CHAPTER
6

Thermodynamics

6.1 Thermodynamic Terms

1. 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)

2. 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)

3. 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)*

6.2 Applications

4. The correct option for free expansion of an ideal gas under adiabatic condition is

(a) $q = 0, \Delta T = 0$ and $w = 0$

(b) $q = 0, \Delta T < 0$ and $w > 0$

(c) $q < 0, \Delta T = 0$ and $w = 0$

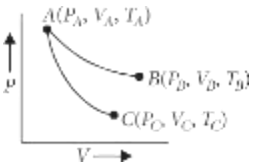
(d) $q > 0, \Delta T > 0$ and $w > 0$ *(NEET 2020)*

5. Under isothermal conditions, a gas at 300 K expands from 0.1 L to 0.25 L against a constant external pressure of 2 bar. The work done by the gas is [Given that 1 L bar = 100 J]

(a) 30 J (b) –30 J

(c) 5 kJ (d) 25 J *(NEET 2019)*

6. Reversible expansion of an ideal gas under isothermal and adiabatic conditions are as shown in the figure.



$AB \rightarrow$ Isothermal expansion

$AC \rightarrow$ Adiabatic expansion

Which of the following options is not correct ?

(a) $\Delta S_{\text{isothermal}} > \Delta S_{\text{adiabatic}}$

(b) $T_A = T_B$

(c) $W_{\text{isothermal}} > W_{\text{adiabatic}}$ *(Odisha NEET 2019)*

7. An ideal gas expands isothermally from 10^{-3} m^3 to 10^{-2} m^3 at 300 K against a constant pressure of 10^5 N m^{-2}. The work done on the gas is

(a) +270 kJ (b) –900 J

(c) +900 kJ (d) –900 kJ

(Odisha NEET 2019)

8. 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)

9. Equal volumes of two monatomic gases, *A* and *B* at same temperature and pressure are mixed. The ratio of specific heats (C_P/C_V) of the mixture will be

(a) 0.83 (b) 1.50

(c) 3.3 (d) 1.67 *(2012)*

10. 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)

11. 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)*

12. 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)*

13. 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)*

14. 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)*

15. 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)*

16. 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, ΔE = 0
(b) $q = \Delta E$ = 500 J, w = 0
(c) $q = w$ = 500 J, ΔE = 0
(d) ΔE = 0, $q = w$ = –500 J *(2001)*

17. 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)*

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

19. 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)*

20. 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, 1991)*

21. For the reactionm, $N_2 + 3H_2$ ☐ $2NH_3$, ΔH = ?
(a) $\Delta E + 2RT$ (b) $\Delta E - 2RT$
(c) $\Delta H = RT$ (d) $\Delta E - RT$ *(1991)*

22. 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)

6.4 Enthalpy Change, $\Delta_r H$ of a Reaction - Reaction Enthalpy

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

24. 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)

25. 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)

26. The following two reactions are known
$Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$; ΔH = –26.8 kJ
$FeO_{(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2(g)}$; ΔH = – 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)*

27. For which one of the following equations is $\Delta H^\circ_{\text{reaction}}$ equal to ΔH°_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)*

28. 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)*

29. 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)*

30. 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) $x \geq y$ *(2001)*

31. In the reaction : $S + 3/2O_2 \rightarrow SO_3 + 2x$ 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)*

32. Given that $C + O_2 \rightarrow CO_2$, $\Delta H^\circ = -x$ kJ
$2CO + O_2 \rightarrow 2CO_2$, $\Delta H^\circ = -y$ 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)*

33. 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)*

6.5 Enthalpies for Different Types of Reactions

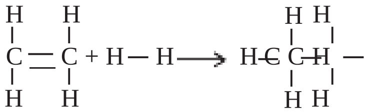
34. The bond dissociation energies of X_2, Y_2 and XY are in the ratio of 1 : 0.5 : 1. ΔH for the formation of XY is –200 kJ mol^{-1}. The bond dissociation energy of X_2 will be
(a) 200 kJ mol^{-1} (b) 100 kJ mol^{-1}
(c) 800 kJ mol^{-1} (d) 400 kJ mol^{-1}
(NEET 2018)

35. 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)*

36. 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 ($\Delta H_{\text{comb}}(CH_4) = 890$ kJ mol^{-1}, $\Delta H_{\text{comb.}}(C_3H_8) = 2220$ kJ mol^{-1}) is
(a) 38 (b) 317 (c) 477 (d) 32
(Karnataka NEET 2013)

37. 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)*

38. 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)

