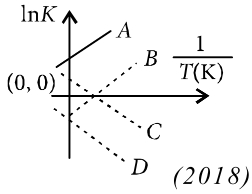
CHAPTER

5

Chemical Thermodynamics

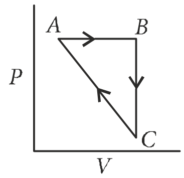
1. Which of the following lines correctly show the temperature dependence of equilibrium constant K, for an exothermic reaction?



(a) A and B
(b) B and C
(c) C and D
(d) A and D
(2018)

2. The combustion of benzene (l) gives $CO_{2(g)}$ and $H_2O_{(l)}$. Given that heat of combustion of benzene at constant volume is -3263.9 kJ mol^{-1} at 25 °C; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be
($R = 8.314$ J K^{-1} mol^{-1})
(a) 4152.6 (b) –452.43 (c) 3260 (d) –3267.6
(2018)

3. An ideal gas undergoes a cyclic process as shown in figure :
$\Delta U_{BC} = -5$ kJ mol^{-1},
$q_{AB} = 2$ kJ mol^{-1},
$W_{AB} = -5$ kJ mol^{-1},
$W_{CA} = 3$ kJ mol^{-1}
Heat absorbed by the system during process CA is



(a) 18 kJ mol^{-1} (b) +5 kJ mol^{-1}
(c) –5 kJ mol^{-1} (d) –18 kJ mol^{-1}
(Online 2018)

4. For which of the following reactions, ΔH is equal to ΔU ?
(a) $2NO_{2(g)} \rightarrow N_2O_{4(g)}$ (b) $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$
(c) $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$ (d) $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$
(Online 2018)

5. Given,
(i) $2Fe_2O_{3(s)} \rightarrow 4Fe_{(s)} + 3O_{2(g)}$; $\Delta_r G° = +1487.0$ kJ mol^{-1}
(ii) $2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$; $\Delta_r G° = -514.4$ kJ mol^{-1}
Free energy change, $\Delta_r G°$ for the reaction $2Fe_2O_{3(s)} + 6CO_{(g)} \rightarrow 4Fe_{(s)} + 6CO_{2(g)}$ will be
(a) –112.4 kJ mol^{-1} (b) –56.2 kJ mol^{-1}
(c) –168.2 kJ mol^{-1} (d) –208.0 kJ mol^{-1}
(Online 2018)

6. $\Delta_f G°$ at 500 K for substance 'S' in liquid state and gaseous state are + 100.7 kcal mol^{-1} and +103 kcal mol^{-1}, respectively. Vapour pressure of liquid 'S' at 500 K is approximately equal to
($R = 2$ cal K^{-1} mol^{-1})
(a) 0.1 atm (b) 10 atm (c) 100 atm (d) 1 atm
(Online 2018)

7. For which of the following processes, ΔS is negative?
(a) $C_{(diamond)} \rightarrow C_{(graphite)}$
(b) $N_2(g, 273\text{ K}) \rightarrow N_2(g, 300\text{ K})$
(c) $H_{2(g)} \rightarrow 2H_{(g)}$
(d) $N_2(g, 1\text{ atm}) \rightarrow N_2(g, 5\text{ atm})$
(Online 2018)

8. Given, $C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)}$; $\Delta_r H° = -393.5$ kJ mol^{-1}
$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$; $\Delta_r H° = -285.8$ kJ mol^{-1}
$CO_{2(g)} + 2H_2O_{(l)} \longrightarrow CH_{4(g)} + 2O_{2(g)}$; $\Delta_r H° = +890.3$ kJ mol^{-1}
Based on the above thermochemical equations, the value of $\Delta_r H°$ at 298 K for the reaction,
$C_{(graphite)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ will be
(a) –74.8 kJ mol^{-1} (b) –144.0 kJ mol^{-1}
(c) + 74.8 kJ mol^{-1} (d) + 144.0 kJ mol^{-1}
(2017)

9. ΔU is equal to
(a) adiabatic work (b) isothermal work
(c) isochoric work (d) isobaric work. *(2017)*

10. For a reaction, $A_{(g)} \rightarrow A_{(l)}$; $\Delta H = -3RT$. The correct statement for the reaction is
(a) $|\Delta H| < |\Delta U|$ (b) $\Delta H = \Delta U \neq 0$
(c) $|\Delta H| > |\Delta U|$ (d) $\Delta H = \Delta U = 0$
(Online 2017)

11. The enthalpy change on freezing of 1 mol of water at 5°C to ice at –5°C is
(Given : $\Delta_{fus}H = 6$ kJ mol^{-1} at 0°C,
$C_p(H_2O, l) = 75.3$ J mol^{-1} K^{-1},
$C_p(H_2O, s) = 36.8$ J mol^{-1} K^{-1})
(a) 5.81 kJ mol^{-1} (b) 6.56 kJ mol^{-1}
(c) 6.00 kJ mol^{-1} (d) 5.44 kJ mol^{-}
(Online 2017)

