NaOH for the KOH sample

3. Which of the following is the most serious *limitation* of ice calorimetry as a method of measuring enthalpies of the given reaction in the narrative?
(a) The method cannot be used to determine enthalpies of endothermic reactions.
(b) The method cannot be used directly to determine enthalpies of reactions that take place at 25°C
(c) Because of the reliance on ice and water, the method cannot be used to determine enthalpies of reactions that involve water or ice as reactants or products.
(d) Although satisfactory for determining the heat of a reaction, this method cannot evaluate a reaction enthalpy.

4. What was the approximate value of the heat of the chemical reaction in the ice calorimetry determination described?
(a) 20 J (b) 14 J
(c) – 7 kJ (d) 20 kJ

5. An experimenter wishes to substitute a mixture of solid and liquid benzene, C_6H_6 (which are in equilibrium at 5.5°C), for the ice-water mixture described above. The enthalpy of fusion of benzene is 10.59 kJ/mol. In which liquid-solid mixture will more grams of solid melt? (You may assume that the enthalpy of combustion of methane is the same at 5.5°C as it is at 0°C).
(a) The ice- water mixture
(b) The liquid-solid benzene mixture
(c) There will be no difference
(d) More information is needed

6. Refer to the thermogravimetric analysis curve in Figure - 3. If the initial mass of the fully hydrated sample was 1.00 g, what was its mass when it had been completely converted to $CuSO_4.3H_2O$?
(a) 0.07 g (b) 0.14 g
(c) 0.85 g (d) 0.93 g

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ				

PASSAGE-2

Dependence of Spontaneity on Temperature : For a process to be spontaneous, at constant temperature and pressure, there must be decrease in free energy of the system in the direction of the process, i.e., $\Delta G_{P,T} < 0$. $\Delta G_{P,T} = 0$ implies the equilibrium condition and $\Delta G_{P,T} > 0$ corresponds to non-spontaneity.

Gibbs-Helmholtz equation relates the free energy change to the enthalpy and entropy changes of the process as :

$$\Delta G_{P,T} = \Delta H - T\Delta S \qquad ...(1)$$

The magnitude of ΔH does not change much with the change in temperature but the entropy factor $T\Delta S$ changes appreciably. Thus, spontaneity of a process depends very much on temperature. For endothermic process, both ΔH and ΔS are positive. The energy factor, the first factor of equation, opposes the spontaneity whereas entropy factor favours it. At low temperature the favourable factor $T\Delta S$ will be small and may be less than ΔH, ΔG will have positive value indicating the non-spontaneity of the process. On raising temperature, the factor $T\Delta S$ increases appreciably and when it exceeds ΔH, ΔG would become negative and the process would be spontaneous.

For an exothermic process, both ΔH and ΔS would be negative. In this case the first factor of eq. 1 favours the spontaneity whereas the second factor opposes it. At high temperature, when $T\Delta S > \Delta H$, ΔG will have positive value, showing thereby non-spontaneity of the process. However, on decreasing temperature, the factor $T\Delta S$ decreases rapidly and when $T\Delta S < \Delta H$, ΔG becomes negative and the process occurs spontaneously. Thus, an exothermic process may be spontaneous at low temperature and non-spontaneous at high temperature.

7. When $CaCO_3$ is heated to a high temperature, it undergoes decomposition into CaO and CO_2 whereas it is quite stable at room temperature. The most likely explanation of it, is

(a) The enthalpy of reaction (ΔH) overweighs the term $T\Delta S$ at high temperature

(b) The term $T\Delta S$ overweighs the enthalpy of reaction at high temperature

(c) At high temperature, both enthalpy of reaction and entropy change become negative

(d) None of these

8. For the reaction at 25°C, $X_2O_{4\,(l)} \longrightarrow 2XO_{2\,(g)}$

$\Delta H = 2.1$ Kcal and $\Delta S = 20$ cal K^{-1}. The reaction would be

(a) spontaneous (b) non-spontaneous

(c) at equilibrium (d) unpredictable

9. For the reaction at 298 K, $2A + B \longrightarrow C$

$\Delta H = 100$ kcal and $\Delta S = 0.050$ kcal K^{-1}. If ΔH and ΔS are assumed to be constant over the temperature range, at what temperature will the reaction become spontaneous?

(a) 1000 K (b) 1500 K

(c) 2000 K (d) 2500 K

10. A rection has a value of $\Delta H = -40$ kcal at 400 K. Above 400 K, the reaction is spontaneous, below this temperature, it is not. The values of ΔG and ΔS at 400 K are respectively

(a) 0, –0.1 cal K^{-1} (b) 0, 100 cal K^{-1}

(c) –10 kcal, –100 cal K^{-1} (d) 0, –100 cal K^{-1}

11. The enthalpy change for a certain reaction at 300 K is –15.0 K cal mol^{-1}. The entropy change under these conditions is –7.2 cal K^{-1}mol^{-1}. The free energy change for the reaction and its spontaneous/non-spontaneous character will be

(a) –12.84 kcal mol^{-1}, spontaneous

(b) 12.84 kcal mol^{-1}, non-spontaneous

(c) –17.16 kcal mol^{-1}, spontaneous

(d) None of these

12. The dissolution of $CaCl_2 \cdot 6H_2O$ in a large volume of water is endothermic to the extent of 3.5 kcal mol^{-1}.

For the reaction,

$$CaCl_{2(s)} \quad 6H_2O_{(l)} \longrightarrow CaCl_2.6H_2O_{(s)}$$

ΔH is –23.2 kcal. The heat of solution of anhydrous $CaCl_2$ in large quantity of water will be

(a) –26.7 kcal mol^{-1} (b) –19.7 kcal mol^{-1}

(c) 19.7 kcal mol^{-1} (d) 26.7 kcal mol^{-1}

PASSAGE-3

Chemical reactions can be viewed from a thermodynamic perspective. Changes in enthalpy (ΔH) and entropy (ΔS) are the two driving forces that determine whether a reaction is spontaneous. Gibb's free energy (ΔG) combines these two factors in one equation : $\Delta G = \Delta H - T\Delta S$

Compound	**ΔH°_f (kJ/mol)**	**S° (J/mol-K)**
$N_{2\,(g)}$	0	192
$H_{2\,(g)}$	0	131
$NH_{3\,(g)}$	–46	192

MARK YOUR RESPONSE	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ
	12. ⓐⓑⓒⓓ				

13. What is $\Delta H°$ for the reaction,

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}\ ?$$

(a) –46 kJ (b) –92,000 J
(c) 0 J (d) 138 kJ

14. What is $\Delta S°$ for the reaction,

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}\ ?$$

(a) –201 J/*K* (b) –192 J/*K*
(c) –131 J/*K* (d) 201 J/*K*

15. At 25°C, the reaction, $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$ is

(a) spontaneous (b) non-spontaneous
(c) rapid (d) slow

16. If the temperature is increased, the equilibrium position of the reaction should

(a) increase (b) stay the same
(c) shift to the left (d) shift to the right

17. At 25°C, myoglobin is a globular protein. At high enough temperatures, however, it will become denatured as in the following reaction,

globular myoglobin → denatured myoglobin

Given that $\Delta H = –175$ kJ/mol and $\Delta S = –397$ J/mol. What is the minimum temperature at which globular myoglobin will become denatured?

(a) 43°C (b) 97°C
(c) 126°C (d) 168°C

PASSAGE-4

The change in value of $\Delta_r H°$ and $\Delta_r S°$ for a reaction with temperature can be found using the following relations

$$\Delta_r H°_{T_2} - \Delta_r H°_{T_1} = \Delta_r C°_p (T_2 - T_1)$$

$$\Delta_r S°_{T_2} - \Delta_r S°_{T_1} = \Delta_r C°_p \ln\left(\frac{T_2}{T_1}\right)$$

Methyl alcohol is produced by the action of CO(*g*) and $H_2(g)$ according to the following equation

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

	CO(g)	**H_2(g)**	**CH_3OH(g)**
$\Delta_f H°$	–114 kj/mol	–	– 201 kj/mol
$S°$ (j/k-mol)	198	29	240
$C°_{p,m}$ (J/mol-K)	29.4	28.8	44

Values given in table are at 300 *K*.

$$\left(\ell n\frac{320}{300} = 0.06\right)$$

18. $\Delta_r S°$ at 320 *K* is (j/mol-K)

(a) – 18.58 (b) – 15.88
(c) 85.81 (d) 81.58

19. $\Delta_r H^{\circ}_{320}$ is (kj/mol)

(a) –387.86 (b) – 87.86
(c) – 187.86 (d) –287.86

20. $\Delta_r G°$ at 320 *K* is (kj/mol)

(a) – 91.81 (b) – 98.18
(c) – 81.91 (d) none of these

PASSAGE-5

Entropy changes for ideal gas are as follows:

(i) Entropy change is terms of temperature and volume is given by

$$\Delta S = nC_v ln\frac{T_2}{T_1} + nR\,ln\frac{V_2}{V_1}$$

It is for *n* moles of an ideal gas from V_1 to V_2 when temperature changes from T_1 to T_2. C_v is the heat capacity at constant volume.

(ii) Entropy change in terms of temperature and pressure:

$$\Delta S = nC_p\, ln\frac{T_2}{T_1} + nRln\frac{P_2}{P_1} \quad \text{(For } n \text{ moles of gas)}$$

C_p is the molar heat capacity at constant pressure.

21. The entropy change for expansion of 14 g of nitrogen when heated from 27°C to 127°C at constant volume and constant pressure will be (in cal/degree) respectively.

(Given, $C_v = 4.94$ cal/mole in this temperature range)

(a) 0.70, 0.99 (b) 0.99, 0.70
(c) 0.50, 0.70 (d) 0.70, 0.50

MARK YOUR RESPONSE	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ
	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	

22. When two moles of an ideal gas $\left(C_{p,m}=\frac{5}{2}R\right)$ is heated from 300 K to 600 K at constant pressure, the value of ΔS is

(a) $\frac{3}{2}Rln2$ (b) $-\frac{3}{2}Rln2$

(c) $5\,R\,ln2$ (d) $\frac{5}{2}Rln2$

23. When two moles of an ideal gas $\left(C_p=\frac{5}{2}R\right)$ is heated from 300 K to 600 K at constant volume, the ΔS is

(a) $5Rln2$ (b) $\frac{3}{2}Rln2$

(c) $3Rln2$ (d) $-3Rln2$

MARK YOUR RESPONSE	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ			

C

REASONING TYPE

In the following questions two Statement-1 (Assertion) and Statement-2 (Reason) are provided. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct. Mark your responses from the following options:

(a) Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1.
(b) Both Statement-1 and Statement-2 are true and Statement-2 is not the correct explanation of Statement-1.
(c) Statement-1 is true but Statement-2 is false.
(d) Statement-1 is false but Statement-2 is true.