39. 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)*

40. 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)*

41. 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)*

42. 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)*

43. 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)*

6.6 Spontaneity

44. For the reaction, $2Cl_{(g)} \rightarrow Cl_{2(g)}$, the correct option is

(a) $\Delta_r H > 0$ and $\Delta_r S > 0$ (b) $\Delta_r H > 0$ and $\Delta_r S < 0$
(c) $\Delta_r H < 0$ and $\Delta_r S > 0$ (d) $\Delta_r H < 0$ and $\Delta_r S < 0$
(NEET 2020)

45. In which case change in entropy is negative?

(a) $2H_{(g)} \rightarrow H_{2(g)}$
(b) Evaporation of water
(c) Expansion of a gas at constant temperature
(d) Sublimation of solid to gas *(NEET 2019)*

46. For a given reaction, ΔH = 35.5 kJ mol^{-1} and ΔS = 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)

47. 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)

48. 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)

49. 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)

50. 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)*

51. For the reaction, $X_2O_{4(l)} \xrightarrow[-1]{} 2XO_{2(g)}$
ΔU = 2.1 kcal, ΔS = 20 cal K at 300 K
Hence, ΔG is

(a) 2.7 kcal (b) – 2.7 kcal
(c) 9.3 kcal (d) –9.3 kcal *(2014)*

52. 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)*

53. In which of the following reactions, standard reaction entropy change ($\Delta S°$) is positive and standard Gibbs 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)*

54. 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)

55. 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)

56. 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)*

57. 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 Gibbs' 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)*

58. 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)*

59. 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)

60. Identify the correct statement for change of Gibbs' 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)*

61. 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)*

62. 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)*

63. 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)*

64. Standard enthalpy and standard entropy changes for the oxidation of ammonia at 298 K are –382.64 kJ mol^{-1} and –145.6 J mol^{-1}, respectively. Standard Gibbs' 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)

65. 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)*

66. 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)*

67. 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)*

68. 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)*

69. 2 moles 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)*

70. $PbO_2 \rightarrow PbO$; $\Delta G_{298} < 0$
$SnO_2 \rightarrow SnO$; $\Delta G_{298} > 0$
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)*

71. 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)*

72. 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)*

6.7 Gibbs Energy Change and Equilibrium

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)*

ANSWER KEY

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

Hints & Explanations

1. (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.

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

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

2. (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. $\therefore \Delta E \neq 0$.

3. (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.

4. (a) : For free expansion of an ideal gas, $P_{ex} = 0$,
$w = -P_{ex}\Delta V = 0$
For adiabatic process, $q = 0$
According to first law of thermodynamics,
$\Delta U = q + w = 0$
As internal energy of an ideal gas is a function of temperature, $\Delta U = 0$, $\therefore \Delta T = 0$

5. (b) : Expansion of a gas against a constant external pressure is an irreversible process. The work done in an irreversible process

$= -P_{ext}\Delta V = -P_{ext}(V_2 - V_1) = -2\,(0.25 - 0.1)$
$= -2 \times 0.15$ L bar $= -0.30 \times 100$ J $= -30$ J

6. (d) : For an ideal gas, internal energy is a function of temperature. Final temperature *i.e.*, T_C for adiabatic process is less than its initial temperature *i.e.*, T_A
$\therefore \quad T_C < T_A$

7. (b) : $w = -PdV = -P(V_2 - V_1)$
$= -10^5 \text{ N m}^{-2}(10^{-2} - 10^{-3}) \text{ m}^3 = -10^5 \text{ N m}^{-2}(9 \times 10^{-3}) \text{ m}^3$
$= -9 \times 10^2$ N m $= -900$ J (∵ 1 J = 1 N m)

8. (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

9. (d) : C_P for monoatomic gas mixture of same volume $= \frac{5}{2}R$, $C_V = \frac{3}{2}R$

$$\therefore \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67$$

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

For free expansion, $w = 0$, adiabatic process, $q = 0$

$\Delta U = q + w = 0$

Internal energy remain constant means $\Delta T = 0$.

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

12. (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.* $\Delta H = \Delta E$

13. (b) : Work $= -P_{ext} \times$ volume change

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

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

14. (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 $\Delta H - \Delta E = P\Delta V$

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

15. (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}

100 g of water $= \frac{75}{18} \times 100$ J K^{-1}

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

$\Rightarrow \Delta T = \frac{10 \times 18}{75} = 2.4\text{ K}$

16. (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, $w = 0$

17. (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

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

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

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

$\Delta H = E_P - E_R = +\text{ve}$

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

20. (c) : During isothermal expansion of an ideal gas,

$\Delta T = 0$, $\Delta E = 0$ $\therefore \Delta H = 0$

$H = E + PV$

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

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

Change in enthalpy is zero, means its enthalpy remains same or unaffected.