12. A gas undergoes change from state A to state B. In this process, the heat absorbed and work done by the gas is 5 J and 8 J, respectively. Now gas is brought back to A by another process during which 3 J of heat is evolved. In this reverse process of B to A
(a) 10 J of the work will be done by the surrounding on gas
(b) 10 J of the work will be done by the gas
(c) 6 J of the work will be done by the surrounding on gas
(d) 6 J of the work will be done by the gas.
(Online 2017)

13. An ideal gas undergoes isothermal expansion at constant pressure. During the process

(a) enthalpy increases but entropy decreases
(b) enthalpy remains constant but entropy increases
(c) enthalpy decreases but entropy increases
(d) both enthalpy and entropy remain constant.
(Online 2017)

14. The heats of combustion of carbon and carbon monoxide are –393.5 and –283.5 kJ mol^{-1} respectively. The heat of formation (in kJ) of carbon monoxide per mole is
(a) 110.5 (b) 676.5
(c) –676.5 (d) –110.5 *(2016)*

15. For the reaction, $A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$, $\Delta H°$ and $\Delta S°$ are, respectively, –29.8 kJ mol^{-1} and –0.100 kJ K^{-1} mol^{-1} at 298 K. The equilibrium constant for the reaction at 298 K is
(a) 1.0×10^{-10} (b) 10
(c) 1 (d) 1.0×10^{10}
(Online 2016)

16. A reaction at 1 bar is non-spontaneous at low temperature but becomes spontaneous at high temperature. Identify the correct statement about the reaction among the following.
(a) ΔH is negative while ΔS is positive.
(b) Both ΔH and ΔS are negative.
(c) ΔH is positive while ΔS is negative.
(d) Both ΔH and ΔS are positive. *(Online 2016)*

17. If 100 moles of H_2O_2 decompose at 1 bar and 300 K, the work done (kJ) by one mole of $O_{2(g)}$ as it expands against 1 bar pressure is

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

(R = 8.3 J K^{-1} mol^{-1})
(a) 124.50 (b) 249.00
(c) 498.00 (d) 62.25 *(Online 2016)*

18. The following reaction is performed at 298 K.
$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$
The standard free energy of formation of $NO_{(g)}$ is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $NO_{2(g)}$ at 298 K? (K_p =1.6×10^{12})
(a) $=; ; 5 - \frac{xz\text{-}63; \times 65^{67}.}{o\text{-}7>=.}$
(b) $0.5[2 \times 86, 600 - R(298)\ln(1.6 \times 10^{12})]$
(c) $R(298)\ln(1.6 \times 10^{12}) - 86600$
(d) $86600 + R(298)\ln(1.6 \times 10^{12})$ *(2015)*

19. The heat of atomization of methane and ethane are 360 kJ/mol and 620 kJ/mol, respectively. The longest wavelength of light capable of breaking the C – C bond is (Avogadro number = 6.02×10^{23}, $h = 6.62 \times 10^{-34}$ Js)
(a) 1.49×10^3 nm (b) 2.48×10^3 nm
(c) 2.48×10^4 nm (d) 1.49×10^4 nm
(Online 2015)

20. For complete combustion of ethanol,

$$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)},$$

the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25 °C. Assuming ideality the enthalpy of combustion, Δ_cH, for the reaction will be (R = 8.314 kJ mol^{-1})
(a) – 1350.50 kJ mol^{-1} (b) – 1366.95 kJ mol^{-1}
(c) – 1361.95 kJ mol^{-1} (d) – 1460.50 kJ mol^{-1}
(2014)

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

22. The incorrect expression among the following is
(a) in isothermal process, $w_{\text{reversible}} = -nRT\ln\frac{V_f}{V_i}$
(b) $\ln K = \frac{\Delta H° - T\Delta S°}{RT}$
(c) $K = e^{-\Delta G°/RT}$ (d) $\frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$ *(2012)*

23. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27°C is
(a) 38.3 J mol^{-1} K^{-1} (b) 35.8 J mol^{-1} K^{-1}
(c) 32.3 J mol^{-1} K^{-1} (d) 42.3 J mol^{-1} K^{-1}
(2011)

24. The standard enthalpy of formation of NH_3 is – 46 kJ mol^{-1}. If the enthalpy of formation of H_2 from its atoms is – 436 kJ mol^{-1} and that of N_2 is –712 kJ mol^{-1}, the average bond enthalpy of N—H bond in NH_3 is
(a) – 1102 kJ mol^{-1} (b) – 964 kJ mol^{-1}
(c) + 352 kJ mol^{-1} (d) + 1056 kJ mol^{-1}
(2010)

25. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when
(a) $T = T_e$ (b) $T_e > T$
(c) $T > T_e$ (d) T_e is 5 times T
(2010)

26. On the basis of the following thermochemical data : ($\Delta_fG°$ $H^+_{(aq)} = 0$).
$H_2O_{(l)} \rightarrow H^+_{(aq)} + OH^-_{(aq)}$; $\Delta H = 57.32$ kJ
$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$; $\Delta H = -286.2$ kJ
The value of enthalpy of formation of OH^- ion at 25°C is
(a) – 22.88 kJ (b) – 228.88 kJ
(c) + 228.88 kJ (d) – 343.52 kJ *(2009)*

27. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is

$$CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}.$$

At 298 K standard Gibb's energies of formation for $CH_3OH_{(l)}$, $H_2O_{(l)}$ and $CO_{2(g)}$ are –166.2, –237.2 and –394.4 kJ mol^{-1} respectively. If standard enthalpy of combustion of methanol is –726 kJ mol^{-1}, efficiency of the fuel cell will be

(a) 80 % (b) 87%
(c) 90% (d) 97% *(2009)*

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

(a) 1000 K (b) 1250 K
(c) 500 K (d) 750 K *(2008)*

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

$$1/2\ Cl_{2(g)} \xrightarrow{1/2\ \Delta_{diss}\overset{\ominus}{H}} Cl_{(g)} \xrightarrow{\Delta_{eg}\overset{\ominus}{H}} Cl^{-}_{(g)} \xrightarrow{\Delta_{hyd}\overset{\ominus}{H}} Cl^{-}_{(aq)}$$

The energy involved in the conversion of $1/2\ Cl_{2(g)}$ to $Cl^{-}_{(aq)}$ (using data, $\Delta_{diss}\overset{\ominus}{H}_{Cl_2} = 240\ kJ\ mol^{-1}$, $\Delta_{eg}\overset{\ominus}{H}_{Cl} = -349\ kJ\ mol^{-1}$, $\Delta_{hyd}\overset{\ominus}{H}_{Cl} = -381\ kJ\ mol^{-1}$) will be

(a) +120 kJ mol^{-1} (b) +152 kJ mol^{-1}
(c) –610 kJ mol^{-1} (d) –850 kJ mol^{-1} *(2008)*

30. Identify the correct statement regarding a spontaneous process:

(a) Lowering of energy in the reaction process is the only criterion for spontaneity.
(b) For a spontaneous process in an isolated system, the change in entropy is positive.
(c) Endothermic processes are never spontaneous.
(d) Exothermic processes are always spontaneous. *(2007)*

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

(a) 41.00 kJ mol^{-1} (b) 4.100 kJ mol^{-1}
(c) 3.7904 kJ mol^{-1} (d) 37.904 kJ mol^{-1} *(2007)*

32. In conversion of limestone to lime,

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

the values of $\Delta H°$ and $\Delta S°$ are +179.1 kJ mol^{-1} and 160.2 J/K respectively at 298 K and 1 bar. Assuming that $\Delta H°$ and $\Delta S°$ do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is

(a) 1118 K (b) 1008 K
(c) 1200 K (d) 845 K *(2007)*

33. ($\Delta H - \Delta U$) for the formation of carbon monoxide (CO) from its elements at 298 K is
($R = 8.314$ JK^{-1} mol^{-1})

(a) –1238.78 J mol^{-1} (b) 1238.78 J mol^{-1}
(c) –2477.57 J mol^{-1} (d) 2477.57 J mol^{-1} *(2006)*

34. The enthalpy changes for the following processes are listed below:

$Cl_{2(g)} = 2Cl_{(g)}$, 242.3 kJ mol^{-1}
$I_{2(g)} = 2I_{(g)}$, 151.0 kJ mol^{-1}
$ICl_{(g)} = I_{(g)} + Cl_{(g)}$, 211.3 kJ mol^{-1}
$I_{2(s)} = I_{2(g)}$, 62.76 kJ mol^{-1}

Given that the standard states for iodine and chlorine are $I_{2(s)}$ and $Cl_{2(g)}$, the standard enthalpy of formation for $ICl_{(g)}$ is

(a) – 14.6 kJ mol^{-1} (b) –16.8 kJ mol^{-1}
(c) +16.8 kJ mol^{-1} (d) +244.8 kJ mol^{-1} *(2006)*

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

(a) $(T_f)_{irrev} > (T_f)_{rev}$
(b) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process
(c) $(T_f)_{rev} = (T_f)_{irrev}$
(d) $T_f = T_i$ for both reversible and irreversible processes. *(2006)*

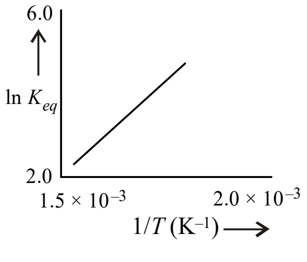
36. The standard enthalpy of formation ($\Delta H_f°$) at 298 K for methane, $CH_{4(g)}$ is –74.8 kJ mol^{-1}. The additional information required to determine the average energy for C – H bond formation would be

(a) the dissociation energy of H_2 and enthalpy of sublimation of carbon
(b) latent heat of vaporisation of methane
(c) the first four ionisation energies of carbon and electron gain enthalpy of hydrogen
(d) the dissociation energy of hydrogen molecule, H_2. *(2006)*

37. If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and ΔH_f for the formation of XY is –200 kJ mol^{-1}. The bond dissociation energy of X_2 will be

(a) 100 kJ mol^{-1} (b) 200 kJ mol^{-1}
(c) 800 kJ mol^{-1} (d) 400 kJ mol^{-1} *(2005)*

