Chapter 6. Thermodynamics

1. For a given reaction, $\Delta H = 35.5$ kJ mol^{-1} and $\Delta S = 83.6$ J K^{-1} mol^{-1}. The reaction is spontaneous at (Assume that ΔH and ΔS do not vary with temperature.)
(a) $T > 425$ K (b) all temperatures
(c) $T > 298$ K (d) $T < 425$ K
(NEET 2017)

2. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy ΔU of the gas in joules will be
(a) –500 J (b) –505 J
(c) +505 J (d) 1136.25 J
(NEET 2017)

3. For a sample of perfect gas when its pressure is changed isothermally from p_i to p_f, the entropy change is given by
(a) $\Delta S = nR \ln\left(\frac{p_f}{p_i}\right)$ (b) $\Delta S = nR \ln\left(\frac{p_i}{p_f}\right)$
(c) $\Delta S = nRT \ln\left(\frac{p_f}{p_i}\right)$ (d) $\Delta S = RT \ln\left(\frac{p_i}{p_f}\right)$
(NEET-II 2016)

4. The correct thermodynamic conditions for the spontaneous reaction at all temperatures is
(a) $\Delta H < 0$ and $\Delta S > 0$
(b) $\Delta H < 0$ and $\Delta S < 0$
(c) $\Delta H < 0$ and $\Delta S = 0$
(d) $\Delta H > 0$ and $\Delta S < 0$ *(NEET-I 2016)*

5. Consider the following liquid-vapour equilibrium.
Liquid $\rightleftharpoons$ Vapour
Which of the following relations is correct?
(a) $\frac{d\ln P}{dT^2} = \frac{-\Delta H_v}{T^2}$ (b) $\frac{d\ln P}{dT} = \frac{\Delta H_v}{RT^2}$
(c) $\frac{d\ln G}{dT^2} = \frac{\Delta H_v}{RT^2}$ (d) $\frac{d\ln P}{dT} = \frac{-\Delta H_v}{RT}$
(NEET-I 2016)

6. The heat of combustion of carbon to CO_2 is –393.5 kJ/mol. The heat released upon formation of 35.2 g of CO_2 from carbon and oxygen gas is
(a) + 315 kJ (b) – 630 kJ
(c) – 3.15 kJ (d) – 315 kJ *(2015)*

7. Which of the following statements is correct for the spontaneous adsorption of a gas?
(a) ΔS is negative and, therefore ΔH should be highly positive.
(b) ΔS is negative and therefore, ΔH should be highly negative.
(c) ΔS is positive and therefore, ΔH should be negative.
(d) ΔS is positive and therefore, ΔH should also be highly positive. *(2014)*

8. For the reaction, $X_2O_{4(l)} \longrightarrow 2XO_{2(g)}$
$\Delta U = 2.1$ kcal, $\Delta S = 20$ cal K^{-1} at 300 K
Hence, ΔG is
(a) 2.7 kcal (b) – 2.7 kcal
(c) 9.3 kcal (d) – 9.3 kcal *(2014)*

9. A reaction having equal energies of activation for forward and reverse reactions has
(a) $\Delta H = 0$ (b) $\Delta H = \Delta G = \Delta S = 0$
(c) $\Delta S = 0$ (d) $\Delta G = 0$
(NEET 2013)

10. When 5 litres of a gas mixture of methane and propane is perfectly combusted at 0°C and 1 atmosphere, 16 litres of oxygen at the same temperature and pressure is consumed. The amount of heat released from this combustion in kJ ($\Delta H_{comb.}$ (CH_4) = 890 kJ mol^{-1}, $\Delta H_{comb.}$ (C_3H_8) = 2220 kJ mol^{-1}) is
(a) 38 (b) 317 (c) 477 (d) 32
(Karnataka NEET 2013)

11. Three thermochemical equations are given below
(i) $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta_r H^\circ = x$ kJ mol^{-1}
(ii) $C_{(graphite)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$; $\Delta_r H^\circ = y$ kJ mol^{-1}
(iii) $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta_r H^\circ = z$ kJ mol^{-1}

Based on the above equations, find out which of the relationship given below is correct.

(a) $z = x + y$ (b) $x = y + z$
(c) $y = 2z - x$ (d) $x = y - z$

(Karnataka NEET 2013)

12. In which of the following reactions, standard reaction entropy change ($\Delta S°$) is positive and standard Gibb's energy change ($\Delta G°$) decreases sharply with increasing temperature?

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

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

(c) $Mg_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow MgO_{(s)}$

(d) $\frac{1}{2}C_{(graphite)} + \frac{1}{2}O_{2(g)} \rightarrow \frac{1}{2}CO_{2(g)}$

(2012)

13. The enthalpy of fusion of water is 1.435 kcal/mol. The molar entropy change for the melting of ice at 0°C is

(a) 10.52 cal/(mol K) (b) 21.04 cal/(mol K)
(c) 5.260 cal/(mol K) (d) 0.526 cal/(mol K)

(2012)

14. Standard enthalpy of vaporisation $\Delta_{vap}H°$ for water at 100°C is 40.66 kJ mol^{-1}. The internal energy of vaporisation of water at 100°C (in kJ mol^{-1}) is

(a) +37.56 (b) – 43.76
(c) +43.76 (d) +40.66

(Assume water vapour to behave like an ideal gas) *(2012)*

15. If the enthalpy change for the transition of liquid water to steam is 30 kJ mol^{-1} at 27°C, the entropy change for the process would be

(a) 10 J mol^{-1} K^{-1} (b) 1.0 J mol^{-1} K^{-1}
(c) 0.1 J mol^{-1} K^{-1} (d) 100 J mol^{-1} K^{-1}

(2011)

16. Enthalpy change for the reaction,
$4H_{(g)} \rightarrow 2H_{2(g)}$ is –869.6 kJ
The dissociation energy of H – H bond is

(a) – 434.8 kJ (b) – 869.6 kJ
(c) + 434.8 kJ (d) + 217.4 kJ *(2011)*

17. Which of the following is correct option for free expansion of an ideal gas under adiabatic condition?

(a) $q = 0, \Delta T \neq 0, w = 0$
(b) $q \neq 0, \Delta T = 0, w = 0$
(c) $q = 0, \Delta T = 0, w = 0$
(d) $q = 0, \Delta T < 0, w \neq 0$ *(2011)*

18. Consider the following processes:

	ΔH (kJ/mol)
$1/2A \rightarrow B$	+150
$3B \rightarrow 2C + D$	–125
$E + A \rightarrow 2D$	+350

For $B + D \rightarrow E + 2C$, ΔH will be

(a) 525 kJ/mol (b) –175 kJ/mol
(c) –325 kJ/mol (d) 325 kJ/mol

(Mains 2011)

19. For an endothermic reaction, energy of activation is E_a and enthalpy of reaction is ΔH (both of these in kJ/mol). Minimum value of E_a will be