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

22. (d) : If $n_p < n_r$; $\Delta n_g = n_p - n_r = -\text{ve}$.

Hence, $\Delta H < \Delta E$.

23. (b) : According to Hess's law, equation (i) is equal to equations (ii) + (iii) *i.e.*, $x = y + z$

24. (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

$H_2O_{(l)}\ H_2O_{(g)}$

$\Delta n_g = 1 - 0 = 1$

$\Delta E = \Delta H - RT$

$\Delta E = (40.66 \times 10^3) - (8.314 \times 373)$

$= 37559$ J/mol or 37.56 kJ/mol

25. (b) : Adding all the equations, we get

	Δ*H*
$A \rightarrow 2B$	300 kJ/mol
$3B \rightarrow 2C + D$	–125 kJ/mol
$2D \rightarrow A + E$	–350 kJ/mol

$B + D \rightarrow E + 2C$; $\Delta H = (300 - 125 - 350)$

$= -175$ kJ/mol

26. (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

27. (c) : For (c), $\Delta H°_{reaction}$

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

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

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

28. (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}.

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

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

29. (a) : $\Delta H^\circ_f = \Sigma H^\circ_{f\,(\text{products})} - \Sigma H^\circ_{f\,(\text{reactants})}$

For the given reaction,

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

$\Delta H^\circ_f = 2 \times \Delta H^\circ_{f\,(H_2O)} - 2 \times \Delta H^\circ_{f\,(H_2O_2)}$

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

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

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

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

Subtracting (ii) from (i), we get

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

i.e., $-x - (-y) = -\text{ve}$

$y - x = -$ ve. Hence, $x > y$.

31. (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 subtracting 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.

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

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

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

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

$$\Delta H^\circ = -x - \left(-\frac{y}{2}\right) = \frac{y - 2x}{2} \text{ kJ}$$

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

$\Delta H^\circ = \Delta H^\circ_{\text{products}} - \Delta H^\circ_{\text{reactants}}$

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

34. (c) : Let *B.E.* of X_2, Y_2 and XY are x kJ mol^{-1}, $0.5x$ kJ mol^{-1} and x kJ mol^{-1} respectively.

$\frac{1}{2}X_2 + \frac{1}{2}Y_2 \rightarrow XY\,; \Delta H = -200 \text{ kJ mol}^{-1}$

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

$\therefore\ -200 = \left[\frac{1}{2} \times (x) + \frac{1}{2} \times (0.5x)\right] - [1 \times (x)]$

B.E. of $X_2 = x = 800 \text{ kJ mol}^{-1}$

35. (None) : Given :

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}, \Delta H = -393.5$ kJ/mol

⇒ Amount of heat released on formation of 44 g CO_2 = 393.5 kJ

∴ Amount of heat released on formation of

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

Note : –ve or +ve sign considering the reaction is exothermic or endothermic.

36. (b) : $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

No. of moles in gaseous mixture

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

No. of moles of $O_2 = \frac{16}{22.4} = 0.71$ moles

Let x moles of CH_4 is there in a gaseous mixture so, number of moles of C_3H_8 would be $0.22 - x$. Then moles of O_2 consumed,

$2x + (0.22 - x)5 = 0.71$ or $x = 0.13$

Total amount of heat liberated

$= 0.13 \times 890 + 0.09 \times 2220 = 315.5$ kJ

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

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

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

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

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

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

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

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

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

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

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

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

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

Hence, enthalpy of formation of HCl $= \frac{-186}{2} = -93 \text{ kJ mol}^{-1}$

40. (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.

Thus, enthalpy of formation of $H_2O_{(l)}$ is $-X_2$ kJ mol^{-1}.

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

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

$= \frac{1}{2}[B.E._{(H_2)} + B.E._{(Cl_2)}] - B.E._{(HCl)} = -90$

$\frac{1}{2}(430 + 240) - B.E._{(HCl)} = -90$

$B.E._{(HCl)} = \frac{1}{2}(430 + 240) + 90 = 425 \text{ kJ mol}^{-1}$

42. (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.

⇒ With weak base some heat is absorbed in dissociation of weak base.

⇒ Heat of neutralisation of weak base with strong acid will be less than –57.33 kJ/mol.

43. (d) : $H - H + Br - Br \rightarrow 2H - Br$

$$\underset{\text{Energy absorbed}}{433 + 192 = 625} \qquad \underset{\text{Energy released}}{2 \times 364 = 728}$$

Net energy released = 728 – 625 = 103 kJ

i.e. $\Delta H° = -103$ kJ

44. (d) : In the reaction, $2Cl_{(g)} \rightarrow Cl_{2(g)}$, the randomness decreases as 2 moles of $Cl_{(g)}$ are converted to 1 mole of $Cl_{2(g)}$, thus, $\Delta_r S < 0$.
And this is an exothermic reaction, thus, $\Delta_r H < 0$.