38. A schematic plot of ln K_{eq} versus inverse of temperature for a reaction is shown in the figure. The reaction must be



(a) exothermic
(b) endothermic
(c) one with negligible enthalpy change
(d) highly spontaneous at ordinary temperature.
(2005)

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

40. For a spontaneous reaction the ΔG, equilibrium constant (K) and E°_{cell} will be respectively
(a) –ve, >1, +ve (b) +ve, >1, –ve
(c) –ve, <1, –ve (d) –ve, >1, –ve *(2005)*

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

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

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

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

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

46. If at 298 K the bond energies of C – H, C – C, C ═ C and H – H bonds are respectively 414, 347, 615 and 435 kJ mol^{-1}, the value of enthalpy change for the reaction $H_2C = CH_{2(g)} + H_{2(g)} \rightarrow H_3C - CH_{3(g)}$ at 298 K will be
(a) +250 kJ (b) –250 kJ
(c) +125 kJ (d) –125 kJ. *(2003)*

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

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

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

ANSWER KEY

1. (a)	**2.** (d)	**3.** (b)	**4.** (b)	**5.** (b)	**6.** (a)	**7.** (d)	**8.** (a)	**9.** (a)	**10.** (c)	**11.** (b)	**12.** (c)
13. (b)	**14.** (d)	**15.** (c)	**16.** (d)	**17.** (*)	**18.** (b)	**19.** (a)	**20.** (b)	**21.** (b)	**22.** (b)	**23.** (a)	**24.** (c)
25. (c)	**26.** (b)	**27.** (d)	**28.** (d)	**29.** (c)	**30.** (b)	**31.** (d)	**32.** (a)	**33.** (a)	**34.** (c)	**35.** (a)	**36.** (a)
37. (c)	**38.** (a)	**39.** (c)	**40.** (a)	**41.** (d)	**42.** (a)	**43.** (d)	**44.** (b)	**45.** (c)	**46.** (d)	**47.** (d)	**48.** (b)

Explanations

1. **(a) :** From thermodynamics, ln $K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$

For exothermic reaction, $\Delta H = -\text{ve}$; Slope $= -\frac{\Delta H^\circ}{R} = +\text{ve}$

So, from graph, line should be A and B.

2. **(d) :** Combustion of benzene,

$$C_6H_{6(l)} + \frac{15}{2}O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)}$$

$\Delta H = \Delta U + \Delta n_g RT$; $\Delta U = -3263.9$ kJ/mol,

$\Delta n_g = 6 - \frac{15}{2} = -1.5$

$R = 8.314$ J K^{-1} mol^{-1}, $T = 25 + 273 = 298$ K

$\Delta H = -3263.9 - 1.5 \times 8.314 \times 298 \times 10^{-3}$
$= -3263.9 - 3.716 = -3267.6$ kJ/mol

3. **(b) :** From the first law of thermodynamics : $\Delta U = q + w$
Where, q = Heat change, w = work done
Now, for state $A \rightarrow B$, $\Delta U_{AB} = q_{AB} + w_{AB} = 2 - 5 = -3$ kJ mol^{-1}
For state $A \rightarrow B \rightarrow C$, $\Delta U_{ABC} = \Delta U_{AB} + \Delta U_{BC} = -3 - 5$
$= -8$ kJ mol^{-1}
$\Delta U_{CBA} = -\Delta U_{ABC} = -(-8) = +8$ kJ mol^{-1}
As, internal energy is a state function, thus,
$\Delta U_{CBA} = \Delta U_{CA} = +8$ kJ mol^{-1} and, $\Delta U_{CA} = q_{CA} + w_{CA}$
$8 = q_{CA} + 3 \Rightarrow q_{CA} = 8 - 3 = +5$ kJ mol^{-1}

4. **(b) :** $\Delta H = \Delta U + \Delta n_g RT$

ΔH will be equal to ΔU if , Δn_g is zero, *i.e.*, moles of gaseous reactants and products are equal.

(a) $2NO_{2(g)} \rightarrow N_2O_{4(g)}$; $\Delta n_g = 1 - 2 = -1$
(b) $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$; $\Delta n_g = (1 + 1) - 2 = 0$
(c) $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$; $\Delta n_g = 2 - (2 + 1) = -1$
(d) $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$; $\Delta n_g = 2 - (1 + 3) = -2$

5. **(b) :** $2Fe_2O_{3(s)} \longrightarrow 4Fe_{(s)} + 3O_{2(g)}$;
$\Delta_r G^\circ = +1487.0$ kJ mol^{-1} ...(i)
$2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)}$; $\Delta_r G^\circ = -514.4$ kJ mol^{-1} ...(ii)
On multiplying equation (ii) by 3 and adding to equation (i), we get the required equation,
$2Fe_2O_{3(s)} \longrightarrow 4Fe_{(s)} + 3O_{2(s)}$; $\Delta_r G^\circ = 1487.0$ kJ mol^{-1}
$6CO_{(g)} + 3O_{2(g)} \longrightarrow 6CO_{2(g)}$; $\Delta_r G^\circ = 3 \times (-514.4)$
$2Fe_2O_{3(s)} + 6CO_{(g)} \longrightarrow 4Fe_{(s)} + 6CO_{2(g)}$;
$\Delta G^\circ = 1487.0 + 3 \times (-514.4) = -56.2$ kJ mol^{-1}