(a) less than ΔH (b) equal to ΔH
(c) more than ΔH (d) equal to zero

(2010)

20. Standard entropies of X_2, Y_2 and XY_3 are 60, 40 and 50 J K^{-1} mol^{-1} respectively. For the reaction $1/2X_2 + 3/2Y_2 \rightleftharpoons XY_3$, $\Delta H = -30$ kJ, to be at equilibrium, the temperature should be

(a) 750 K (b) 1000 K
(c) 1250 K (d) 500 K *(2010)*

21. Match List I (Equations) with List II (Type of processes) and select the correct option.

List I Equations	List II Type of processes
A. $K_p > Q$	(i) Non- spontaneous
B. $\Delta G° < RT \ln Q$	(ii) Equilibrium
C. $K_p = Q$	(iii) Spontaneous and endothermic
D. $T > \frac{\Delta H}{\Delta S}$	(iv) Spontaneous

(a) A - (i), B - (ii), C - (iii), D - (iv)
(b) A - (iii), B - (iv), C - (ii), D - (i)
(c) A - (iv), B - (i), C - (ii), D - (iii)
(d) A - (ii), B - (i), C - (iv), D - (iii)

(Mains 2010)

22. Three moles of an ideal gas expanded spontaneously into vacuum. The work done will be

(a) infinite (b) 3 Joules
(c) 9 Joules (d) zero

(Mains 2010)

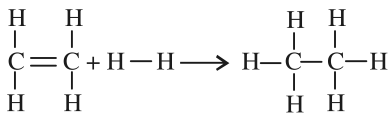
23. For vaporization of water at 1 atmospheric pressure, the values of ΔH and ΔS are 40.63 kJ mol^{-1} and 108.8 J K^{-1} mol^{-1}, respectively. The temperature when Gibb's energy change (ΔG) for this transformation will be zero, is

(a) 273.4 K (b) 393.4 K
(c) 373.4 K (d) 293.4 K
(Mains 2010)

24. The following two reactions are known
$Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$; $\Delta H = -26.8$ kJ
$FeO_{(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2(g)}$; $\Delta H = -16.5$ kJ
The value of ΔH for the following reaction
$Fe_2O_{3(s)} + CO_{(g)} \rightarrow 2FeO_{(s)} + CO_{2(g)}$ is
(a) + 10.3 kJ (b) – 43.3 kJ
(c) – 10.3 kJ (d) + 6.2 kJ
(Mains 2010)

25. The values of ΔH and ΔS for the reaction,
$C_{(graphite)} + CO_{2\,(g)} \rightarrow 2CO_{\,(g)}$
are 170 kJ and 170 J K^{-1}, respectively. This reaction will be spontaneous at
(a) 910 K (b) 1110 K
(c) 510 K (d) 710 K *(2009)*

26. From the following bond energies:
H — H bond energy : 431.37 kJ mol^{-1}
C = C bond energy : 606.10 kJ mol^{-1}
C — C bond energy : 336.49 kJ mol^{-1}
C — H bond energy : 410.50 kJ mol^{-1}
Enthalpy for the reaction,



will be
(a) – 243.6 kJ mol^{-1} (b) – 120.0 kJ mol^{-1}
(c) 553.0 kJ mol^{-1} (d) 1523.6 kJ mol^{-1}
(2009)

27. Bond dissociation enthalpy of H_2, Cl_2 and HCl are 434, 242 and 431 kJ mol^{-1} respectively. Enthalpy of formation of HCl is
(a) –93 kJ mol^{-1} (b) 245 kJ mol^{-1}
(c) 93 kJ mol^{-1} (d) –245 kJ mol^{-1}
(2008)

28. For the gas phase reaction,
$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
which of the following conditions are correct?
(a) $\Delta H < 0$ and $\Delta S < 0$
(b) $\Delta H > 0$ and $\Delta S < 0$
(c) $\Delta H = 0$ and $\Delta S < 0$
(d) $\Delta H > 0$ and $\Delta S > 0$ *(2008)*

29. Which of the following are not state functions?
(I) $q + w$ (II) q
(III) w (IV) $H - TS$
(a) (I), (II) and (III) (b) (II) and (III)
(c) (I) and (IV) (d) (II), (III) and (IV)
(2008)

30. Consider the following reactions:
(i) $H^+_{(aq)} + OH^-_{(aq)} = H_2O_{(l)}$, $\Delta H = -X_1$ kJ mol^{-1}
(ii) $H_{2(g)} + 1/2O_{2(g)} = H_2O_{(l)}$, $\Delta H = -X_2$ kJ mol^{-1}
(iii) $CO_{2(g)} + H_{2(g)} = CO_{(g)} + H_2O_{(l)}$, $\Delta H = -X_3$ kJ mol^{-1}
(iv) $C_2H_{2(g)} + 5/2O_{2(g)} = 2CO_{2(g)} + H_2O_{(l)}$, $\Delta H = +X_4$ kJ mol^{-1}
Enthalpy of formation of $H_2O_{(l)}$ is
(a) $+X_3$ kJ mol^{-1} (b) $-X_4$ kJ mol^{-1}
(c) $+X_1$ kJ mol^{-1} (d) $-X_2$ kJ mol^{-1}.
(2007)

31. Given that bond energies of H – H and Cl – Cl are 430 kJ mol^{-1} and 240 kJ mol^{-1} respectively and ΔH_f for HCl is –90 kJ mol^{-1}, bond enthalpy of HCl is
(a) 380 kJ mol^{-1} (b) 425 kJ mol^{-1}
(c) 245 kJ mol^{-1} (d) 290 kJ mol^{-1}
(2007)

32. Identify the correct statement for change of Gibb's energy for a system (ΔG_{system}) at constant temperature and pressure.
(a) If $\Delta G_{system} < 0$, the process is not spontaneous.
(b) If $\Delta G_{system} > 0$, the process is spontaneous.
(c) If $\Delta G_{system} = 0$, the system has attained equilibrium.
(d) If $\Delta G_{system} = 0$, the system is still moving in a particular direction. *(2006)*

33. Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta E$?
(a) $2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$
(b) $H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$
(c) $C_{(s)} + 2H_2O_{(g)} \rightarrow 2H_{2(g)} + CO_{2(g)}$
(d) $PCl_{5(g)} \rightarrow PCl_{3(g)} + Cl_{2(g)}$ *(2006)*

34. The enthalpy and entropy change for the reaction:
$Br_{2(l)} + Cl_{2(g)} \rightarrow 2BrCl_{(g)}$
are 30 kJ mol^{-1} and 105 J K^{-1} mol^{-1} respectively. The temperature at which the reaction will be in equilibrium is
(a) 300 K (b) 285.7 K
(c) 273 K (d) 450 K *(2006)*