1. **Statement-1** : T, P and V are state variables or state functions.
Statement-2 : Their values depend on the state of the system and how it is reached.

2. **Statement-1** : A process is called adiabatic if the system does not exchange heat with the surroundings.
Statement-2 : It does not involve increase or decrease in temperature of the system.

3. **Statement-1** : There is exchange in internal energy in a cyclic process.
Statement-2 : Cyclic proces is the one in which the sytem returns to its initial state after a number of reactions.

4. **Statement-1** : For an isothermal reversible process $Q=-W$ i.e. work done by the system equals the heat absorbed by the system.
Statement-2 : Enthalpy change (ΔH) is zero for isothermal process.

5. **Statement-1** : At constant temperature and pressure whatever heat absorbed by the system is used in doing work.
Statement-2 : Internal energy change is zero.

6. **Statement-1** : Enthalpy of formation of graphite is zero but of diamond is not zero.
Statement-2 : Enthalpy of formation of most stable allotrope is taken as zero.

7. **Statement-1** : When a solid melts, decrease in enthalpy is observed.
Statement-2 : Melting of a solid is endothermic.

8. **Statement-1** : The value of enthalpy of neutralization of weak acid and strong base is numerically less than 57.1 kJ.
Statement-2 : All the OH^- ions furnished by 1 g equivalent of strong base are not completely neutralized.

9. **Statement-1** : Enthalpy changes are positive when $Na_2SO_4.10H_2O$, $CuSO_4.5H_2O$ and salt like NaCl, KCl etc. which do not form hydrates are dissolved in water. But enthalpy changes are negative when anhydrous salts capable of forming hydrates are dissolved in water.
Statement-2 : The difference in the behaviour is due to large difference in the molecular weight of hydrated and anhydrous salts. The substance with larger molecular weight usually show positive enthalpy changes on dissolutions.

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	

10. **Statement-1** : Many endothermic reactions that are not spontaneous at room temperature become spontaneous at high temperature.

Statement-2 : Entropy of the system increases with increase in temperature.

11. **Statement-1** : An exothermic process, non-spontaneous at high temperature, may become spontaneous at low temperature.

Statement-2 : With decrease in temperature, randomness (entropy) decreases.

12. **Statement-1** : A reaction which is spontaneous and accompanied by decrease of randomness must be exothermic.

Statement-2 : All exothermic reactions are accompanied by decrease of randomness.

13. **Statement-1** : The endothermic reactions are favoured at lower temperature and the exothermic reactions are favoured at higher temperature.

Statement-2 : When a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of change.

14. **Statement-1** : The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.

Statement-2 : The volume occupied by the molecules of an ideal gas is zero.

15. **Statement-1** : Endothermic process is favoured by low temperatures.

Statement-2 : For the process ΔG becomes negative when $T\Delta G > \Delta H$.

16. **Statement-1** : For an isothermal process involving an ideal gas Gibbs and Helmbaltz free energy charges are equal, i.e. $\Delta G = \Delta A$.

Statement-2 : In isothermal process for an ideal gas system both ΔE and ΔH are zero.

17. **Statement-1** : Idealized heat engine can convert heat completely into work.

Statement-2 : The temperature of sink can not be below the temperature of the codest part of the universe.

18. **Statement-1** : The entropy of fusion of solid and vaporization of liquid is positive.

Statement-2 : Both the change of solid into liquid and liquid into vapour takes place with increase of disorder.

19. **Statement-1** : The process of dissolution of gases in water is always an endothermic process.

Statement-2 : The dissolution of gases in water proceeds with negative value of ΔS.

20. **Statement-1** : An exothermic process which is non-spontaneous at high temperature may become spontaneous at a low temperature.

Statement-2 : There occurs a decrease in entropy factor as the temperature is decreased.

21. **Statement-1** : The reaction between sodium (Na) and oxygen (O_2) to form sodium oxide (Na_2O) and sodium peroxide (Na_2O_2) is spontaneous.

Statement-2 : The formation of sodium oxide and sodium peroxide proceeds vigorously.

22. **Statement-1** : The heat absorbed by a system (q) under condition of constant volume ($\Delta V = 0$) is fully used up in increasing energy instead of doing work (i.e. $W = 0$)

Statement-2 : Mechanical work (PdV) is zero at constant volume.

23. **Statement-1** : The work done in an isothermal expansion is more in magnitude as compared to that involved in adiabatic expansion.

Statement-2 : In the graph of pressure (P on y-axis) against volume (V on x-axis), the curve decreases more rapidly for reversible adiabatic expansion than in the P-V graph (P on y-axis and V on x-axis) for reversible isothermal expansion starting from same initial state.

MARK YOUR RESPONSE	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ
	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ
	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ	

D MULTIPLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONE OR MORE is/are correct.

1. Which of the following is/are not path dependent ?
(a) Work (b) Heat change
(c) Work + heat change (d) $q_{rev/T}$

2. Which of the following relations are correct for a perfect gas ?

(a) $\left(\frac{\partial U}{\partial V}\right)_T = 0$ (b) $\left(\frac{\partial H}{\partial P}\right)_T = 0$

(c) $\left(\frac{\partial T}{\partial P}\right)_H = 0$ (d) $\left(\frac{\partial U}{\partial T}\right)_V = 0$

3. For an isothermal irreversible expansion of 1 mole of a perfect gas, indicate the correct relation :
(a) $\Delta U = 0$ (b) $\Delta H = 0$

(c) $q = -RT\left(1 - \frac{P_2}{P_1}\right)$ (d) $W = RT\ln\frac{P_2}{P_1}$

4. A particular state of system is arrived at starting from a given state in two different ways, (1) following reversible path and (2) irreversible path. Which of the following relations will be correct for the system if the processes are isothermal ?
(a) $\Delta S_{rev} = \Delta S_{irr}$ (b) $q_{rev} = q_{irr}$

(c) $\Delta S_{rev} = \Delta S_{irr} = \frac{q_{rev}}{T}$ (d) $\Delta S_{irr} = \frac{q_{irr}}{T} \neq \Delta S_{rev}$

5. What could be the correct statements about idealized Carnot's heat engine working between temperatures T_2 (source) and T_1 (sink) ?

(a) Efficiency $\eta = \frac{T_2 - T_1}{T_2}$, which is maximum
(b) Complete conversion of heat into work is possible i.e. , η can be unity
(c) Power of the engine is maximum
(d) Power of the engine is zero

6. A definite amount of an ideal gas is subjected to an expansion from initial pressure P_1 to final pressure P_2 under (i) isothermal and (ii) adiabatic conditions. Indicate the correct statements :

(a) $\Delta V_{(isothermal)} = \Delta V_{(adiabatic)}$

(b) $\Delta V_{(isothermal)} > \Delta V_{(adiabatic)}$

(c) V vs P plot is steeper for isothermal expansion
(d) V vs P plot is steeper for adiabatic expansion

7. The standard enthalpy of formation of CO_2 will be given by :
(a) standard enthalpy of combustion of diamond
(b) standard enthalpy of combustion of graphite
(c) standard enthalpy of combustion of CO
(d) sum of standard enthalpy of formation and enthalpy of combustion of CO

8. Enthalpy changes of which of the following reactions ***do not*** represent the enthalpy of formation of NO?

(a) $\frac{1}{2}N_{2(g)} + \frac{1}{3}O_{3(g)} \rightarrow NO_{(g)}$

(b) $N_{(g)} + O_{(g)} \rightarrow NO_{(g)}$

(c) $NO_{2(g)} \rightarrow NO_{(g)} + \frac{1}{2}O_{2(g)}$

(d) $\frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow NO_{(g)}$

9. Which of the following expressions represent Gibbs-Helmholtz equation ?
(a) $\Delta G = \Delta H + T\Delta S$
(b) $-\Delta G = T\Delta S - \Delta H$

(c) $\Delta G = \Delta H + T\left(\frac{d(\Delta G)}{dT}\right)_P$

(d) $\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_p = -\frac{\Delta H}{T^2}$

10. Which of the following is/are endothermic reaction(s) ?

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

(b) $H_2O_{(\ell)} \rightarrow H_{2(g)} + \frac{1}{2}O_{2(g)}$

(c) $C_2H_{6(g)} \rightarrow C_2H_{4(g)} + H_{2(g)}$

(d) $S_{(rhombic)} \rightarrow S_{(monoclinic)}$

11. Which of the following is always negative ?
(a) enthalpy of hydration
(b) enthalpy of neutralization
(c) enthalpy of hydrogenation
(d) enthalpy of solution

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ
	11. ⓐⓑⓒⓓ				

12. $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}, \quad \Delta H = -94.05\,\text{kcal mol}^{-1}$

$C_{(diamond)} + O_{2(g)} \rightarrow CO_{2(g)}, \quad \Delta H = -94.50\,\text{kcal mol}^{-1}$

Then, which of the following is/are correct ?

(a) $C_{(diamond)} \rightarrow C_{(graphite)}, \quad \Delta H = 450\text{cal mol}^{-1}$

(b) $C_{(graphite)} \rightarrow C_{(diamond)}, \quad \Delta H = 450\text{cal mol}^{-1}$

(c) Graphite is stabler than diamond

(d) Diamond is stabler allotrope than graphite.

13. At 300K, the reactions which have the following values of thermodynamic parameters, occur spontaneously:

(a) $\Delta G° = -400\text{kJ mol}^{-1}$

(b) $\Delta H° = 200\text{kJ mol}^{-1}, \; \Delta S° = -4\text{JK}^{-1}\text{mol}^{-1}$

(c) $\Delta H° = -200\text{kJ mol}^{-1}, \; \Delta S° = 4\text{JK}^{-1}\text{mol}^{-1}$

(d) $\Delta H° = 200\text{kJ mol}^{-1}, \; \Delta S° = -40\text{JK}^{-1}\text{mol}^{-1}$

14. Which of the following statement(s) is/are correct ?

(a) The system of constant entropy and constant volume will attain the equilibrium in a state of minimum energy

(b) The entropy of the universe is on the increase

(c) The process would be spontaneous when $(\Delta S)_{E,V} < 0, \; (\Delta E)_{S,V} > 0$

(d) The process would be spontaneous when $(\Delta S)_{E,V} > 0, \; (\Delta E)_{S,V} < 0$

15. The dependence of enthalpy of the reaction on temperature,

$C_3H_{8(g)} + 5O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(\ell)}$ is represented by the expression(s) (C_p and C_v are the molar heat capacities at constant pressure and constant volume.)