6. **(a) :** $\underset{(\Delta_f G^\circ = 100.7 \text{ kcal mol}^{-1})}{S_{(l)}} \longrightarrow \underset{(\Delta_f G^\circ = 103 \text{ kcal mol}^{-1})}{S_{(g)}}$

ΔG for this transformation is :
$\Delta G^\circ = 103 - 100.7 = 2.3$ kcal mol^{-1} $= 2.3 \times 10^3$ cal mol^{-1}
$\Delta G^\circ = -RT \ln K$
$2.3 \times 10^3 = -2.303 \times 2 \times 500 \log K \Rightarrow \log K = -1 \Rightarrow K = 0.1$
$K = p_s = 0.1$ atm

7. **(d) :** Entropy change, ΔS is given as : $\Delta S = nC_p \ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$
For isothermal process, temperature is constant.

$\Delta S = 0 + nR\ln\frac{1}{5} = -1.6\,nR \quad \therefore \quad \Delta S < 0$

While in all other cases, the entropy increases.

8. **(a) :** $C_{(\text{graphite})} + O_{2(g)} \longrightarrow CO_{2(g)}$; $\Delta_r H^\circ = -393.5$ kJ mol^{-1} ...(i)

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$; $\Delta_r H^\circ = -285.8$ kJ mol^{-1} ...(ii)

$CO_{2(g)} + 2H_2O_{(l)} \longrightarrow CH_{4(g)} + 2O_{2(g)}$; $\Delta_r H^\circ = +890.3$ kJ mol^{-1} ...(iii)

$C_{(\text{graphite})} + 2H_{2(g)} \longrightarrow CH_{4(g)}$; $\Delta_r H^\circ = ?$
On applying the mathematical operation,
(i) + (ii) × 2 + (iii), we get
$C_{(\text{graphite})} + O_{2(g)} \longrightarrow CO_{2(g)}$; $\Delta_r H^\circ = -393.5$ kJ mol^{-1}
$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$; $\Delta_r H^\circ = -571.6$ kJ mol^{-1}
$CO_{2(g)} + 2H_2O_{(l)} \longrightarrow CH_{4(g)} + 2O_{2(g)}$; $\Delta_r H^\circ = +890.3$ kJ mol^{-1}
$C_{(\text{graphite})} + 2H_{2(g)} \longrightarrow CH_{4(g)}$;
$\Delta_r H^\circ = [-393.5 + (-571.6) + 890.3]$ kJ mol^{-1} $= -74.8$ kJ mol^{-1}

9. **(a) :** According to 1st law of thermodynamics
$\Delta U = q + w$ ...(i)
where, ΔU = change in internal energy, q = heat, w = work done
For adiabatic process, $q = 0$
$\therefore \quad \Delta U = w$
i.e., change in internal energy is equal to adiabatic work.

10. **(c) :** $\Delta U = \Delta H - \Delta n_g RT$
$\Delta U = -3RT - (0 - 1)RT \qquad (\because \Delta n_g = n_P - n_R)$
$\Delta U = -2RT$
Hence, $|\Delta H| > |\Delta U|$

11. **(b) :** Total energy change involves the following steps :
Change of 1 mol of water at 5°C to 1 mol of water at 0°C.
Change of 1 mol of water at 0°C to 1 mol of ice at 0°C.
Change of 1 mol of ice at 0°C to 1 mol of ice at – 5°C.
$\therefore$ Total $\Delta H = C_p(H_2O_{(l)})\Delta T + \Delta H_{\text{freezing}} + C_p(H_2O_{(s)})\Delta T$
$= 75.3 \times (0 - 5) + (-6 \times 10^3) + 36.8(-5 - 0)$
$= -376.5 - 6000 - 184 = 6.56$ kJ mol^{-1}

12. **(c) :** From A to B;
$q = +5$ J, $w = -8$ J (work done by the system)
According to first law of thermodynamics,
$\Delta U = q + w = 5 - 8 = -3$ J
From B to A; $\Delta U = +3$ J
(As internal energy is state function and does not depend on path)
$q = -3$ J (heat evolved), $w = \Delta U - q = +3 - (-3) = +6$ J
Thus, 6 J work will be done by the surrounding on gas.

13. (b) : For an isothermal expansion of an ideal gas at constant pressure, $\Delta H = nC_p\Delta T = 0$; $\Delta S = nR\ln(V_f/V_i) > 0$

14. (d) : The required equation $C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$; $\Delta H_f = ?$

Given that, $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H_1 = -393.5$ kJ/mol^{-1} ...(i)

$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H_2 = -283.5$ kJ mol^{-1} ...(ii)

Subtracting eqn (ii) from eqn (i) will give the required equation.