35. The enthalpy of hydrogenation of cyclohexene is -119.5 kJ mol^{-1}. If resonance energy of benzene is -150.4 kJ mol^{-1}, its enthalpy of hydrogenation would be
(a) -358.5 kJ mol^{-1} (b) -508.9 kJ mol^{-1}
(c) -208.1 kJ mol^{-1} (d) -269.9 kJ mol^{-1}
(2006)

36. Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction?
(a) Exothermic and increasing disorder
(b) Exothermic and decreasing disorder
(c) Endothermic and increasing disorder
(d) Endothermic and decreasing disorder
(2005)

37. A reaction occurs spontaneously if
(a) $T\Delta S < \Delta H$ and both ΔH and ΔS are +ve
(b) $T\Delta S > \Delta H$ and ΔH is +ve and ΔS is –ve
(c) $T\Delta S > \Delta H$ and both ΔH and ΔS are +ve
(d) $T\Delta S = \Delta H$ and both ΔH and ΔS are +ve
(2005)

38. The absolute enthalpy of neutralisation of the reaction:
$MgO_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_2O_{(l)}$ will be
(a) -57.33 kJ mol^{-1}
(b) greater than -57.33 kJ mol^{-1}
(c) less than -57.33 kJ mol^{-1}
(d) 57.33 kJ mol^{-1} *(2005)*

39. If the bond energies of H–H, Br–Br, and H–Br are 433, 192 and 364 kJ mol^{-1} respectively, the $\Delta H°$ for the reaction $H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$ is
(a) -261 kJ (b) $+103$ kJ
(c) $+261$ kJ (d) -103 kJ *(2004)*

40. Standard enthalpy and standard entropy changes for the oxidation of ammonia at 298 K are -382.64 kJ mol^{-1} and -145.6 kJ mol^{-1}, respectively. Standard Gibb's energy change for the same reaction at 298 K is
(a) -221.1 kJ mol^{-1} (b) -339.3 kJ mol^{-1}
(c) -439.3 kJ mol^{-1} (d) -523.2 kJ mol^{-1}
(2004)

41. Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is
(a) $\Delta S_{system} + \Delta S_{surroundings} > 0$
(b) $\Delta S_{system} - \Delta S_{surroundings} > 0$
(c) $\Delta S_{system} > 0$ only
(d) $\Delta S_{surroundings} > 0$ only. *(2004)*

42. The work done during the expansion of a gas from a volume of 4 dm^3 to 6 dm^3 against a constant external pressure of 3 atm is (1 L atm = 101.32 J)
(a) -6 J (b) -608 J
(c) $+304$ J (d) -304 J *(2004)*

43. For the reaction,
$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(l)}$
at constant temperature, $\Delta H - \Delta E$ is
(a) $+RT$ (b) $-3RT$ (c) $+3RT$ (d) $-RT$
(2003)

44. The densities of graphite and diamond at 298 K are 2.25 and 3.31 g cm^{-3}, respectively. If the standard free energy difference ($\Delta G°$) is equal to 1895 J mol^{-1}, the pressure at which graphite will be transformed into diamond at 298 K is
(a) 9.92×10^8 Pa (b) 9.92×10^7 Pa
(c) 9.92×10^6 Pa (d) 9.92×10^5 Pa
(2003)

45. What is the entropy change (in J K^{-1} mol^{-1}) when one mole of ice is converted into water at 0°C? (The enthalpy change for the conversion of ice to liquid water is 6.0 kJ mol^{-1} at 0°C.)
(a) 20.13 (b) 2.013 (c) 2.198 (d) 21.98
(2003)

46. Formation of a solution from two components can be considered as
(i) Pure solvent → separated solvent molecules, ΔH_1
(ii) Pure solute → separated solute molecules, ΔH_2
(iii) Separated solvent and solute molecules → solution, ΔH_3
Solution so formed will be ideal if
(a) $\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$
(b) $\Delta H_{soln} = \Delta H_1 + \Delta H_2 - \Delta H_3$
(c) $\Delta H_{soln} = \Delta H_1 - \Delta H_2 - \Delta H_3$
(d) $\Delta H_{soln} = \Delta H_3 - \Delta H_1 - \Delta H_2$ *(2003)*

47. For which one of the following equations is $\Delta H°_{react}$ equal to $\Delta H°_f$ for the product?
(a) $N_{2(g)} + O_{3(g)} \rightarrow N_2O_{3(g)}$
(b) $CH_{4(g)} + 2Cl_{2(g)} \rightarrow CH_2Cl_{2(l)} + 2HCl_{(g)}$
(c) $Xe_{(g)} + 2F_{2(g)} \rightarrow XeF_{4(g)}$
(d) $2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$ *(2003)*

48. The molar heat capacity of water at constant pressure, C , is 75 J K^{-1} mol^{-1}. When 1.0 kJ of heat is supplied to 100 g of water which is free to expand, the increase in temperature of water is
(a) 1.2 K (b) 2.4 K (c) 4.8 K (d) 6.6 K *(2003)*

49. Unit of entropy is
(a) J K^{-1} mol^{-1} (b) J mol^{-1}
(c) $J^{-1}K^{-1}$ mol^{-1} (d) J K mol^{-1} *(2002)*

50. In a closed insulated container a liquid is stirred with a paddle to increase the temperature which of the following is true?
(a) $\Delta E = W \neq 0, q = 0$ (b) $\Delta E = W = q \neq 0$
(c) $\Delta E = 0, W = q \neq 0$ (d) $W = 0, \Delta E = q \neq 0$. *(2002)*

51. Heat of combustion ΔH for $C_{(s)}$, $H_{2(g)}$ and $CH_{4(g)}$ are –94, –68 and –213 kcal/mol, then ΔH for $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ is
(a) –17 kcal (b) –111 kcal
(c) –170 kcal (d) –85 kcal *(2002)*

52. Which reaction is not feasible?
(a) $2KI + Br_2 \rightarrow 2KBr + I_2$
(b) $2KBr + I_2 \rightarrow 2KI + Br_2$
(c) $2KBr + Cl_2 \rightarrow 2KCl + Br_2$
(d) $2H_2O + 2F_2 \rightarrow 4HF + O_2$ *(2002)*

53. 2 mole of ideal gas at 27°C temperature is expanded reversibly from 2 lit. to 20 lit. Find entropy change. (R = 2 cal/mol K)
(a) 92.1 (b) 0 (c) 4 (d) 9.2 *(2002)*

54. Change in enthalpy for reaction,
$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$
if heat of formation of $H_2O_{2(l)}$ and $H_2O_{(l)}$ are –188 and –286 kJ/mol respectively, is
(a) –196 kJ/mol (b) +196 kJ/mol
(c) +948 kJ/mol (d) –948 kJ/mole *(2001)*