(a) $\left[\dfrac{d(\Delta H)}{dt}\right]_p = \Delta C_p$

(b) $\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$

(c) $\Delta H_2 - \Delta H_1 = \Delta C_v(T_2 - T_1)$

(d) $\Delta E_2 - \Delta E_1 = \Delta C_v(T_2 - T_1)$

16 Enthapy of atomization of $C_2H_{6(g)}$ and $C_3H_{8(g)}$ are 620 and 880 kJmol^{-1} respectively. The C – C and C – H bond energies are respectively

(a) 80 and 60 kJmol^{-1} (b) 80 and 90 kJmol^{-1}

(c) 70 and 90 kJmol^{-1} (d) 100 and 80 kJmol^{-1}

17. For the reaction between CO_2 and graphite,

$CO_{2(g)} + C_{(s)} \longrightarrow 2CO_{(g)}$; $\Delta H = 170\text{kJ}$ and $\Delta S = 170\,\text{JK}^{-1}$. The reaction will be spontaneous at

(a) 300 K (b) 500 K

(c) 900 K (d) 1100 K

18. While of the following thermodynamic relations is/are correct?

(a) $dG = VdP - SdT$ (b) $dU = PdV + TdS$

(c) $dH = VdP + TdS$ (d) $dG = VdP + SdT$

19. In a process involving *n* moles of an ideal gas, the entropy change of the system is given by

(a) $nC_v \ln\dfrac{T_2}{T_1} + nR\ln\dfrac{V_2}{V_1}$

(b) $nC_p \ln\dfrac{T_2}{T_1} + nR\ln\dfrac{V_2}{V_1}$

(c) $nC_v \ln\dfrac{T_2}{T_1} + nR\ln\dfrac{P_1}{P_2}$

(d) $nC_v \ln\dfrac{T_2}{T_1} + nR\ln\dfrac{V_1}{V_2}$

20. Consider the reaction,

$C_6H_{12}O_{6(g)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(\ell)}$.

Which of the following expressions is/are correct ?

(a) $\Delta H^{\circ}_{\text{reaction}}$

$= 6\Delta H^{\circ}_f(CO_2) + 6\Delta H^{\circ}_f(H_2O) - \Delta H^{\circ}_f(C_6H_{12}O_6)$

(b) $\Delta G°_{\text{reaction}}$

$= 6\Delta G°_f(CO_2) + 6\Delta G°_f(H_2O) - \Delta G°_f(C_6H_{12}O_6)$

(c) $\Delta S°_{\text{reaction}}$

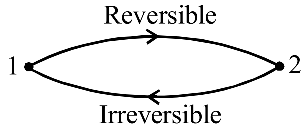
$= 6S°(CO_2) + 6S°(H_2O) - S°(C_6H_{12}O_6)$

(d) $\Delta S°_{\text{reaction}}$

$= 6S°(CO_2) + 6S°(H_2O) - 6S°(C_6H_{12}O_6) - 6S°(O_2)$

MARK YOUR RESPONSE	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ
	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ	

21. For the cyclic process given below, which of the following relations is/are correct ?



(a) $\Delta S = S_2 - S_1 = \int_1^2 \frac{\delta q_{\text{rev}}}{T}$

(b) $\Delta S = S_1 - S_2 = \int_2^1 \frac{\delta q_{\text{irr}}}{T}$

(c) $\Delta S_{\text{cycle}} = 0 = \int_1^2 \frac{\delta q_{\text{rev}}}{T} + \int_2^1 \frac{\delta q_{\text{irr}}}{T}$

(d) $\Delta S_{\text{cycle}} = 0 > \int_1^2 \frac{\delta q_{\text{rev}}}{T} + \int_2^1 \frac{\delta q_{\text{irr}}}{T}$

22. An ideal gas system undergoes expansion from pressure P_1 to P_2 under (I) adiabatic and (II) isothermal conditions. Then

(a) $\Delta U(\text{I}) < 0$ and $\Delta U(\text{II}) = 0$

(b) $\Delta U(\text{I}) = 0$ and $\Delta U(\text{II}) < 0$

(c) $\Delta V(\text{I}) < \Delta V(\text{II})$

(d) $\Delta V(\text{I}) > \Delta V(\text{II})$

23. Choose the correct statements.

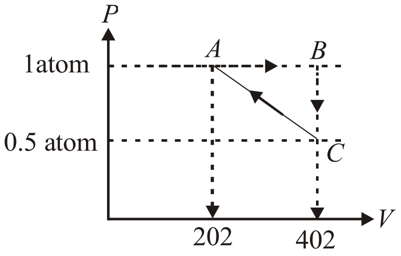
(a) First law of thermodynamics is also known as the law of thermal equilibrium.

(b) It is not possible to find out the heat of combustion at room temperature.

(c) The triple point of water is one of the reference points on the thermodynamic scale of temperature.

(d) One degree kelvin is equal to $\frac{1}{273.16}$ of the triple point of water.

24. On the basis of the following graph (P–V graph), choose the correct statements.



(a) The entropy change for the over all process is zero.

(b) For the over all process $\Delta H > \Delta E$.

(c) Total work done, $W = q$

(d) Total work = – 620.77 J

25. Select the process(es) that take place with increase of entropy

(a) $3O_2(g) \longrightarrow 2O_3(g)$

(b) Sugar + Water $\longrightarrow$ Solution

(c) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

(d) $H_2(g) + Cl_2(g) \longrightarrow$ Mixture

26. Select those which are not state function.

(a) heat (b) work

(c) enthalpy (d) change in enthalpy

27. Which of the following are correct for an isothermal reversible expansion of an ideal gas

(a) $\Delta E = 0$

(b) $\Delta H = 0$

(c) $W = nRTln\frac{P_1}{P_2}$

(d) $W = -q$

MARK YOUR RESPONSE	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ	24. ⓐⓑⓒⓓ	25. ⓐⓑⓒⓓ
	26. ⓐⓑⓒⓓ	27. ⓐⓑⓒⓓ			

28. In an adiabatic process, the work done during expansion or compression of an ideal gas is equal to

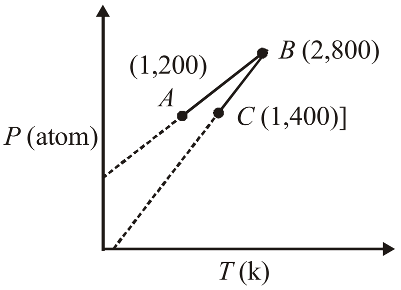
(a) $nC_v\Delta T$

(b) $\dfrac{nR}{\gamma-1}(T_2-T_1)$

(c) $-nRP_{\text{ext}}\left[\dfrac{T_2P_1-T_1P_2}{P_1P_2}\right]$

(d) $-2.303\, n\, RT \log\dfrac{V_2}{V_1}$

29. One mole of an ideal gas is subjected to a reversible process that involves two steps ($A\rightarrow B$ and $B\rightarrow C$). The pressure at A and C is same. Consider the graph and choose correct statements.



(a) Work done $A\rightarrow B$ is zero

(b) In path $A\rightarrow B$ work will be done on the gas by the surroundings

(c) Volume of gas at C = 2 × Volume of gas at A

(d) Volume of gas at B is 32.8

MARK YOUR RESPONSE	28. ⓐⓑⓒⓓ	29. ⓐⓑⓒⓓ			

E

MATRIX-MATCH TYPE

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labeled 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 following :**

Column I	**Column II**
(A) $\Delta S_{Total} = 0$	p. Adiabatic
(B) $\Delta S_{System} = R\, ln\,\dfrac{V_2}{V_1}$	q. Reversible Process
(C) $\mu_{J.T.} = 0$	r. Perfect gas
(D) PV^{γ} = a constant	s. Isothermal process

2. **Match the following :**

Column I	**Column II**
(A) Complete conversion of heat into work in Carnot's engine takes place at sink temperature	p. Critical temperature
(B) Molecular motion disappears at	q. Inversion temperature
(C) $\mu_{J.T.} = 0$	r. –273.15° C
(D) Liquefaction of a real gas is not possible above	s. 0 K

MARK YOUR RESPONSE

1.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

2.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

3. **Match the following**

Column I		Column II
(A) Standard enthalpy of a reaction ($\Delta H°$)	p.	$-RTlnK$
(B) Free energy change of a reaction (ΔG)	q.	$RT^2\left(\dfrac{d\Delta G}{dT}\right)_p$
(C) Standard free energy of a reaction ($\Delta G°$)	r.	$-\left(\dfrac{d\Delta G}{dT}\right)_p$
(D) Entropy change of a reaction (ΔS)	s.	$-nFE_{cell}$

4. **Match the following**

Column I		Column II
(A) $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$	p.	Work done by the system
(B) $KCl_{(s)} + H_2O_{(\ell)} \rightarrow KCl_{(aq)}$	q.	Work done on the system
(C) $CaC_{2(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} + C_2H_{2\,(g)}$	r.	$\Delta S > 0$
(D) $NH_4Cl_{(s)} \rightarrow NH_{3(g)} + HCl_{(g)}$	s.	$\Delta S < 0$

5. **Match the following**

Column I		Column II
(A) $2N_2O \rightarrow 2N_{2(g)} + O_{2(g)} + \text{Heat}$	p.	Spontaneous at low tempertature
(B) $H_2O_{(g)} \rightarrow H_2O_{(l)}$	q.	Spontaneous at high temperature
(C) $2NH_{3(g)} + \text{Heat} \rightarrow N_{2(g)} + 3H_{2(g)}$	r.	Non-spontaneous at all temperatures
(D) $3O_{2(g)} + \text{Heat} \rightarrow 2O_{3(g)}$	s.	Spontaneous at all temperatures

6. **Match the heat changes (at 298K and 1 atm. pressure) of the reactions listed in column I with the quantities listed in column II :**

Column I		Column II
(A) $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$	p.	Standard enthalpy of CO_2
(B) $C_{graphite} + O_{2(g)} \rightarrow CO_{2(g)}$	q.	Enthalpy of reaction
(C) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$	r.	Enthalpy of combustion of CO
(D) $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$	s.	Standard enthalpy of H_2O

MARK YOUR RESPONSE

3.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

4.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

5.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

6.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

7. **Match the enthalpy changes listed in Column II with the reactions listed in Column I.**

	Column I		**Column II**
(A)	$HCl_{(aq)} + NH_4OH_{(aq)}$	p.	$\Delta H = 57.3$ kJ
(B)	$H_2SO_{4(aq)}$ + Excess of $KOH_{(aq)}$	q.	$\Delta H = -57.3$ kJ
(C)	0.5L of 1 $M\, H_2SO_4$ + Excess of NaOH	r.	$\lvert\Delta H\rvert < 57.3$ kJ
(D)	$H_2O_{(\ell)} \longrightarrow H^+_{(aq)} + OH^-_{(aq)}$	s.	$\Delta H = -114.6$ kJ

8.