$\Rightarrow \Delta H_f = \Delta H_1 - \Delta H_2 = -393.5 - (-283.5) = -110$ kJ mol^{-1}

15. (c) : $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ = -29.8$ kJ mol^{-1} + 0.1×298 kJ mol^{-1} = 0

Also, $\Delta G^\circ = -2.303\ RT \log K \Rightarrow 0 = -2.303\ RT \log K$

$\log K = 0 \Rightarrow K = 1$

16. (d) : $\Delta G = \Delta H - T\Delta S$

According to the above reaction if $\Delta H > 0$ and $\Delta S > 0$ then the process is spontaneous at high temperature and non spontaneous at low temperature.

17. (*) : $\underset{100\text{ moles}}{2H_2O_{2(l)}} \rightleftharpoons 2H_2O_{(l)} + \underset{50\text{ moles}}{O_{2(g)}}$

$w = -p_{ext} \cdot dV = -p_{ext}(V_f - V_i) = -p_{ext}(V_f)$ $(\because V_i = 0)$

Now, for oxygen, $PV = nRT$

$\Rightarrow w = -nRT = -(1)(8.3)(300)$ (for one mole of oxygen)

$= -2490$ J $= -2.49$ kJ

$\therefore$ The work done by one mole of oxygen is 2.49 kJ.

* (None of the given options is correct.)

18. (b) : Given : $T = 298$ K, $\Delta G^\circ_{f(NO)} = 86.6$ kJ/mol,

$\Delta G^\circ_{f(NO_2)} = ?$, $K_p = 1.6 \times 10^{12}$

$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$

$\Delta G^\circ_r = 2\Delta G^\circ_{f(NO_2)} - 2\Delta G^\circ_{f(NO)} - \Delta G^\circ_{f(O_2)}$

$\Delta G^\circ_r = 2\Delta G^\circ_{f(NO_2)} - 2 \times 86{,}600$

$\Delta G^\circ_r = -RT\ \ln K_p$

$2\Delta G^\circ_{f(NO_2)} - 2 \times 86{,}600 = -R(298)\ \ln(1.6 \times 10^{12})$

$$\Delta G^\circ_{f(NO_2)} = \frac{7\times=;\ 1;\ 55 - o\text{-}7>=.\ xz\text{-}63\ \times 65^{67}.}{7}$$

$= 0.5\ [2 \times 86{,}600 - R(298)\ \ln(1.6 \times 10^{12})]$

19. (a) : In CH_4, $4 \times BE_{(C-H)} = 360$ kJ/mol

$\therefore\ BE_{(C-H)} = 90$ kJ/mol

In C_2H_6, $BE_{(C-C)} + 6 \times BE_{(C-H)} = 620$ kJ/mol

$\therefore\ BE_{(C-C)} = 80$ kJ/mol $\therefore\ BE_{(C-C)} = \dfrac{=5\times 65^{8}}{;\ 357\times 65^{78}}$ Q4y {xqo×xq

V{ $1b = \dfrac{}{\lambda}$

$$\therefore\ \lambda = \frac{;\ 3\ 7\times 65^{-89}\times 8\times 65^{=}\times;\ 357\times 65^{78}}{=5\times 65^{8}} = 1.49 \times 10^{-6}\text{ m}$$

$\therefore\ \lambda = 1.49 \times 10^3$ nm

20. (b) : Given; $\Delta E = -1364.47$ kJ mol^{-1}, $\Delta n_g = 2 - 3 = -1$

$T = 25 + 273 = 298$ K

$\Delta H = \Delta E + \Delta n_g RT = -1364.47 + (-1) \times 8.314 \times 10^{-3} \times 298$

$= -1364.47 - 1 \times 8.314 \times 10^{-3} \times 298$

$= -1364.47 - 2477.57 \times 10^{-3} = -1366.95$ kJ mol^{-1}

(Note : Given value of R is wrong, it should be 8.314 J K^{-1} mol^{-1} or 8.314×10^{-3} kJ K^{-1} mol^{-1}.)

21. (b) : As it absorbs heat, $q = +208$ J

$$w_{rev} = -2.303nRT\log_{10}\left(\frac{V_2}{V_1}\right)$$

$$= -2.303 \times (0.04) \times 8.314 \times 310\ \log_{10}\left(\frac{375}{50}\right)$$

$\therefore\ w_{rev} = -207.76 \approx -208$ J

22. (b) : $\Delta G^\circ = -RT\ln K$, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta H^\circ - T\Delta S^\circ = -RT\ln K \Rightarrow \ln K = -\left(\dfrac{\Delta H^\circ - T\Delta S^\circ}{RT}\right)$

23. (a) : Entropy change for an isothermal process is

$$\Delta S = 2.303nR\log\left(\frac{V_2}{V_1}\right) = 2.303 \times 2 \times 8.314 \times \log\left(\frac{100}{10}\right)$$