55. When 1 mol of gas is heated at constant volume temperature is raised from 298 to 308 K. Heat supplied to the gas is 500 J. Then which statement is correct?
(a) $q = w = 500$ J, $\Delta E = 0$
(b) $q = \Delta E = 500$ J, $w = 0$
(c) $q = w = 500$ J, $\Delta E = 0$
(d) $\Delta E = 0$, $q = w = -500$ J *(2001)*

56. Enthalpy of $CH_4 + 1/2\ O_2 \rightarrow CH_3OH$ is negative. If enthalpy of combustion of CH_4 and CH_3OH are x and y respectively. Then which relation is correct?
(a) $x > y$ (b) $x < y$
(c) $x = y$ (d) $x\ ^3\ y$ *(2001)*

57. $PbO_2 \rightarrow PbO$; $\Delta G_{298} < 0$
$SnO_2 \rightarrow SnO$; $\Delta G_{298} > 0$
Most probable oxidation state of Pb and Sn will be
(a) Pb^{4+}, Sn^{4+} (b) Pb^{4+}, Sn^{2+}
(c) Pb^{2+}, Sn^{2+} (d) Pb^{2+}, Sn^{4+} *(2001)*

58. Cell reaction is spontaneous when
(a) $\Delta G°$ is negative (b) $\Delta G°$ is positive
(c) $\Delta E°_{red}$ is positive (d) $\Delta E°_{red}$ is negative. *(2000)*

59. $2Zn + O_2 \rightarrow 2ZnO$; $\Delta G° = -616$ J
$2Zn + S_2 \rightarrow 2ZnS$; $\Delta G° = -293$ J
$S_2 + 2O_2 \rightarrow 2SO_2$; $\Delta G° = -408$ J
$\Delta G°$ for the following reaction
$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$ is
(a) –731 J (b) –1317 J
(c) –501 J (d) +731 J *(2000)*

60. At 27°C latent heat of fusion of a compound is 2930 J/mol. Entropy change is
(a) 9.77 J/mol-K (b) 10.77 J/mol-K
(c) 9.07 J/mol-K (d) 0.977 J/mol-K *(2000)*

61. For the reaction,
$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ which one is true
(a) $\Delta H = \Delta E - RT$ (b) $\Delta H = \Delta E + RT$
(c) $\Delta H = \Delta E + 2RT$ (d) $\Delta H = \Delta E - 2RT$ *(2000)*

62. In an endothermic reaction, the value of ΔH is
(a) negative (b) positive
(c) zero (d) constant. *(1999)*

63. In the reaction: $S + 3/2\ O_2 \rightarrow SO_3 + 2x$ kcal and $SO_2 + 1/2\ O_2 \rightarrow SO_3 + y$ kcal, the heat of formation of SO_2 is
(a) $(2x + y)$ (b) $(x - y)$
(c) $(x + y)$ (d) $(2x - y)$ *(1999)*

64. Identify the correct statement regarding entropy.
(a) At absolute zero of temperature, the entropy of all crystalline substances is taken to be zero.
(b) At absolute zero of temperature, the entropy of a perfectly crystalline substance is +ve.
(c) At absolute zero of temperature, entropy of a perfectly crystalline substance is taken to be zero.
(d) At 0°C, the entropy of a perfectly crystalline substance is taken to be zero. *(1998)*

65. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litres. The ΔE for this process is ($R = 2$ cal $mol^{-1}K^{-1}$)
(a) 1381.1 cal (b) zero
(c) 163.7 cal (d) 9 L atm *(1998)*

66. Given that $C + O_2 \rightarrow CO_2$, $\Delta H^o = -x$ kJ
$2CO + O_2 \rightarrow 2CO_2$, $\Delta H^o = -y$ kJ
The enthalpy of formation of carbon monoxide will be
(a) $\frac{y-2x}{2}$ (b) $2x - y$
(c) $y - 2x$ (d) $\frac{2x-y}{2}$ *(1997)*

67. Which of the following is the correct equation?
(a) $\Delta U = \Delta W + \Delta Q$ (b) $\Delta U = \Delta Q - W$
(c) $\Delta W = \Delta U + \Delta Q$ (d) None of these *(1996)*

68. If enthalpies of formation for $C_2H_{4(g)}$, $CO_{2(g)}$ and $H_2O_{(l)}$ at 25°C and 1 atm pressure are 52, – 394 and – 286 kJ/mol respectively, then enthalpy of combustion of $C_2H_{4(g)}$ will be
(a) + 141.2 kJ/mol (b) + 1412 kJ/mol
(c) – 141.2 kJ/mol (d) – 1412 kJ/mol *(1995)*

69. A chemical reaction is catalyzed by a catalyst *X*. Hence *X*
(a) reduces enthalpy of the reaction
(b) does not affect equilibrium constant of reaction
(c) decreases rate constant of the reaction
(d) increases activation energy of the reaction. *(1995)*

70. Standard state Gibb's free energy change for isomerization reaction *cis*-2-pentene $\rightleftharpoons$ *trans*-2-pentene is –3.67 kJ/mol at 400 K. If more *trans*-2-pentene is added to the reaction vessel, then
(a) equilibrium remains unaffected
(b) equilibrium is shifted in the forward direction
(c) more *cis*-2-pentene is formed
(d) additional *trans*-2-pentene is formed. *(1995)*

71. For a reaction to occur spontaneously
(a) ΔH must be negative
(b) ΔS must be negative
(c) ($\Delta H - T\Delta S$) must be negative
(d) ($\Delta H + T\Delta S$) must be negative. *(1995)*

72. During isothermal expansion of an ideal gas, its
(a) internal energy increases
(b) enthalpy decreases
(c) enthalpy remains unaffected
(d) enthalpy reduces to zero. *(1994, 91)*

73. Following reaction occurring in an automobile
$2C_8H_{18(g)} + 25O_{2(g)} \rightarrow 16CO_{2(g)} + 18H_2O_{(g)}$
The sign of ΔH, ΔS and ΔG would be
(a) –, +, + (b) +, +, –
(c) +, –, + (d) –, +, – *(1994)*

74. For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, $\Delta H = ?$
(a) $\Delta E + 2RT$ (b) $\Delta E - 2RT$
(c) $\Delta H = RT$ (d) $\Delta E - RT$ *(1991)*

75. If ΔH is the change in enthalpy and ΔE, the change in internal energy accompanying a gaseous reaction, then
(a) ΔH is always greater than ΔE
(b) $\Delta H < \Delta E$ only if the number of moles of the products is greater than the number of moles of the reactants
(c) ΔH is always less than ΔE
(d) $\Delta H < \Delta E$ only if the number of moles of products is less than the number of moles of the reactants. *(1990)*