	Column I **(Function)**		**Column II** **(Variables on which the function depends)**
(A)	ΔH	p.	T
(B)	ΔG	q.	P
(C)	ΔE	r.	mass
(B)	ΔS	s.	V

9.

	Column I		**Column II**
(A)	Reversible isothermal expansion of an ideal gas	p.	$W = -2.30\,RT \log \frac{V_2}{V_1}$
(B)	Reversible adiabatic compression of an ideal gas	q.	PV^{γ} = constant
(C)	Irreversible adiabatic expansion of an ideal gas	r.	$W = \frac{nR}{\gamma - 1}(T_2 - T_1)$
(D)	Irreversible isothermal compression of an ideal gas	s.	$\Delta H = 0$

MARK YOUR RESPONSE

7.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

8.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

9.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

F

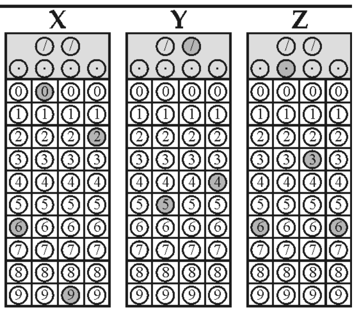
NUMERIC/INTEGER ANSWER TYPE

The answer to each of the questions is either numeric (eg. 304, 40, 3010, 3 etc.) or a fraction (2/3, 23/7) or a decimal (2.35, 0.546).

The appropriate bubbles below the respective question numbers in the response grid have to be darkened.

For example, if the correct answers to question X, Y & Z are 6092, 5/4 & 6.36 respectively then the correct darkening of bubbles will look like the following.

For single digit integer answer darken the extreme right bubble only.



1. The reaction $2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}; \Delta H \quad -560\,kJ$ is carried out in a container of constant volume. Two moles of CO and one mole of O_2 are taken in a container of 1 L at 500 *K* whereby they 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 in kJ) of ΔU at 500 *K* (1 L atm = 0. kJ).

2. Enthalpy of combustion of ethanol, carbon and hydrogen are –1362, – 393 and – 286 kJ mol^{-1} respectively. Compute C – C bond energy (in kJ mol^{-1}) using following data.

$\Delta H^\circ_{vap}(C_2H_5OH) \quad 44\,kJ\,mol^{-1}$

$\Delta H_f(C) \quad 715\,kJ\,mol^{-1} \quad BE(C-H) \quad 415\,kJ\,mol^{-1}$

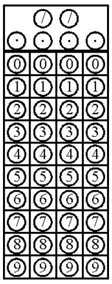
$\Delta H^\circ_f(H) \quad 218\,kJ\,mol^{-1} \quad BE(C-O) \quad 356\,kJ\,mol^{-1}$

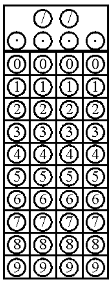
$\Delta H^\circ_f(O) \quad 249\,kJ\,mol^{-1}, \quad BE(O-H) \quad 463\,kJ\,mol^{-1}$

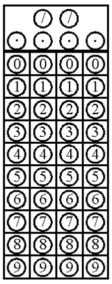
3. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for CH_4 as fuel (2 L/hour of CH_4 and 12 L/hour of O_2) is to be readjusted for an equimolar mixture of ethane and butane under the same condition of temperature and pressure. In order to get the same calorific output what should be the rate of supply of oxygen (in Litre/hr)? Assume the gases to behave ideally and losses due to incomplete combustion, etc., are the same for both the fuels.

Enthalpy of combustion : $CH_4 = -810\,kJ\,mol^{-1}$; $C_2H_6 = -1560\,kJ$; $C_4H_{10} = -2880\,kJ\,mol^{-1}$

MARK YOUR RESPONSE

1.


2.


3.


Answerkey

A SINGLE CORRECT CHOICE TYPE

1.	a	**2.**	d	**3.**	c	**4.**	b	**5.**	d	**6.**	a	**7.**	c	**8.**	a	**9.**	d	**10.**	b
11.	b	**12.**	d	**13.**	c	**14.**	b	**15.**	c	**16.**	c	**17.**	d	**18.**	b	**19.**	c	**20.**	a
21.	c	**22.**	d	**23.**	c	**24.**	d	**25.**	b	**26.**	b	**27.**	b	**28.**	c	**29.**	b	**30.**	a
31.	b	**32.**	d	**33.**	b	**34.**	c	**35.**	b	**36.**	d	**37.**	d	**38.**	d	**39.**	b	**40.**	b
41.	c	**42.**	b	**43.**	b	**44.**	d	**45.**	b	**46.**	a	**47.**	c	**48.**	b	**49.**	c	**50.**	c
51.	d	**52.**	c	**53.**	d	**54.**	c	**55.**	d	**56.**	b	**57.**	b	**58.**	b	**59**	c	**60**	b
61	d	**62**	d	**63**	a	**64**	d	**65**	a	**66**	d	**67**	d	**68**	c	**69**	b	**70**	b
71	d	**72**	d	**73**	a	**74**	a	**75**	b										

B COMPREHENSION TYPE

1	(a)	**5**	(b)	**9**	(d)	**13**	(b)	**17**	(d)	**21**	(a)
2	(c)	**6**	(c)	**10**	(d)	**14**	(a)	**18**	(a)	**22**	(c)
3	(b)	**7**	(b)	**11**	(a)	**15**	(a)	**19**	(b)	**23**	(c)
4	(c)	**8**	(a)	**12**	(b)	**16**	(c)	**20**	(c)		

C REASONING TYPE

1	(c)	**5**	(a)	**9**	(c)	**13**	(d)	**17**	(a)	**21**	(b)
2	(c)	**6**	(a)	**10**	(b)	**14**	(b)	**18**	(a)	**22**	(a)
3	(a)	**7**	(d)	**11**	(b)	**15**	(d)	**19**	(d)	**23**	(a)
4	(b)	**8**	(c)	**12**	(c)	**16**	(a)	**20**	(b)		

D MULTIPLE CORRECT CHOICE TYPE

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

E MATRIX-MATCH TYPE

1. A-q; B-q, r, s; C-r; D-p, q, r

2. A-r, s; B-r, s; C-q; D-p

3. A-q; B-s; C-p; D-r

4. A-q, s; B-r; C-p, r; D-p, r

5. A-s; B-p; C-q; D-r

6. A-r; B-p; C-s; D-q

7. A-r; B-s; C-q; D-p

8. A-p, q, r; B-p, q, r, s; C-p, r, s; D-p, q, r, s

9. A-p, s; B-q, r; C-r; D-s

F NUMERIC/INTEGER ANSWER TYPE

1	557	**2**	331	**3**	10.95

Solutions

A SINGLE CORRECT CHOICE TYPE

2. **(d)** $V_f \quad \dfrac{P_iV_i}{P_f} \quad \dfrac{(5\text{ bar})\times(2\text{ dm}^3)}{1\text{ bar}} \quad 10\text{ dm}^3$

Work, $w = -P_{\text{ext}}(V_f - V_i) = -(1\text{ bar})(10-2)\text{ dm}^3$
$= -1\times10^5\text{ Pa}\times8\times10^{-3}\text{ m}^3 = -800\text{ J}$

3. **(c)** $\Delta H = \Delta U + (P_2V_2 - P_1V_1) = 30 + (4\times5 - 2\times3) = 44\text{ L atm}$

4. **(b)** $q = -w_{\text{rev}} = -\left(-2.303nRT\log\dfrac{P_1}{P_2}\right)$

$= 2.303\times\dfrac{40}{4}\times2\times300\log\dfrac{1}{10} \quad -13.82\text{ k cal}$

7. **(c)** $\Delta H = (-40.8)\times\dfrac{1.8}{18} = -4.08\text{ k J};$

$\Delta S \quad \dfrac{\Delta H}{T} \quad \dfrac{-4.08\times10^3}{373.15} \quad -10.93\text{ JK}^{-1}$

8. **(a)** In adiabatic process, $q = 0$, $\Delta U = q + w = w = -100$ J

9. **(d)** $\Delta H = \Delta U + \Delta n_{(g)}RT$; $\Delta n_{(g)} = 1$ in (d); $\Delta n_{(g)} \quad 0$ in other cases.

10. **(b)** Heat of combustion determined by bomb calorimeter is at constant volume, i.e. ΔU.

$2C_6H_{6(\ell)} \quad 15O_{2(g)} \rightarrow 12CO_{2(g)} \quad 6H_2O_{(\ell)}$

Hence, $\Delta H - \Delta U = \Delta nRT = (12-15)\times8.314\times300$

$= -7.483\text{ kJ}$

12. **(d)** Ozone (O_3), the allotropic form of oxygen is of higher energy (by 68 kcal mol^{-1}) than O_2. Hence, O_3 can not be taken as the reference or standard state.