$= 38.294$ J mol^{-1} K^{-1} ≈ 38.3 J mol^{-1} K^{-1}

24. (c) : $1/2N_2 + 3/2H_2 \longrightarrow NH_3$

$B.E.$ 712 436

$$\therefore\ (\Delta H^\circ_f)_{NH_3} = \left[\frac{1}{2}B.E._{N_2} + \frac{3}{2}B.E._{H_2} - 3B.E._{N-H}\right]$$

$$-46 = \left[\frac{1}{2} \times 712 + \frac{3}{2} \times 436 - 3B.E._{N-H}\right]$$

$-46 = 356 + 654 - 3B.E._{N-H}$

$3B.E._{N-H} = 1056$

$B.E._{N-H} = \dfrac{1056}{3} = 352$ kJ mol^{-1}

25. (c) : According to Gibbs formula, $\Delta G = \Delta H - T\Delta S$

Since ΔH and ΔS, both are +ve, for $\Delta G < 0$, the value of $T > T_e$.

26. (b) : The reaction for the formation of $OH^-_{(aq)}$ is

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H^+_{(aq)} + OH^-_{(aq)}$

This is obtained by adding the two given equations.

$\therefore\ \Delta H$ for the above reaction = 57.32 + (–286.2) = –228.88 kJ

27. (d) : For the given reaction,

$CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$, $\Delta H = -726$ kJ mol^{-1}

also, $\Delta G^\circ_f[CH_3OH_{(l)}] = -166.2$ kJ mol^{-1}

$\Delta G^\circ_f[H_2O_{(l)}] = -237.2$ kJ mol^{-1} and $\Delta G^\circ_f[CO_{2(g)}] = -394.4$ kJ mol^{-1}

Now, $\Delta G^\circ_{reaction} = \sum \Delta G^\circ_{f\text{ products}} - \sum \Delta G^\circ_{f\text{ reactants}}$

$= [-394.4 + 2 \times (-237.2)] - (-166.2) = -702.6$ kJ mol^{-1}

$$\%\text{ Efficiency} = \frac{\Delta G}{\Delta H} \times 100 = \frac{-702.6}{-726} \times 100 = 96.77\% \approx 97\%$$

28. (d) : $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightarrow XY_3$

$\Delta S^0_{reaction} = \Delta S^0_{products} - \Delta S^0_{reactants}$

$\therefore\ \Delta S^0_{reaction} = \Delta S^0_{XY_3} - \frac{1}{2}\Delta S^0_{X_2} - \frac{3}{2}\Delta S^0_{Y_2}$

$= 50 - \frac{1}{2} \times 60 - \frac{3}{2} \times 40 = -40$ J K^{-1} mol^{-1}

Using equation, $\Delta G = \Delta H - T\Delta S$

We have $\Delta H = -30$ kJ, $\Delta S = -40$ J K^{-1} mol^{-1} and at equilibrium

$\Delta G = 0$. Therefore $T = \dfrac{\Delta H}{\Delta S} = \dfrac{-30 \times 1000}{-40} = 750$ K

29. (c) : $\frac{1}{2}\mathrm{Cl}_{2(g)} \rightarrow \mathrm{Cl}_{(g)}$; $\Delta H_1 = \frac{1}{2}\Delta_{diss}H^{\ominus}_{\mathrm{Cl}_2} = \frac{240}{2} = 120\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{Cl}_{(g)} \rightarrow \mathrm{Cl}^-_{(g)}$; $\Delta H_2 = \Delta_{eg}H^{\ominus}_{\mathrm{Cl}} = -349\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{Cl}^-_{(g)} + aq \rightarrow \mathrm{Cl}^-_{(aq)}$; $\Delta H_3 = \Delta_{hyd}H^{\ominus} = -381\ \mathrm{kJ\ mol^{-1}}$

The required reaction is $\frac{1}{2}\mathrm{Cl}_{2(g)} \rightarrow \mathrm{Cl}^-_{(aq)}$; ΔH

Then $\Delta H = \frac{1}{2}\Delta_{diss}H^{\ominus} + \Delta_{eg}H^{\ominus} + \Delta_{hyd}H^{\ominus}$

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

30. (b) : In an isolated system, there is neither exchange of energy nor matter between the system and surrounding. For a spontaneous process in an isolated system, the change in entropy is positive, *i.e.* $\Delta S > 0$.
Most of the spontaneous chemical reactions are exothermic. A number of endothermic reactions are spontaneous *e.g.* melting of ice (an endothermic process) is a spontaneous reaction.
The two factors which are responsible for the spontaneity of a process are
(i) tendency to acquire minimum energy
(ii) tendency to acquire maximum randomness.