45. (a) : If $\Delta n_g < 0$ then $\Delta S < 0$

46. (a) : For a spontaneous reaction,

$\Delta G < 0$ *i.e.*, $\Delta H - T\Delta S < 0$

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

$$T > \left(\frac{33.5 \times 1000}{83.6} = 424.6\right) \approx 425\text{ K}$$

∴ $T > 425$ K

47. (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

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

48. (a, c) : $\Delta G = \Delta H - T\Delta S$

If $\Delta H < 0$ and $\Delta S > 0$

$\Delta G = (-ve) - T(+ve)$

then at all temperatures, $\Delta G = -ve$, spontaneous reaction.

If $\Delta H < 0$ and $\Delta S = 0$

$\Delta G = (-ve) - T(0) = -ve$ at all temperatures.

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

50. (b) : Using Gibbs'-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.

51. (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

∴ $\Delta H = 2.1 + 2 \times 2 \times 10^{-3} \times 300 = 3.3$ 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

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

53. (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 the product side 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 the term $(-T\Delta S)$ more negative and ΔG will decrease.

54. (c) : $\Delta H_{fus} = 1.435$ kcal/mol

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_{fus}} = \frac{1.435 \times 10^3}{273} = 5.26\text{ cal/(mol K)}$$

55. (d) : We know that $\Delta G = \Delta H - T\Delta S$

$0 = \Delta H - T\Delta S$ [∵ $\Delta G = 0$ as transition of $H_2O_{(l)} \rightleftharpoons H_2O_{(v)}$ is at equilibrium]

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

56. (a) : Given reaction is :

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

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

$$= 50 - \left(\frac{1}{2}(60) + \frac{3}{2}(40)\right)$$

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

At equilibrium $\Delta G° = 0$

$\Delta H° = T\Delta S°$

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

57. (c) : According to Gibbs 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}

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

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

Given : $\Delta H = 170$ kJ = 170×10^3 J, $\Delta S = 170$ J K^{-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.

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

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

59. (d) : Gas phase reaction,

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

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

Δn_g = Change in number of moles of products and reactants species.

Since Δn_g = +ve, hence ΔH = +ve

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

Therefore, $\Delta S = S_{\text{products}} - S_{\text{reactants}}$

ΔS = +ve.

60. (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.

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

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

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

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

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

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

ΔG = –ve for spontaneous reaction.

When ΔS = +ve, ΔH = +ve and $T\Delta S > \Delta H \Rightarrow \Delta G$ = –ve

64. (b) : $\Delta G = \Delta H - T\Delta S$

$$= -382.64 - 298\left(\frac{-145.6}{1000}\right)$$

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

65. (a) : For spontaneous process, $\Delta S_{\text{total}} > 0$.

$\therefore \quad \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

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

67. (a) : $\Delta G° = -P\Delta V$ = Work done

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

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

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

$= 11.08 \times 10^8$ Pa $\approx 9.92 \times 10^8$ Pa $(\because 1 \text{ atm} = 101325 \text{ Pa})$

68. (a) : Entropy change (ΔS) is given by $\Delta S = \dfrac{q_{rev}}{T}$

$\therefore \quad$ Unit of entropy = J K^{-1}mol^{-1}

69. (d) : The change of entropy $dS = \dfrac{q_{rev}}{T}$

From the first law of thermodynamics,

$$dq = dU + PdV = C\,dT + PdV$$

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

$$\Rightarrow \frac{dq}{T} = C_V \frac{dT}{T} + \frac{RdV}{V} \quad \left[\text{For 1 mole of a gas, } \frac{P}{T} = \frac{R}{V}\right]$$

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

$$\Rightarrow \Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad \text{[for one mole of ideal gas]}$$

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

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

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

Entropy change for 2 moles of gas

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

70. (d) : The sign and magnitude of Gibbs free energy is a criterion of spontaneity for a process.

When $\Delta G > 0$ or +ve, it means $G_{\text{products}} > G_{\text{reactants}}$ 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.

$$\overset{+4}{Sn}O_2 \to \overset{+2}{Sn}O;\ \Delta G > 0$$

(more favourable)

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

$$\overset{+4}{Pb}O_2 \to \overset{+2}{Pb}O;\ \Delta G < 0$$

(more favourable)

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

72. (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.

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 of gaseous products, therefore ΔS is positive.

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