13. **(c)** 1 mole of $H_2SO_4 \equiv 2$ equiv.;

$\Delta H_N = 2\times(-57.3) = -114.6\text{ kJ}$

16. **(c)** Number of equiv. of $HNO_3 = 1\times0.5 = 0.5$; equivalents of KOH $= 2\times0.1 = 0.2$ (limiting reagent)

Enthalpy change = Number of equivalents × ΔH_N
$= 0.2\times(-57.3) = -11.46\text{ kJ}$

17. **(d)**

$$\begin{array}{l} H_2C_2O_{4(aq)} \rightarrow 2H^+_{aq} + C_2O^{2-}_{4(aq)};\ \Delta H \quad x\text{ kJ} \\ \underline{[H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(\ell)},\ \Delta H = -57.3\text{kJ}]\times2} \\ H_2C_2O_4 + 2OH^- \rightarrow 2H_2O_{(\ell)} + C_2O_4^{2-},\ \Delta H = x - 114.6\text{ kJ} \end{array}$$

But $x - 114.6 = -106$ (given) $\Rightarrow x = 8.6\text{ kJ mol}^{-1}$

18. **(b)** $CH_{4(g)} + 2O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(\ell)},\ \Delta H = -890\text{ k J}$ .....(i)

$2H_2O_{(\ell)} \rightarrow 2H_2O_{(g)},\ \Delta H = 2\times40.5 \quad 81\text{ kJ}$ ......(ii)

(i) + (ii), $CH_{4(g)} + 2O_{2(g)} \rightarrow 2CO_{2(g)} \quad 2H_2O_{(g)}$,

$\Delta H = -890 \quad 81 \quad -809\text{ kJ}$

19. **(c)** For 5 moles of gas at T, $PV_1 = 5RT$
For 5 moles of gas at T-2, $PV_2 = 5R(T-2)$
Hence, $PV_2 - PV_1 = P(V_2 - V_1) = P\Delta V$
$= 5R[T-2-T] = -10R$
or, $-P\Delta V = 10R$ (ΔV is negative, W is +ive)

21. **(c)** $C_3H_{8(g)} + 5O_2 \rightarrow 3CO_{2(g)} + 4H_2O_{(l)},\ \Delta H \quad x_3$

$\Delta H_r \quad x_3 \quad 3\Delta H_f(CO_2) + 4\Delta H_f(H_2O)$

$- \Delta H_f(C_3H_8) - 5\Delta H_f(O_2)$

$= 3x_1 + 4x_2 - \Delta H_f(C_3H_8) - 5\times0$

or $\Delta H_f(C_3H_8) \quad 3x_1 \quad 4x_2 - x_3$

22. **(d)** $CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)},\ \Delta H \quad 360\text{ k cal}$

Hence, C–H bond energy $\dfrac{360}{4} \quad 90\text{k cal mol}^{-1}$

$C_2H_{6(g)} \rightarrow 2C_{(g)} + 6H_{(g)}, \Delta H \quad 620\text{k cal}$

Hence, $H_{C-C} \quad 6H_{C-H} \quad 620$

or $H_{C-C} \quad 620 - 6H_{C-H} \quad 620 - 6\times90 \quad 80\text{ k cal}$

23. **(c)** $\Delta H_c(C_2H_6) - \Delta H_c(CH_4) = -368.2 - (-210.8)$

$= -157.4$

$\Delta H_c(C_3H_8) - \Delta H_c(C_2H_6) = -526.2 - (-368.4)$

$= -157.8$

Thus, average $\Delta H_c(-CH_2) = -\dfrac{157.4 \quad 157.8}{2}$

$= -157.6\text{ kcal mol}^{-1}$

Then, $\Delta H_c(C_6H_{14}) = \Delta H_c(C_3H_8) + 3\Delta H_c(-CH_2)$

$= -526.2 \quad 3(-157.6) \quad -999\text{ k cal}$

24. **(d)** $\Delta H_{\text{hyd}} = \Delta H_{\text{sol}} - \Delta H_{\text{lattice}} = 1 - 180$

$= -179 \text{ k cal mol}^{-1}$

Thus, $\Delta H_{\text{hyd}}(\text{Na}^+) + \Delta H_{\text{hyd}}(\text{Cl}^-) = -179$

or, $\Delta H_{\text{hyd}}(\text{Na}^+) + \frac{2}{3}\Delta H_{\text{hyd}}(\text{Na}^+) = -179$

or, $\Delta H_{\text{hyd}}(\text{Na}^+) = -107.4 \text{k cal mol}^{-1}$

27. **(b)** $\Delta S_{\text{freezing}} = n \times \frac{\Delta H_{\text{freezing}}}{T_f} = \frac{90}{18} \times \frac{(-6.0 \times 10^3 \text{ J})}{273.15}$

$= -109.83 \text{ JK}^{-1}$

28. (c) ΔH_N for strong acid with strong base = –13.7 k cal equiv^{-1}

$\Delta H_{\text{ion}}(\text{CH}_3\text{COOH}) = -12.5 - (-13.7) = +1.2 \text{ k cal mol}^{-1}$

$\Delta H_{\text{ion}}(\text{NH}_4\text{OH}) = -10.5 - (-13.7) - \Delta H_{\text{ion}}(\text{CH}_3\text{COOH})$

$= 13.7 - 10.5 - 1.2 = 2 \text{ k cal mol}^{-1}$

30. **(a)** $\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{X}_2 \rightarrow \text{HX}$, Let x = enthalpy of X–X bond

$\Delta H_f(\text{HX}) = -50 = \frac{1}{2}\Delta H_{\text{H-H}} + \frac{1}{2}\Delta H_{\text{X-X}} - \Delta H_{\text{H-X}}$

$= \frac{1}{2} \times 2x + \frac{1}{2}x - 2x = -\frac{x}{2}$

or, $x = 50 \times 2 = 100 \text{ k J mol}^{-1}$

31. **(b)** $\Delta H_{\text{S-S}} + 2\Delta H_{\text{H-S}} = 239$ $\quad 2\Delta H_{\text{H-S}} = 175$

Hence, $\Delta H_{\text{S-S}} = 239 - 175 = 64 \text{ kcal mol}^{-1}$

Then, ΔH for $8\text{S}_{(g)} \rightarrow \text{S}_{8(g)}$ is $8 \times (-64) = -512$k cal

32. **(d)** $\text{CuSO}_{4(s)} + 5\text{H}_2\text{O}_{(g)} \rightarrow \text{CuSO}_4.5\text{H}_2\text{O}_{(s)}$,

$\Delta H = -71.5 \text{ k cal}$

$5\text{H}_2\text{O}_{(\ell)} \rightarrow 5\text{H}_2\text{O}_{(g)}$, $\Delta H = 5 \times 10.5 \text{ k cal}$

Adding the two eqn.,

$\text{CuSO}_{4(s)} + 5\text{H}_2\text{O}_{(\ell)} \rightarrow \text{CuSO}_4.5\text{H}_2\text{O}_{(s)}$

$\Delta H = -71.5 + 52.5 = -19.0 \text{ k cal mol}^{-1}$

40. **(b)** Use the relation $C_p - C_v = R$

42. **(b)** $\text{S}_{(s)} + 3\text{F}_{2(g)} \rightarrow \text{SF}_{6(g)}$, $\Delta H = -1100 \text{ kJ mol}^{-1}$

Hence, $\Delta H_f(\text{S}_{(g)}) + 6\Delta H_f(\text{F}_{(g)}) - 6\Delta H_{\text{S-F}} = -1100$

or $275 + 6 \times 80 - 6\Delta H_{\text{S-F}} = -1100 \Rightarrow \Delta H_{\text{S-F}} = 309.16$

43. **(b)** $\Delta U = q + w = q - P\Delta V = 200\text{J} - 10^5 \text{P}_\text{a} \times (5-4) \times 10^{-3} \text{m}^3$

$= 200\text{J} - 100 \text{ P}_\text{a} \text{ m}^3 = 200 \text{ J} - 100 \text{ J} = 100 \text{ J}$

44. **(d)** In the polymerisation of $\text{CH}_2 = \text{CH}_2$ into $(-\text{CH}_2 - \text{CH}_2-)_\text{n}$, one C = C double bond is changed into 2 C–C bonds.

Hence, $\Delta H = \Delta H_{\text{C=C}} - 2\Delta H_{\text{C-C}} = 590 - 2 \times 331$

$= -72 \text{ k J mol}^{-1}$

Number of moles of C_2H_4 polymerised $= \frac{56}{28} = 2$

Enthalpy change $= 2 \times (-72) = -144$ kJ

45. **(b)** $\text{Na}_{(s)} + \frac{1}{2}\text{Cl}_{2(g)} \rightarrow \text{NaCl}_{(s)}, \Delta H = -410 \text{kJ}$

$\Delta H_{\text{sub}}(\text{Na}) + IE(\text{Na}_{(g)}) + \frac{1}{2}\Delta H_{\text{Cl-Cl}}$

$- EA(\text{Cl}) + \Delta H_{\text{lattice}}(\text{NaCl}) = -410$

or $108 + 493 + \frac{1}{2} \times 242 - 368 + \Delta H_{\text{lattice}}(\text{NaCl}) = -410$

or $\Delta H_{\text{lattice}}(\text{NaCl}) = -744 \text{ kJ mol}^{-1}$

46. **(a)** $\text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{(\ell)}, \Delta H = -285.8 \text{kJ}$ .....(i)

$\text{H}_2\text{O}_{(\ell)} \rightarrow \text{H}^+_{(aq)} + \text{OH}^-_{aq}, \Delta H = 57.3 \text{kJ}$ .....(ii)

$\frac{1}{2}\text{H}_{2(g)} + \text{aq} \rightarrow \text{H}^+_{(aq)} + \text{e}^-, \Delta H = 0$

(by convention) ....(iii)

$(\text{i}) + (\text{ii}) - (\text{iii}), \frac{1}{2}\text{H}_{2(g)} + \frac{1}{2}\text{O}_{2\,(g)} + \text{e}^- + \text{aq} \rightarrow \text{OH}^-_{(aq)}$

$\Delta H = -285.8 + 57.3 = -228.5 \text{ kJ}$

48. **(b)** $\frac{1}{2}\text{H}_{(g)} + \frac{1}{2}\text{Cl}_{2(g)} \rightarrow \text{HCl}_{(g)}$

$\Delta S° = \Sigma\ S°\ (\text{Products}) - \Sigma\ S°\ (\text{reactants})$

$= S°_{\text{HCl}} - \left(\frac{1}{2}S°_{\text{H}_2} + \frac{1}{2}S°_{\text{Cl}_2}\right) = 187 - \frac{1}{2}(131 + 223)$

$= 10 \text{ JK}^{-1}$

49. **(c)** $\text{HA} + \text{aq} \rightarrow \text{H}^+_{(aq)} + \text{A}^-_{(aq)}, \Delta H = x \text{ kJ mol}^{-1}$

$\text{H}^+_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{H}_2\text{O}_{(\ell)}\ \Delta H = -57.3 \text{ kJ mol}^{-1}$

Hence, $\text{HA} + \text{OH}^-_{(aq)} \rightarrow \text{H}_2\text{O}_{(\ell)} + \text{A}^-_{(aq)},$

$\Delta H = x - 57.3$

But $\Delta H = x - 57.3 = -56.1$ (given), $x = 1.2 \text{ kJ mol}^{-1}$

It no self ionization of HA occurs at all, $\Delta H(\text{ionization}) = 1.5 \text{ kJ mol}^{-1}$

Hence, % ionization in 1 *M* solution

$$= \frac{(1.5-1.2)}{1.5} \times 100 = 20$$

50. **(c)** $\frac{1}{2}N_{2(g)} + \frac{3}{2}F_{2(g)} \rightarrow NF_{3(g)}, \Delta H = -113 \text{ kJ}$

or, $\frac{1}{2}\Delta H_{N\equiv N} + \frac{3}{2}\Delta H_{F-F} - 3\Delta H_{N-F} = -113 \text{ kJ}$

If x kJ mol^{-1} is the energy of F-F bond, then energy of $N \equiv N$ bond = $6x$

Hence, $\frac{1}{2} \times 6x + \frac{3}{2} \times x - 3 \times 273 = -113 \text{ kJ}$ or

$x = 156.9 \text{ kJ mol}^{-1}$ = F - F bond energy

$N \equiv N$ bond energy $= 6 \times 156.9 = 941.4 \text{ kJ mol}^{-1}$

52. **(c)** H_2SO_4 is a dibasic acid. Equimolar equal volume of H_2SO_4 contains twice the number of equivalents as compared to HNO_3 and so also the heat produced.