Answer Key

1.	(a)	**2.**	(b)	**3.**	(b)	**4.**	(a, c)	**5.**	(b)	**6.**	(None)	**7.**	(b)	**8.**	(b)	**9.**	(a)		
10.	(b)	**11.**	(b)	**12.**	(a)	**13.**	(c)	**14.**	(a)	**15.**	(d)	**16.**	(c)	**17.**	(c)	**18.**	(b)	**19.**	(c)
20.	(a)	**21.**	(c)	**22.**	(d)	**23.**	(c)	**24.**	(d)	**25.**	(b)	**26.**	(b)	**27.**	(a)	**28.**	(d)	**29.**	(b)
30.	(d)	**31.**	(b)	**32.**	(c)	**33.**	(b)	**34.**	(b)	**35.**	(c)	**36.**	(a)	**37.**	(c)	**38.**	(c)	**39.**	(d)
40.	(b)	**41.**	(a)	**42.**	(b)	**43.**	(b)	**44.**	(None)	**45.**	(d)	**46.**	(a)	**47.**	(c)	**48.**	(b)		
49.	(a)	**50.**	(a)	**51.**	(a)	**52.**	(b)	**53.**	(d)	**54.**	(a)	**55.**	(b)	**56.**	(a)	**57.**	(d)	**58.**	(a)
59.	(a)	**60.**	(a)	**61.**	(a)	**62.**	(b)	**63.**	(d)	**64.**	(c)	**65.**	(b)	**66.**	(a)	**67.**	(b)	**68.**	(d)
69.	(b)	**70.**	(c)	**71.**	(c)	**72.**	(c)	**73.**	(d)	**74.**	(b)	**75.**	(d)						

EXPLANATIONS

1. (a) : For a spontaneous reaction,
$\Delta G < 0$ *i.e.*, $\Delta H - T\Delta S < 0$

$$T > \frac{\Delta H}{\Delta S}$$

$$T > \left(\frac{35.5 \times 1000}{83.6} = 424.6 \approx 425 \text{ K}\right)$$

$\therefore\ T > 425$ K

2. (b) : $w = -P_{ext}\Delta V = -2.5(4.50 - 2.50)$
$= -5$ L atm $= -5 \times 101.325$ J $= -506.625$ J
$\Delta U = q + w$
As, the container is insulated, thus $q = 0$
Hence, $\Delta U = w = -506.625$ J

3. (b) : For an ideal gas undergoing reversible expansion, when temperature changes from T_i to T_f and pressure changes from p_i to p_f,

$$\Delta S = nC_p \ln\frac{T_f}{T_i} + nR\ln\frac{p_i}{p_f}$$

For an isothermal process, $T_i = T_f$ so, ln 1 = 0

$$\therefore\ \Delta S = nR\ln\frac{p_i}{p_f}$$

4. (a, c) : $\Delta G = \Delta H - T\Delta S$
If $\Delta H < 0$ and $\Delta S > 0$
$\Delta G = (-\text{ve}) - T(+\text{ve})$
then at all temperatures, $\Delta G = -$ve, spontaneous reaction.
If $\Delta H < 0$ and $\Delta S = 0$
$\Delta G = (-\text{ve}) - T(0) = -$ve at all temperatures.

5. (b) : This is Clausius—Clapeyron equation.

6. (None) : Given :
$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$, $\Delta H = -393.5$ kJ/mol
$\Rightarrow$ Amount of heat released on formation of 44 g $CO_2 = 393.5$ kJ
$\therefore$ Amount of heat released on formation of

$$35.2 \text{ g } CO_2 = \frac{393.5}{44} \times 35.2 = 314.8 \approx 315 \text{ kJ}$$

7. (b) : Using Gibb's-Helmholtz equation,
$\Delta G = \Delta H - T\Delta S$
During adsorption of a gas, entropy decreases *i.e.* $\Delta S < 0$
For spontaneous adsorption, ΔG should be negative, which is possible when ΔH is highly negative.

8. (b) : $\Delta H = \Delta U + \Delta n_g RT$
Given, $\Delta U = 2.1$ kcal, $\Delta n_g = 2$,
$R = 2 \times 10^{-3}$ kcal, $T = 300$ K
$\therefore\ \Delta H = 2.1 + 2 \times 2 \times 10^{-3} \times 300 = 3.3$ kcal
Again, $\Delta G = \Delta H - T\Delta S$
Given, $\Delta S = 20 \times 10^{-3}$ kcal K^{-1}
On putting the values of ΔH and ΔS in the equation, we get
$\Delta G = 3.3 - 300 \times 20 \times 10^{-3}$
$= 3.3 - 6 \times 10^3 \times 10^{-3} = -2.7$ kcal

9. (a) : $\Delta H = (E_a)_f - (E_a)_b = 0$

10. (b) : $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

$$CH_4 + C_3H_8 = \frac{5}{22.4} = 0.22 \text{ moles}$$

$$O_2 = \frac{16}{22.4} = 0.71 \text{ moles}$$

$2x + (0.22 - x)5 = 0.71$
$x = 0.13$
Heat liberated $= 0.13 \times 890 + 0.09 \times 2220 = 316$ kJ

11. (b) : According to Hess's law, equation (i) is equal to equations (ii) + (iii).

12. (a) : $C_{(graphite)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$

$$\Delta n_g = 1 - \frac{1}{2} = \frac{1}{2}$$

As amount of gaseous substance is increasing in product, thus ΔS is positive for this reaction.
And we know that $\Delta G = \Delta H - T\Delta S$
As ΔS is positive, thus increase in temperature will make $T\Delta S$ more negative and ΔG will decrease.

13. (c) : $\Delta H_f = 1.435$ kcal/mol

$$\Delta S = \frac{\Delta H_f}{T_f} = \frac{1.435 \times 10^3}{273} = 5.26 \text{ cal/mol K}$$

14. (a) : $\Delta_{vap}H° = 40.66$ kJ mol^{-1}
$T = 100 + 273 = 373$ K, $\Delta E = ?$
$\Delta H = \Delta E + \Delta n_g RT \Rightarrow \Delta E = \Delta H - \Delta n_g RT$
Δn_g = number of gaseous moles of products − number of gaseous moles of reactants
$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$
$\Delta n_g = 1 - 0 = 1$
$\Delta E = \Delta H - RT$
$\Delta E = (40.66 \times 10^3) - (8.314 \times 373)$
$= 37559$ J/mol or 37.56 kJ/mol

15. (d) : We know that $\Delta G = \Delta H - T\Delta S$
$0 = \Delta H - T\Delta S$ $[\because \Delta G = 0]$

$$\Delta S = \frac{\Delta H}{T} = \frac{30 \times 10^3}{300} = 100 \text{ J mol}^{-1} \text{ K}^{-1}$$

16. (c) : The dissociation energy of H – H bond is $\frac{869.6}{2} = 434.8$ kJ

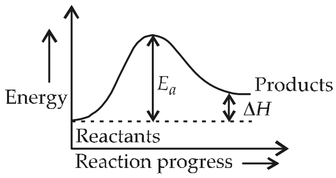
17. (c) : For free expansion of an ideal gas under adiabatic condition $q = 0$, $\Delta T = 0$, $w = 0$.