54. **(c)** In the second experiment, the heat produced is twice that in first case but at the same time thermal capacity of the resulting solution (twice as that in first case) is doubled. Hence, temperature rise will be the same.

55. **(d)** ΔH_f^o (water) can not be calculated) unless bond energies of H-H and O =O bonds are given.

59. **(c)** $Mn_{(s)} + 2HNO_{3(aq)} \longrightarrow Mn(NO_3)_{2(aq)} + H_{2(g)}$;

Moles of H_2 = Moles of Mn $= \frac{110}{55} = 2$

Work done due to expansion

$= -P\Delta V = -\Delta nRT = -2 \times 8.314 \times 300 = -4988.4 \text{ J}$

60. $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$

$$\Delta C_p = C_p(H_2O) - C_p(H_2) - \frac{1}{2}C_p(O_2)$$

$$= 33.58 - (28.90 + \frac{1}{2} \times 29.36) = -10 \text{ JK}^{-1}$$

$\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$;

$\Delta H_2 = \Delta H_1 + \Delta C_p(373 - 298)$

$= -241.8 \text{ kJ} - 10 \times 75 \text{ J} = -242.55 \text{ kJ}$

61. **(d)** $C_2H_5OH_{(\ell)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(\ell)}$;

$\Delta H = 2 - 3 = -1$

No. of moles of $C_2H_5OH = \frac{46}{46} = 1$;

$q_p - q_v = \Delta nRT = (-1) \times 8.314 \times 300 = -2.49 \text{ kJ}$

63. **(a)** $\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$

$\Delta H_2 - 24 = (0.031 - 0.055)(100 - 50)$

$\Rightarrow \Delta H_2 = 22.8 \text{ cal g}^{-1}$

64. **(d)** (i) $CuSO_{4(s)} + \text{aqua} \longrightarrow CuSO_{4(aq)}$

$\Delta H = \frac{-1.451}{0.1} = -14.51 \text{ k cal mol}^{-1}$

(ii) $CuSO_4.5H_2O_{(s)} + \text{aqua} \longrightarrow CuSO_{4(aq)}$

$\Delta H = \frac{0.264}{0.1} = 2.64 \text{ k cal mol}^{-1}$

From (i) – (ii), $CuSO_{4(s)} + 5H_2O_{(\ell)} \longrightarrow CuSO_4.5H_2O_{(s)}$;

$\Delta H = -17.15 \text{ k cal mol}^{-1}$

65. **(a)** C_v for diatomic ideal gas $= \frac{3}{2}RT + R = \frac{5}{2}R \text{ mol}^{-1}$

C_p for diatomic gas $= C_v + R = \frac{5}{2}R + R = \frac{7}{2}R \text{ mol}^{-1}$

Enthalpy increase of 2 moles $= \frac{7}{2}R \times 2 = 7R$

67. **(d)** Moles of the acid neutralized $= \frac{200}{1000} \times 0.1 = 0.02$

Moles of acid remaining undissociated

$$= 0.02\left(1 - \frac{25}{100}\right) = 0.015$$

Heat evolved during neutralization for 100% ionization $= 13700 \times 0.02 = 274 \text{ cal}$

Heat used up for dissociation of 0.015 mole $= 274 - 244 = 30 \text{ cal}$

Heat of dissociation per mole

$$= \frac{30}{0.015} = 2000 \text{ cal} = 2.0 \text{ k cal}$$

68. **(d)** Let x mole of KOH be neutralized by the strong acid HA. Then, moles neutralized by $HB = 1 - x$

Hence, $-13.7 \times x + (-12.7) \times (1 - x) = -13.5$

$$\Rightarrow \quad x = 0.8; \quad \frac{x}{1-x} = \frac{0.8}{0.2} = 4$$

69. **(b)** For isothermal and reversible expansion of an ideal gas

$$\Delta S = 2.303 nR \log \frac{V_2}{V_1}$$

$$= 2.303 \times \frac{2.8}{28} \times 8.314 \log \frac{10}{1} = 1.915 \text{JK}^{-1}$$

70. **(b)** $\mathrm{C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}}$

$\mathrm{C_{(s)} + O = O \longrightarrow O = C = O}$

$$\Delta H_{\text{combustion}} = \Delta H_{\mathrm{C_{(s)} \to C_{(g)}}} + \Delta H_{\mathrm{O=O}} - 2\Delta H_{\mathrm{C=O}}$$

$= 718 + 498 - 2 \times 339 = 538 \text{ kJ mol}^{-1}$

Resonance energy

$= \Delta H_f(\text{experimental}) - \Delta H_f(\text{calculated})$

$= -393 - 538 = -931 \text{ kJ mol}^{-1}$

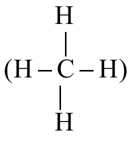
71. **(d)** If $n_p < n_r$ then $\Delta n_{(g)} = n_p - n_r =$ '–'ve

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

$\therefore$ $\Delta H = \Delta E$ – some quantity [$\because \Delta n$ is – tive]

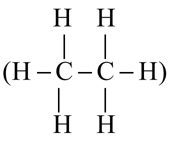
or $\Delta H < \Delta E$

72. **(d)** In case of dissociation of $\mathrm{CH_4}$, the dissociation energy is equal to the energy required to break four C – H



bonds $\left(\mathrm{H}-\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}-\mathrm{H}\right)$

$\therefore$ C – H bond energy $= \dfrac{360}{4} = 90$



In case of dissociation of $\mathrm{C_2H_6}$ $\left(\mathrm{H}-\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}-\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}-\mathrm{H}\right)$

6 C – H bonds and one C – C bond break

$\therefore$ C – C bond energy $= 620 - 6 \times 90$

$= 620 - 540$

$= 80$ k cal/mol

73. **(a)** For an adiabatic process, q = 0

For ideal gas $C_v = \dfrac{3}{2}R$ (given)

We know that during adiabatic expansion of an ideal gas, the work is done at the expense of internal energy of the gas. Therefore

$$dE = C_v \times dT = -PdV$$

or $\quad C_v dT = -\dfrac{nRT}{V}.dV \quad \left[\because P = \dfrac{nRT}{V}\right]$

or $\quad \dfrac{C_v}{nR} \cdot \dfrac{dT}{T} = -\dfrac{dV}{V}$

Integrating between limits, we get

$$\int_{T_1}^{T_2} \frac{C_v}{nR} \frac{dT}{T} = -\int_{V_1}^{V_2} \frac{dV}{V}$$

or $\quad \dfrac{C_v}{nR} \ell n \dfrac{T_2}{T_1} = \ell n \dfrac{V_1}{V_2}$

or $\quad \dfrac{C_v}{nR} \log \dfrac{T_2}{T_1} = \log \dfrac{V_1}{V_2}$

or $\quad \dfrac{3}{2} \log \dfrac{T_2}{300} = \log \dfrac{10}{20}$ (Substituting given values)

or $\quad \dfrac{T_2}{300} = 0.63$

or $\quad T_2 = 189\,K$

$\Delta E = nC_v R(T_2 - T_1)$ (For adiabatic process)

$= 1 \times \dfrac{3}{2} \times 8.314 \times (189 - 300) = -1384$ J.

$\Delta E = w = -1384$ J.

74. **(a)** The formation of $\mathrm{CH_3OCH_3}$ may be represented as

$$2\mathrm{C}(s) + 3\mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \to \mathrm{H_3C - 0 - CH_3}; \Delta H = ?$$

It invoves vapourisation of 2 gram atoms of solid carbon and breaking 3 moles of H – H bonds and $\dfrac{1}{2}$ mole of O = O bonds resulting in the formation of 6 C – H bonds and 2 C – O bonds. Thus the heat of formation of $\mathrm{CH_3 - O - CH_3}$ is given by

$$\Delta H = (2 \times 125 + 3 \times 103 + \frac{1}{2} \times 177) - (6 \times 87 + 2 \times 70)$$

$= -14.5\,k$cal

75. **(b)** Given: $Q_v = \frac{2\times 5023}{x+21.4}$

$\therefore \quad Q_v = \frac{590\times 5023}{590+21.24} = 4850 \text{ cal}$

[$\because$ $CuCl_2.10H_2O + 590H_2O = CuCl_2.600H_2O + Q_v$]

Also given
$CuCl_2 + 600H_2O = CuCl_2.600\,H_2O + 11080$ cal
(anhydrous)

$\therefore \quad CuCl_2 + 10H_2O \rightleftharpoons CuCl_2.10H_2O + (11080-4850)\text{cal}$

Hence heat of solution of $CuCl_2$ in 10 moles of water = 6230 cal

B COMPREHENSION TYPE

1. **(a)** Heat evolved for the dissolution of 5.6 g of KOH in 100 g of water
= mass of solution × sp. heat × temperature rise
$= 105.6 \times 4.18 \times (37-24)$ J = 5.738 kJ

Hence, $\Delta H_{\text{solution}}$ for KOH $= \frac{-5.738\times 5.6}{56}$

$= -57.38 \text{ kJ mol}^{-1}$

2. **(c)** On doubling the amount of KOH, heat evolved will be doubled. However, on doubling the amount of water at the same time, thermal capacity of the solution will also be doubled. Hence, ΔT will practically remain the same.

3. **(b)** The correct answer is (b). The measured enthalpy of reaction would be at constant temperature of 0°C and has to be modified using other informations. The choice (a) is incorrect because with the absorption of heat more ice will be formed.

4. **(c)** From the change in volume due to melting of ice the mass of ice that melts, is calculated. Using specific heat of fusion of ice, heat evolved is calculated.

Mass of ice melted $= \frac{-1.82}{-0.091} = 20.0$ g

$q_{\text{reaction}} = -q_{\text{ice}} = -20.0 \times 334 = -6680 \text{ J} = -7 \text{ kJ}$

5. **(b)** The latent heat of solid benzene $= \frac{10.59 \text{ kJ mol}^{-1}}{78.1 \text{ g mol}^{-1}}$

$= 0.136 \text{ kJ g}^{-1} = 136 \text{ J g}^{-1}$
Since the corresponding value for ice-water is higher, 334 J g^{-1}, the heat produced during the reaction will melt a greater mass of solid benzene.

6. **(c)** Molar mass of $CuSO_4.5H_2O = 249.7 \text{ g mol}^{-1}$

Moles of $CuSO_4.5H_2O = \frac{1}{249.7} \text{ g mol}^{-1}$

Molar mass of $CuSO_4.3H_2O = 213.7 \text{ g mol}^{-1}$

Mass of $CuSO_4.3H_2O$ formed $= \frac{1\times 213.7}{249.7} = 0.85$ g

7. **(b)** ΔH for the process :

$$CaCO_{3\,(s)} \longrightarrow CaO_{\,(s)} + CO_{2\,(g)}$$

is positive and so also ΔS. At low temperature $\Delta H > T\Delta S$, so $\Delta G = \Delta H - T\Delta S$ will be positive signalling non-spontaneity of the process. At high temperature, $\Delta H < T\Delta S$ and ΔG will be negative signalling the spontaneity of the process.

8. **(a)** $\Delta G = \Delta H - T\Delta S = 2.1 \text{ kcal} - 298 \times 20 \times 10^{-3} \text{ kcal} = -3.86$ kcal. Since ΔG for the process is negative, so it would be spontaneous.

9. **(d)** The reaction will be at equilibrium when $\Delta G = 0$, $\Delta G = \Delta H - T\Delta S = 0$;

$T = \frac{\Delta H}{\Delta S} = \frac{100 \text{ kcal}}{0.050 \text{ kcal K}^{-1}} = 2000 \text{ K}$. Hence, the reaction will become spontaneous at temperature greater than 2000 K.

10. **(d)** $\Delta G = \Delta H - T\Delta S = 0$ at 400 K.

$\Delta S = \frac{\Delta H}{T} = \frac{-40\times 10^3 \text{ cal}}{400} = -100 \text{ cal K}^{-1}$. At 400 K the reaction is at equilibrium i.e., $\Delta G = 0$.

11. **(a)** $\Delta G = \Delta H - T\Delta S = -15.0 \text{ kcal} - 300 \times (-7.2 \text{ cal K}^{-1}) \times 10^{-3} = -12.84$ kcal.

12. **(b)** $CaCl_2.6H_2O + H_2O_{\,(l)} \longrightarrow Ca^{2+}_{(aq)} + 2Cl^{-}{}_{(aq)}$
$\Delta H° = 3.5 \text{ kcal mol}^{-1}$

$CaCl_{2(s)} + 6H_2O \longrightarrow CaCl_2.6H_2O_{(s)}$
$\Delta H° = -23.2 \text{ kcal mol}^{-1}$

Adding : $CaCl_2 + H_2O_{\,(l)} \longrightarrow Ca^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)}$
$\Delta H° = 3.5 - 23.2 \text{ kcal} = -19.7 \text{ kcal mol}^{-1}$

13. **(b)** $\Delta H°_{\text{reaction}} = 2\Delta H°_f(NH_3) - \Delta H°_f(N_2) - 3\Delta H°_f(H_2)$
$= 2\times(-46) - 0 - 3\times 0 = -92$ kJ

14. **(a)** $\Delta S°_{\text{reaction}} = \Sigma S°_{\text{products}} - \Sigma S°_{\text{reactants}}$

$= 2S°_{(NH_3)} - S°_{(N_2)} - 3S°_{(H_2)}$

$= 2\times 192 - 192 - 3\times 131 = -201 \text{ JK}^{-1}$

15. **(a)** $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -92 \text{ kJ} - 298(-201 \text{ JK}^{-1})$

$= -32.1 \text{ kJ}$; spontaneous

16. **(c)** Since the reaction is exothermic ($\Delta H^\circ = -92$ kJ), equilibrium constant will decrease on raising the temperature. Hence, equilibrium will shift towards left.

17. **(d)** $\Delta G = 0 = \Delta H - T\Delta S = -175 \times 10^3 - T(-397)$

$\Rightarrow T = 441 \text{ K} = 168^\circ\text{C}$

18. **(a)** $\Delta_r S^\circ{}_{320} = \Delta_r S^\circ{}_{300} + \Delta_r C_p [320 - 300]$

$\Delta_r S^o_{300} = S^o_{CH_3OH} - S^o_{CO} - 2S^o_{H_2}$

$= 240 - 198 - 2 \times 29$

$= -16$ J/K-mol

$\therefore \quad \Delta_r S^\circ{}_{320} = -16 + \Delta_r . C^\circ_p \, ln\frac{T_2}{T_1}$

$= -16 - 43 \, ln\frac{320}{300}$

$[\Delta_r C^\circ_p = 44 - 29.4 - 2 \times 28.8 = -43$ J/K-mol$]$

$= -18.58$ J/mol-K

19. **(b)** $\Delta_r H^\circ_{320} = \Delta_r H^\circ_{300} + \Delta_r C^\circ_p (T_2 - T_1)$

$= -201 - (-114) + \frac{-43 \times 20}{1000} \qquad [\Delta_r C^\circ_p = -43 \text{ J}]$

$= -87 + \frac{-43 \times 20}{1000}$

$= -87 - 0.86$

$= -87.86$

20. **(c)** $\Delta_r G^\circ_{320} = \Delta_r H^\circ_{320} - T\Delta_r S^\circ_{320}$ [Gibbs-Helmholtz eqn.]

$= -87.86 - \frac{320 \times (-18.58)}{1000}$

$= -81.91 \quad [\because \Delta_r H^\circ_{320} = -87.86 ; \Delta_r S^\circ_{320} = -18.58]$

21. **(a)** At constant volume,

$$\Delta S = nC_v ln\frac{T_2}{T_1}$$

Given n = 14 g of nitrogen

$= \frac{14}{28}$ mole or 0.5 mole

$\therefore \quad \Delta S = 0.5 \times 4.94 \times 2.303 \log\frac{400}{300}$

$\left[ln\frac{T_2}{T_1} = 2.303 \log\frac{T_2}{T_1}\right]$

$= 0.70 \text{ cal K}^{-1}$

At constant pressure

$$\Delta S = nC_p ln\frac{T_2}{T_1}$$

Since $C_p = C_v + R$

$\therefore \quad C_p = 4.94 + 2.0 = 6.94$ cal/mole

$\therefore \quad \Delta S = \frac{1}{2} \times 6.94 \times 2.303 \log\frac{400}{300} \; [\because n = \frac{1}{2}]$

$= 0.99 \text{ cal K}^{-1}$

22. **(c)** Using the relation, $\Delta S = nC_p \ln\frac{T_2}{T_1}$

We get,

$\Delta S = 2 \times \frac{5}{2} R ln\frac{600}{300} = 5 \, R ln 2$

23. **(c)** $\Delta S = n \, C_v \, ln\frac{T_2}{T_1}$

$= 2 \times \left(\frac{5}{2} - 1\right) R ln 2 \qquad [\because C_v = C_p - R]$

$= 2 \times \frac{3}{2} R ln 2 = 3 \, R ln 2$

C REASONING TYPE

1. **(c)** Values of state functions depend only on the state of the system and not on how it is reached.

2. **(c)** It may involve increase or decrease in temperature of the system. Systems in which such processes occur, are thermally insulated from the surroundings.

3. **(a)** As internal energy is a state function so its value depends on intial and final states of the system. In case of cyclic system initial and final states are same. So $\Delta E = 0$, and similarly $\Delta H = 0$.

4. **(b)** In an isothermal process change in internal energy (ΔE) is zero (as it is a function of temperature).
$\therefore$ According to first law of thermodynamics
$\because Q + W = \Delta E$. Hence $Q = -W$ (if $\Delta E = 0$)
If a system undergoes a change in which internal energy of the system remains constant (i.e. $\Delta E = 0$) then $-W = Q$. This means that work done by the system equals the heat absorbed by the system.

5. **(a)** $Q = -W$ if $\Delta E = 0$

6. **(a)** Reason is the correct explanation of Assertion.

7. **(d)** When a solid melts, increase in enthalpy is observed.

8. **(c)** The value of enthalpy of neutralisation of weak acid by strong base is less than 57.1 kJ. This is due to the reason that the part of energy liberated during combination of H^+ and OH^+ ions is utilised in the ionisation of weak acid.

9. **(c)** The exothermic or endothermic behaviour of dissolution depends only upon the nature of the salt and not on its molecular weight.

10. **(b)** The factor $T\Delta S$ increases with increase in temperature.

11. **(b)** Exothermic reaction is non-spontaneous when ΔS is –ve and temperature is high. With decrease in temperature $T\Delta S$ becomes smaller than ΔH in magnitude and so ΔG becomes –ve.

12. **(c)** An exothermic reaction may be accompanied by increase or decrease of randomness.

13. **(d)** The statement is clearly wrong in context to Le-chatelier's principle, which states that "increase in temperature shifts the equilibrium in the forward direction of those reactions which proceed with absorption of heat (**endothermic reactions**), and in the backward direction of those reactions which proceed with the evolution of heat (**exothermic reactions**)." E is clearly true again according to Le-chatelier principle.

14. **(b)** Here both assertion and reason are correct. There is no force of attraction between molecules of an ideal gas and no work has to be done in tearing apart the molecules during expansion.

19. **(d)** Assertion is false, Reason is true.
Gases dissolve in water exothermically.

20. **(b)** Both assertion and reason are true but reason is not the correct explanation of assertion.
For a process to be spontaneous ΔG must be negative.
$\Delta G = \Delta H - T\Delta S$
Exothermic process (ΔH is negative) is non-spontaneous if ΔS is negative and temperature is high because in such condition $T\Delta S > \Delta H$. ($\Delta G = \Delta H - T\Delta S = +$ tive). When temperature is decreased, $T\Delta S < \Delta H$ ($\Delta G = \Delta H - T\Delta S = -$tive) and so the reaction becomes spontaneous.

21. **(b)** Both assertion and reason are correct but reason is not the correct explanation of assertion.
A spontaneous reaction may be a fast reaction or it may be a slow reaction.

22. **(a)** Both assertion and reason are true and reason is the correct explanation of assertion.

23. **(a)** Both assertion and reason are true and reason is the correct explanation of assertion.

D MULTIPLE CORRECT CHOICE TYPE

13. **(a, c)** $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$: In case of options (a), (c) and (d), ΔG° is negative .