18. (b) : Adding all the equations

$$\begin{array}{ll} & \Delta H \\ A \rightarrow 2B & 300\text{ kJ/mol} \\ 3B \rightarrow 2C + D & -125\text{ kJ/mol} \\ \underline{2D \rightarrow A + E} & \underline{-350\text{ kJ/mol}} \\ B + D \rightarrow E + 2C\,; & \end{array}$$

$\Delta H = (300 - 125 - 350) = -175$ kJ/mol

19. (c) : Refer to the figure.



We find that the least E_a will be more than ΔH for an endothermic reaction since $E_{products} > E_{reactants}$.

20. (a) : Given reaction is :

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3$$

We know, $\Delta S° = \Sigma S°_{products} - \Sigma S°_{reactants}$

$= 50 - (30 + 60) = -40$ J K^{-1} mol^{-1}

At equilibrium $\Delta G° = 0$

$\Delta H° = T\Delta S°$

$$\therefore\quad T = \frac{\Delta H°}{\Delta S°} = \frac{-30 \times 10^3\text{ J mol}^{-1}}{-40\text{ J K}^{-1}\text{ mol}^{-1}} = 750\text{ K}$$

21. (c) : When $K_p > Q$, rate of forward reaction > rate of backward reaction.

∴ Reaction is spontaneous.

When $\Delta G° < RT \ln Q$, $\Delta G°$ is positive, reverse reaction is feasible, thus reaction is non spontaneous.

When $K_p = Q$, rate of forward reaction = rate of backward reaction.

∴ Reaction is in equilibrium.

When $T\Delta S > \Delta H$, ΔG will be negative only when $\Delta H = +$ve.

∴ Reaction is spontaneous and endothermic.

22. (d) : Since the ideal gas expands spontaneously into vacuum, $P_{ext} = 0$, hence work done is also zero.

23. (c) : According to Gibb's equation,

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

when $\Delta G = 0$, $\Delta H = T\Delta S$

Given, $\Delta H = 40.63$ kJ mol^{-1} = 40.63×10^3 J mol^{-1}

$\Delta S = 108.8$ J K^{-1} mol^{-1}

$$\therefore\quad T = \frac{\Delta H}{\Delta S} = \frac{40.63 \times 10^3}{108.8} = 373.43\text{ K}$$

24. (d) : $Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$

$\Delta H = -26.8$ kJ ...(i)

$FeO_{(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2(g)}$ $\Delta H = -16.5$ kJ ...(ii)

$Fe_2O_{3(s)} + CO_{(g)} \rightarrow 2FeO_{(s)} + CO_{2(g)}$ $\Delta H = ?$ ...(iii)

Eq. (iii) can be obtained as :

(i) – 2(ii)

$= -26.8 - 2(-16.5) = -26.8 + 33.0 = +6.2$ kJ

25. (b) : For the reaction to be spontaneous, $\Delta G = -$ve.

Given, $\Delta H = 170$ kJ $= 170 \times 10^3$ J

$\Delta S = 170$ J K^{-1} mol^{-1}

Applying, $\Delta G = \Delta H - T\Delta S$, the value of $\Delta G = -$ve only when $T\Delta S > \Delta H$, which is possible only when $T = 1110$ K.

∴ $\Delta G = 170 \times 10^3 - (1110 \times 170) = -18700$ J

Thus, reaction is spontaneous at $T = 1110$ K

26. (b) : For the given reaction, enthalpy of reaction can be calculated as

= B.E.(reactant) – B.E.(product)

$= [\text{B.E.}_{(C=C)} + \text{B.E.}_{(H-H)} + 4 \times \text{B.E.}_{(C-H)}] - [\text{B.E.}_{(C-C)} + 6 \times \text{B.E.}_{(C-H)}]$

$= [606.10 + 431.37 + 4 \times 410.50] - [336.49 + 6 \times 410.50]$

$= 2679.47 - 2799.49 = -120.02$ kJ mol^{-1}

27. (a) : $H_2 + Cl_2 \rightarrow 2HCl$

$\Delta H_{reaction} = \Sigma(\text{B.E})_{reactant} - \Sigma(\text{B.E})_{product}$

$= [(\text{B.E})_{H-H} + (\text{B.E})_{Cl-Cl}] - [2\text{B.E}_{(H-Cl)}]$

$= 434 + 242 - (431) \times 2$

$\Delta H_{reaction} = -186$ kJ

Heat of formation is the amount of heat absorbed or evolved when one mole of substance is directly obtained from its constituent element.

Hence, enthalpy of formation of HCl $= \frac{-186}{2}$ kJ

$= -93$ kJ mol^{-1}

28. (d) : Gas phase reaction

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

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

Δn = Change in number of moles of product and reactant species.

Since $\Delta n_g = +$ve, hence $\Delta H = +$ve

also one mole of PCl_5 is dissociated into two moles of PCl_3 and Cl_2 in the same phase.

Therefore, $\Delta S = S_{product} - S_{reactant}$

$\Delta S = +$ve.

29. (b) : State functions or state variables are those which depend only on the state of the system and not on how the state was reached.

$$\left.\begin{array}{l} q + w = \Delta E \text{ (internal energy)} \\ H - TS = G \text{ (free energy)} \end{array}\right\} \text{State functions}$$

Path function depends on the path followed during a process as well as the end states. Work and heat are the path functions.

30. (d) : The amount of heat absorbed or released when 1 mole of a substance is directly obtained from its constituent elements is called the heat of formation or enthalpy of formation.
Equation (i) represents neutralisation reaction, (iii) represents hydrogenation reaction and (iv) represents combustion reaction.

31. (b) : $HCl \rightarrow \frac{1}{2}H_2 + \frac{1}{2}Cl_2$

$\Delta H = \Sigma \text{ B.E.}_{\text{(products)}} - \Sigma \text{ B.E.}_{\text{(reactants)}}$

$= \frac{1}{2}[\text{B.E.}_{(H_2)} + \text{B.E.}_{(Cl_2)}] - \text{B.E.}_{(HCl)}$

$= \frac{1}{2}(430 + 240) - (-90) = \frac{1}{2} \times 670 + 90$

$= 335 + 90 = 425 \text{ kJ mol}^{-1}$

32. (c) : The criteria for spontaneity of a process in terms of ΔG is as follows:

- If ΔG is negative, the process is spontaneous.
- If ΔG is positive, the process does not occur in the forward direction. It may occur in the backward direction.
- If ΔG is zero, the system is in equilibrium.

33. (b) : $\Delta H = \Delta E + \Delta n_g RT$

For $H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$

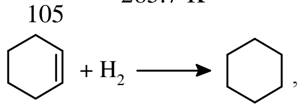
$\Delta n_g = 2 - (1 + 1) = 0.$ *i.e.* $\Delta H = \Delta E$

34. (b) : $Br_{2(l)} + Cl_{2(g)} \rightarrow 2BrCl_{(g)}$

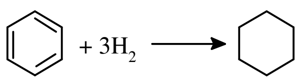
$\Delta H = 30 \text{ kJ mol}^{-1}, \Delta S = 105 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta S = \frac{\Delta H}{T}$ *i.e.* $105 = \frac{30}{T} \times 1000$

$\therefore \quad T = \frac{30 \times 1000}{105} = 285.7 \text{ K}$

35. (c) : 

, $\Delta H = -119.5 \text{ kJ mol}^{-1}$



Enthalpy of hydrogenation of benzene

$= 3 \times \Delta H - \text{resonance energy}$

$= 3 \times (-119.5) - (-150.4) = -358.5 + 150.4$

$= -208.1 \text{ kJ mol}^{-1}$

36. (a) : For spontaneous reaction ΔH = –ve, ΔS = +ve
Spontaneity depends upon both critical minimum energy and maximum randomness / disorder.

37. (c) : $\Delta G = \Delta H - T\Delta S$

ΔG = –ve for spontaneous reaction

When ΔS = +ve, ΔH = +ve

and $T\Delta S > \Delta H \Rightarrow \Delta G = -\text{ve}$

38. (c) : MgO is the oxide of weak base and we know that heat of neutralisation of 1 eq. of strong acid with strong base is –57.33 kJ/mol.
$\Rightarrow$ with weak base some heat is absorbed in dissociation of weak base.
$\Rightarrow$ Heat of neutralisation of weak base with strong acid will be less than –57.33 kJ/mol.

39. (d) : $\underset{\substack{433 \; + \; 192 \\ = 625}}{H-H + Br-Br} \rightarrow \underset{\substack{2 \times 364 \\ = 728}}{2H-Br}$

Energy absorbed Energy released

Net energy released = 728 – 625 = 103 kJ

i.e. $\Delta H = -103$ kJ

40. (b) : $\Delta G = \Delta H - T\Delta S = -382.64 - 298\left(\frac{-145.6}{1000}\right)$

$= -382.64 + 43.38 = -339.3 \text{ kJ mol}^{-1}$

41. (a) : $\Delta S = R \ln \frac{V_2}{V_1}$

Here the volume of gas increases from V_1 to V_2 at constant temperature T.
Since $V_2 > V_1$, it is obvious that the spontaneous (irreversible) isothermal expansion of a gas is accompanied by an increase in the entropy of the system and its surroundings considered together.

$\Delta S_{sys} + \Delta S_{surr} > 0$

42. (b) : Work = $-P_{ext}$ × volume change

$= -3 \times 101.32 \times (6 - 4) = 6 \times 101.32$

$= -607.92 \text{ J} \approx -608 \text{ J}$

43. (b) : $C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(l)}$

$\Delta n_g = 3 - 6 = -3$

$\Delta H = \Delta E + P\Delta V$ or $\Delta H - \Delta E = P\Delta V$

$\Delta H - \Delta E = \Delta n_g RT = -3RT$

44. (None) $\Delta G = -P\Delta V$ = Work done

$$\Delta V = \left(\frac{12}{3.31} - \frac{12}{2.25}\right) \times 10^{-3} \text{ L} = -1.71 \times 10^{-3} \text{ L}$$

ΔG = Work done = $-(-1.71 \times 10^{-3}) \times P \times 101.3$ J

$$P = \frac{1895}{1.71 \times 10^{-3} \times 101.3} = 10.93 \times 10^3 \text{ atm}$$

$= 11.07 \times 10^8$ Pa

45. (d) : $S = \frac{q_{rev}}{T} = \frac{6000}{273} = 21.978\ \text{J K}^{-1}\ \text{mol}^{-1}$

46. (a) : Heat of solution is defined as the amount of heat evolved or absorbed when one mole of the substance is dissolved in excess of the solvent. For hydrated salt and for salts which do not form hydrates, ΔH is positive and for anhydrous salts, it is negative.

47. (c) : For (c) $\Delta H°_{\text{reaction}}$

$= \Delta H°_f(XeF_4) - [\Delta H°_f(Xe) + 2\Delta H°_f(F_2)]$

Enthalpies of formation of elementary substances Xe and F_2 are taken as zero.

Thus, $\Delta H°_{\text{reaction}} = \Delta H°_f(XeF_4)$

48. (b) : Molar heat capacity = 75 J K^{-1} mol^{-1}

18 g of water = 1 mole = 75 J K^{-1} mol^{-1}

1 g of water = $\frac{75}{18}$ J K^{-1}

$Q = m \cdot C \cdot \Delta t$ or $1000 = 100 \times \frac{75}{18} \times \Delta t$

$\Rightarrow \quad \Delta t = \frac{10 \times 18}{75} = 2.4$ K

49. (a) : Entropy change (dS) is given by $dS = \frac{dq_r}{T}$

$\therefore$ Unit of entropy = J/K mol (entropy per unit mole) = J $K^{-1}mol^{-1}$

50. (a) : The mathematical form of first law of thermodynamics : $q = \Delta E + W$

Since the system is closed and insulated, $q = 0$

Paddle work is done on system. $\therefore$ $W \neq 0$.

Temperature and hence internal energy of the system increases. $\therefore$ $\Delta E \neq 0$.

51. (a) : (i) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H_i = -94$ kcal/mole

(ii) $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$; $\Delta H_{ii} = -68 \times 2$ kcal/mole

(iii) $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$; $\Delta H_{iii} = -213$ kcal/mole

(iv) $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$; $\Delta H_{iv} = ?$

By applying Hess's law we can compute ΔH_{iv}.

$\therefore \quad \Delta H_{iv} = \Delta H_i + \Delta H_{ii} - \Delta H_{iii}$

$= (-94 - 68 \times 2 + 213)$ kcal $= -17$ kcal

52. (b) : The halogen are highly electronegative elements - their non-metallic character gradually decreases from fluorine to iodine. F > Cl > Br > I. Fluorine can displace chlorine, bromine and iodine. Chlorine can displace bromine and iodine and bromine can displace iodine from their salts. Iodine cannot displace flourine, chlorine and bromine. Hence reaction (b) is not feasible.