16. **(b)** $C_2H_{6(g)} \longrightarrow 2C_{(g)} + 6H_{(g)}$

$$\Delta H_{C-C} + 6\Delta H_{C-H} = 620\,\text{kJmol}^{-1}$$

$C_3H_{8(g)} \longrightarrow 3C_{(g)} + 8H_{(g)}$;

$$2\Delta H_{C-C} + 8\Delta H_{C-H} = 880\,\text{kJmol}^{-1}$$

Hence, $\Delta H_{C-C} = 80\ \text{kJmol}^{-1}$;
$\Delta H_{C-H} = 90\ \text{kJmol}^{-1}$

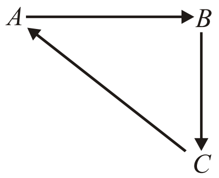
17. **(d)** For equilibrium $\Delta G = 0 = \Delta H - T\Delta S$,

$$T = \frac{\Delta H}{\Delta S} = \frac{170 \times 10^3}{170} = 1000\,\text{K}$$

The reaction would be spontaneous at temperature greater than 1000 K, so as to have ΔG to be negative.

23. **(b, c)** Zeroth law of thermodynamics is called the law of thermal equilibrium.

24. **(a, d)** The over all process can be depicted as



Thus it is a cyclic process.
Hence, $\Delta E = 0$, $\Delta H = 0$, $\Delta S = 0$ (cyclic process)
and $\Delta E = q + W$ (Ist law)
$\therefore\ 0 = q + W$
or $q = -W$

Total work done = $W_{A\to B}+W_{B\to C}+W_{C\to A}$

$$\therefore \quad W=-P(V_B-V_A)+0+2.303\,nRT\log\frac{V_C}{V_A}$$

$$=-(40-20)+0+2.303\times 1\times 0.082\times\log\frac{V_C}{V_A}$$

= – 6.13 litre-atmosphere
= –620.77J

25. **(b)** Dissolution of solid in liquid results in more randomness i.e. increase in entropy.

Mixing of gases results in increase in entropy.

26. **(a, b)** Both H & ΔH are state functions, independent of path.

27. **(a, b, d)** For such a process ,

$$W=-nRT\ell n\frac{P_1}{P_2}$$

28. **(a, b, c)** The expression

$$W=-2.303\,RT\log\frac{V_2}{V_1}$$

29. **(c, d)** Volume of A,

$$V_A=\frac{1\times R\times 200}{1}=200R\quad[\because PV=nRT]$$

$$=200\times 0.082=16.4\text{ L}$$

gives work in isothermal and reversible expansion of an ideal gas

$$V_B=\frac{0.082\times 800}{2}=32.8\text{L}$$

$$V_C=\frac{6.082\times 400}{1}=32.8\text{L}$$

Since $V_B > V_A$, expansion of gas occurs along A and B and work is done by the gas.

E MATRIX-MATCH TYPE

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

(A) For a reversible process, $\Delta S_{\text{system}} = -\Delta S_{\text{surr}}$.

or $\Delta S_{\text{system}}+\Delta S_{\text{surr}}=\Delta S_{\text{Total}}=0$

(B) From first law, $dE=\delta q_{\text{rev}}+W=\delta q_{\text{rev}}-PdV$

$$\delta q_{\text{rev}}=TdS=dE+P\,dV=CvdT+PdV$$

$$dS=C_v\frac{dT}{T}+\frac{PdV}{T}=Cv\frac{dT}{T}+R.\frac{dV}{V}=R\frac{dV}{V}$$

($dT = 0$ for isothermal process)

$$dS=\int_1^2 R\frac{dV}{T}$$

Integrating $\int_1^2 dS=S_2-S_1=\Delta S=\int_1^2 R\frac{dV}{V}=R\ln\frac{V_2}{V_1}$

(C) In perfect gas intermolecular forces do not exit.

Hence, $\left(\frac{dP}{dT}\right)_H=\mu_{\text{J.T.}}=0$

(D) For adiabatic and reversible process,

$$\delta q_{\text{rev}}=0=dE+PdV=CvdT+RT\frac{dV}{V}$$

(for ideal gas)

$$\frac{dT}{T}=-\frac{R}{C_v}\times\frac{dV}{V}=-\frac{Cp-C_v}{C_v}\times\frac{dV}{V}=-(\gamma-1)\frac{dV}{V}$$

Integrating, $\int_1^2\frac{dT}{T}=\ln\frac{T_2}{T_1}$

$$=-\int_1^2(\gamma-1)\frac{dV}{V}=-(\gamma-1)\ln\frac{V_2}{V_1}=(\gamma-1)\ln\frac{V_1}{V_2}$$

$$=\ln\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$\frac{T_2}{T_1}=\left(\frac{V_1}{V_2}\right)^{\gamma-1}$ for ideal gas $\frac{T_2}{T_1}=\frac{P_2V_2}{P_1V_1}$

Hence, $\frac{P_2V_2}{P_1V_1}=\left(\frac{V_1}{V_2}\right)^{\gamma-1}$ $P_1V_1^{\gamma}=P_2V_2^{\gamma}=\text{a constant}$

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

(A) Efficiency of Carnot's heat engine, $x=\frac{T_2-T_1}{T_2}=1$

when

T_1 = temperature of sink = 0 K (or – 273.15° C)

(B) Molecules cease to move at 0 *K* (or – 273.15° C)

(C) At inversion temperature a real gas does not exhibit Joule-Thompson effect.

4. **A-q, s; B-r; C-p, r; D-p, r**

(A) $\Delta n \quad 2-(2 \quad 1) \quad -1$. System contract at constant pressure. Hence, work is done by the surroundings on the system. Also $\Delta S \quad 0$.

(B) On dissolution, disorder increases and hence $\Delta S \quad 0$.

(C) $\Delta n = +1$. Disorder increases and the system expands against external pressure. Hence, $\Delta S > 0$ and work is done by the system.

(D) $\Delta n = +2$. Both the disorder and volume of the system increase. Hence $\Delta S > 0$ and *W* is negative (work is done by the system).

5. **A-s; B-p; C-q; D-r**

(A) $\Delta n = +1$, $\Delta S > 0$. ΔH is negative. $\Delta G = \Delta H - T\Delta S$ is negative at all temperatures, i.e. process is spontaneous at all temperatures.

(B) The process is exothermic, i.e. ΔH is negative. Also $\Delta S \quad 0$. ΔG would be negative at low temperatures.

(C) $\Delta H \quad 0$; $\Delta n = \quad 2$, so $\Delta S > 0$. Hence ΔG would be negative at high temperatures.

(D) $\Delta H \quad 0$; $\Delta n \quad -1$, so $\Delta S \quad 0$. Hence, ΔG would be positive at all temperatures.

6. **A-r; B-p; C-s; D-q**

(A) The reaction is combustion of CO.

(B) One mole of CO_2 in its standard state is formed from the constituent elements from their standard states.

(C) One mole of $H_2O_{(l)}$ is formed from the constituent elements in their standard states.

(D) Heat effect is simply the enthalpy of reaction.

7. **A-r; B-s; C-q; D-p**

(A) NH_4OH is a weak base. Hence $|\Delta H| < 57.3$ kJ (Heat of neutralization of strong acid with strong base)

(B) One mole of H_2SO_4 = 2 equivalents are neutralized with strong base. Hence, $\Delta H = 2 \times (-57.3) = -114.6$ kJ

(C) 0.5 L of 1 *M* H_2SO_4 = 0.5 mole of H_2SO_4 = 2 × 0.5 = 1 equivalent. Hence, $\Delta H = -57.3$ kJ

(D) ΔH = – Heat change accompanying the union of H and OH^- = – (– 57.3) = 57.3 kJ.

F NUMERIC/INTEGER ANSWER TYPE

1. **Ans : 557 kJ**

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

$(\because \Delta V \quad 0)$

$\Delta U = \Delta H - V\Delta P = -550 - [1 \times (40-70) \times 0.1] = -557$ kJ, Absolute value = **557 kJ**

2. **Ans : 331 kJ mol^{-1}**

$$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} \quad 3H_2O_{(l)}$$

(combustion)

$$\Delta H_{comb}(C_2H_5OH) = 2\Delta H \;{}_f(CO_2)$$

$$+3\Delta H^\circ{}_f(H_2O) - \Delta H \;{}_f(C_2H_5OH)$$

$$-1362 = 2 \times (-393) + 3(-286) - \Delta H^o{}_f(C_2H_5OH)$$

$$\Delta H \;{}_f(C_2H_5OH) \quad -282\,\text{kJmole}^{-1}$$

$$2C_{(s)} \quad 3H_{2(g)} \quad \frac{1}{2}O_{2(g)} \rightarrow C_2H_5OH_{(\ell)}$$

$$\Delta H_f(C_2H_5OH) = 2\Delta H_f(C) + 6\Delta H_f(H) \; +$$

$$\Delta H_f(O) - 5BE(C-H) - BE(C-C)$$

$$-BE(C-O) - BE(O-H) - \Delta H_{vap}(C_2H_5OH)$$

– 282 = 2 × 715 + 6 × 218 + 249 – 5 × 415 – *BE* (C – C) – 356 – 463 – 44

BE (C – C) = **331 kJ mol^{-1}**

3. **Ans : 10.95 L hr^{-1}**

Number of moles of gas α Volume (*V*) ; moles = KV

$$CH_4 + 2O_2 \longrightarrow CO_2 \quad 2H_2O$$

Rate of supply of $CH_4 = K \times 2\,\text{mol hr}^{-1}$

Rate of supply of $O_2 = 3 \times 2 \times 2K \quad 12K\,\text{mol hr}^{-1}$

Colorific output = – 810 × 2K = – 1620 $K\,\text{kJ hr}^{-1}$

$$C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O; \Delta H = -1560\,\text{kJ}$$

$$C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O; \Delta H = -2880\,\text{kJ}$$

For 1 : 1 mole mixture of C_2H_6 and C_4H_{10}

Enthalpy of combustion $= -\left(\frac{1560}{2}+\frac{2880}{2}\right)$

$= -2220$ kJ mol^{-1}

For the same calorific outfit, rate of supply of the fuel mixture $= -\frac{1620K}{-2220} = \frac{27K}{37}$ mole hr^{-1} $= \frac{27}{37}$ L hr^{-1}

= 0.73 L hr^{-1}

Rate of supply of $O_2 = \frac{1}{2}\times\frac{27}{37}\times\frac{7}{2}\times 3+\frac{1}{2}\times\frac{27}{37}\times\frac{13}{2}\times 3 =$

$\frac{81}{4\times 37}(7+13) = \frac{81\times 5}{37} =$ **10.95 L hr^{-1}**

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