53. (d) : The change of entropy $dS = \frac{dq_r}{T}$

From the first law of thermodynamics,

$dQ = dU + PdV = C_V dT + PdV$

$\Rightarrow \quad \frac{dQ}{T} = C_V \frac{dT}{T} + \frac{P}{T} dV$

$\Rightarrow \quad \frac{dQ}{T} = C_V \frac{dT}{T} + \frac{RdV}{V} \quad \left[\frac{P}{T} = \frac{R}{V}\right]$

$\therefore \quad dS = C_V \frac{dT}{T} + R\frac{dV}{V}$

$\Rightarrow \quad \Delta S = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}$

[for one mole of ideal gas]

Here $T_2 = T_1 = 27°C = 300$ K. $\therefore$ $\ln\frac{T_2}{T_1} = 0$

$\therefore \quad \Delta S = R\ln\frac{V_2}{V_1} = 2\ln\frac{20}{2} = 2\ln 10 = 4.605$

$\therefore \quad \Delta S = 4.605$ cal/mol-K

Entropy change for 2 moles of gas

$= 2 \times 4.605$ cal/K $= 9.2$ cal/K

54. (a) : $\Delta H°_f = \Sigma H°_{f\,(\text{product})} - \Sigma H°_{f\,(\text{reactant})}$

For the given reaction

$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$

$\Delta H°_f = 2 \times \Delta H°_{f\,(H_2O)} - 2 \times \Sigma H°_{f\,(H_2O_2)}$

$= 2 \times -286\ \text{kJ mol}^{-1} - 2 \times (-188)\ \text{kJ mol}^{-1}$

$= -196\ \text{kJ mol}^{-1}$

55. (b) : $\Delta H = \Delta E + P\Delta V$

When $\Delta V = 0$; $w = 0$.

$\Delta H = \Delta E + 0$ or $\Delta H = \Delta E$

As $\Delta E = q + w$, $\Delta E = q$

In the present problem, $\Delta H = 500$ J,

$\Delta H = \Delta E = 500$ J, $q = 500$ J, $w = 0$

56. (a) : $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, $\Delta H_1 = -x$ kJ ...(i)

$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$, $\Delta H_2 = -y$ kJ ...(ii)

Subtracting (ii) from (i), we get

$CH_4 + \frac{1}{2}O_2 \rightarrow CH_3OH$, $\Delta H_3 = -$ve

i.e., $-x - (-y) = -$ve

$y - x = -$ ve

Hence, $x > y$.

57. (d) : The sign and magnitude of Gibb's free energy is a criterion of spontaneity for a process. When $\Delta G > 0$ or +ve, it means $G_{\text{product}} > G_{\text{reactant}}$ as $\Delta G = G_{\text{products}} - G_{\text{reactants}}$ the reaction will not take place spontaneously, *i.e.* the reaction should be spontaneous in reverse direction.

$\underset{+4}{SnO_2} \rightarrow \underset{+2}{SnO}$; $\Delta G > 0$

(more favourable)

$\Delta G < 0$ or –ve, the reaction or change occurs spontaneously.

$\underset{+4}{PbO_2} \rightarrow \underset{+2}{PbO}$; $\rightarrow \Delta G < 0$

(more favourable)

58. (a) : For a cell reaction to be spontaneous $\Delta G°$ should be negative. As $\Delta G° = -nFE°_{cell}$, so the value will be –ve only when $E°_{cell}$ is +ve.

59. (a) : For the reactions,

$2ZnS \rightarrow 2Zn + S_2$; $\Delta G° = +293$ J ...(1)

$2Zn + O_2 \rightarrow 2ZnO$; $\Delta G° = -616$ J ...(2)

$S_2 + 2O_2 \rightarrow 2SO_2$; $\Delta G° = -408$ J ...(3)

The $\Delta G°$ for the reaction,

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$ can be obtained by adding eq. (1), (2) and (3).

So, $\Delta G° = 293 - 616 - 408 = -731$ J

60. (a) : $\Delta S = \dfrac{Q}{T} = \dfrac{2930}{300} = 9{\cdot}77$ J/mol K

61. (a) : $\Delta H = \Delta E + P\Delta V$

also $PV = nRT$ (ideal gas equation)

or $P\Delta V = \Delta n_g RT$

Δn_g = change in number of gaseous moles

$\therefore \quad \Delta H = \Delta E + \Delta n_g RT \Rightarrow \Delta n_g = 2 - 3 = -1$

$\Rightarrow \quad \Delta H = \Delta E - RT$

62. (b) : In endothermic reactions, energy of reactants is less than energy of products. Thus, $E_R < E_P$.

$\Delta H = E_P - E_R = +$ve

63. (d) : $S + \frac{3}{2}O_2 \rightarrow SO_3 + 2x$ kcal ...(i)

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 + y$ kcal (ii)

By substracting equation (ii) from (i) we get,

$S + O_2 \rightarrow SO_2 + (2x - y)$ kcal

The heat of formation of SO_2 is $(2x - y)$ kcal/mole.

64. (c) : The entropy of a substance increases with increase in temperature. However at absolute zero the entropy of a perfectly crystalline substance is taken as zero, which is also called as third law of thermodynamics.

65. (b) : Change in internal energy depends upon temperature. At constant temperature, the internal energy of the gas remains constant, so $\Delta E = 0$

66. (a) : $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H = -x$ kJ ...(i)

$CO_{(g)} + \dfrac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H = -\dfrac{y}{2}$ kJ ...(ii)

By substracting equation (ii) from (i) we get,

$C_{(s)} + \dfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$;

$\Delta H = -x - \left(-\dfrac{y}{2}\right) = \dfrac{y - 2x}{2}$ kJ

67. (b) : This is the mathematical relation of first law of thermodynamics. Here ΔU = change in internal energy; ΔQ = heat absorbed by the system and W = work done by the system.

68. (d) : $C_2H_4 + 3O_2 \rightarrow 2\,CO_2 + 2\,H_2O$

$\Delta H = \Delta H_{products} - \Delta H_{reactants}$

$= 2 \times (-394) + 2 \times (-286) - (52 + 0) = -1412$ kJ/mol

69. (b) : Since a catalyst affects equally both forward and backward reactions, therefore it does not affect equilibrium constant of reaction.

70. (c) : If more *trans*-2-pentene is added, then its concentration in right hand side will increase. But in order to maintain the constant K, concentration of *cis*-2-pentene will also increase. Therefore more *cis*-2-pentene will be formed.

71. (c) : For a reaction to be spontaneous, ΔG (Gibb's free energy change) must be negative.

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

ΔH = change in enthalpy, ΔS = change in entropy.

72. (c) : During isothermal expansion of an ideal gas, $\Delta T = 0$.

Now we know $H = E + PV$

$\because \quad \Delta H = \Delta E + \Delta(PV) = \Delta E + \Delta(nRT)$

$\therefore \quad \Delta H = \Delta E + nR\Delta T = 0 + 0 = 0$

73. (d) : (i) The given reaction is a combustion reaction, therefore ΔH is less than 0. Hence, ΔH is negative.

(ii) Since there is increase in the number of moles, therefore ΔS is positive

(iii) Since reaction is spontaneous, therefore ΔG is negative.

74. (b) : $\Delta n_g = 2 - 4 = -2$, $\Delta H = \Delta E - 2RT$

75. (d) : If $n_p < n_r$; $\Delta n_g = n_p - n_r = -$ve.

Hence $\Delta H < \Delta E$.