31. (d) : $\Delta U = \Delta H - \Delta nRT = 41000 - 1 \times 8.314 \times 373$
$= 41000 - 3101.122 = 37898.878\ \mathrm{J\ mol^{-1}} = 37.9\ \mathrm{kJ\ mol^{-1}}$

32. (a) : For $\Delta G° = \Delta H° - T\Delta S°$
For a spontaneous process $\Delta G° < 0$ *i.e.* $\Delta H° - T\Delta S° < 0$
or $\Delta H° < T\Delta S°$ or, $T\Delta S° > \Delta H°$
or $T > \frac{\Delta H°}{\Delta S°}$ *i.e.* $T > \frac{179.1 \times 1000}{160.2}$ or $T > 1117.9\ \mathrm{K} \approx 1118\ \mathrm{K}$

33. (a) : $\Delta H - \Delta U = \Delta n_g RT$

$\mathrm{C} + \frac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{CO}$; $\Delta n_g = 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2}$

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

34. (c) : $\frac{1}{2}\mathrm{I}_{2\,(s)} + \frac{1}{2}\mathrm{Cl}_{2\,(g)} \rightarrow \mathrm{ICl}_{\,(g)}$

$$\Delta H_{\mathrm{ICl}(g)} = \left[\frac{1}{2}\Delta H_{\mathrm{I}_2(s)\rightarrow\mathrm{I}_2(g)} + \frac{1}{2}\Delta H_{\mathrm{I-I}} + \frac{1}{2}\Delta H_{\mathrm{Cl-Cl}}\right] - [\Delta H_{\mathrm{I-Cl}}]$$

$$= \left[\frac{1}{2} \times 62.76 + \frac{1}{2} \times 151.0 + \frac{1}{2} \times 242.3\right] - [211.3]$$

$= [31.38 + 75.5 + 121.15] - 211.3 = 228.03 - 211.3 = 16.73\ \mathrm{kJ/mol}$

35. (a) : If a gas was to expand by a certain volume reversibly, then it would do a certain amount of work on the surroundings. If it was to expand irreversibly it would have to do the same amount of work on the surroundings to expand in volume, but it would also have to do work against frictional forces. Therefore the amount of work have greater modulus but –ve sign.
$W_{\mathrm{irrev.}} > W_{\mathrm{reve.}}$; $(T_f)_{\mathrm{irrev.}} > (T_f)_{\mathrm{rev.}}$

36. (a) : $\mathrm{C} + 2\mathrm{H}_2 \rightarrow \mathrm{CH}_4$; $\Delta H° = -74.8\ \mathrm{kJ\ mol^{-1}}$
In order to calculate average energy for C – H bond formation we should know the following data.
$\mathrm{C}_{(\mathrm{graphite})} \rightarrow \mathrm{C}_{(g)}$; ΔH°_f = enthalpy of sublimation of carbon
$\mathrm{H}_{2(g)} \rightarrow 2\mathrm{H}_{(g)}$; $\Delta H°$ = bond dissociation energy of H_2

37. (c) : Let the bond dissociation energy of XY, X_2 and Y_2 be x kJ mol^{-1}, x kJ mol^{-1} and $0.5x$ kJ mol^{-1} respectively.

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

$\Delta H_{\mathrm{reaction}}$ = [(sum of bond dissociation energy of all reactants) – (sum of bond dissociation energy of product)]

$$= \left[\frac{1}{2}\Delta H_{X_2} + \frac{1}{2}\Delta H_{Y_2} - \Delta H_{XY}\right] = \frac{x}{2} + \frac{0.5x}{2} - x = -200$$

$\therefore \quad x = \frac{200}{0.25} = 800\ \mathrm{kJ\ mol^{-1}}$

38. (a) : $\ln\frac{K_2}{K_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$\ln\frac{6}{2} = \frac{\Delta H}{R}[1.5 \times 10^{-3} - 2 \times 10^{-3}] \Rightarrow \ln 3 = \frac{\Delta H}{R} \times (-0.5 \times 10^{-3})$

ΔH of reaction comes out to be negative. Hence reaction is exothermic.

39. (c) : $\mathrm{N}_2 + 3\mathrm{H}_2 \rightarrow 2\mathrm{NH}_3$
$\Delta H = \Delta U + \Delta nRT = \Delta U - 2RT$ $(\Delta n = 2 - 4 = -2)$
$\therefore \Delta H < \Delta U$

40. (a) : For spontaneous process, ΔG = –ve
Now $\Delta G = -RT \ln K$; When $K > 1$, ΔG = –ve
Again $\Delta G° = -nFE°$; When $E°$ = +ve, $\Delta G°$ = –ve

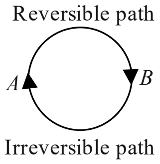
41. (d) : $\mathrm{C}_{(s)} + \mathrm{O}_{2(g)} \rightarrow \mathrm{CO}_{2(g)}$; $\Delta H = -393.5\ \mathrm{kJ\ mol^{-1}}$ .. (i)

$\mathrm{CO}_{(g)} + \frac{1}{2}\mathrm{O}_{2(g)} \rightarrow \mathrm{CO}_{2(g)}$; $\Delta H = -283\ \mathrm{kJ\ mol^{-1}}$ ... (ii)

On subtraction equation (ii) from equation (i), we get
$\mathrm{C}_{(s)} + \mathrm{O}_{2(g)} \rightarrow \mathrm{CO}_{(g)}$; $\Delta H = -110.5\ \mathrm{kJ\ mol^{-1}}$
The enthalpy of formation of carbon monoxide per mole $= -110.5\ \mathrm{kJ\ mol^{-1}}$

42. (a) : $W = -P\Delta V = -1 \times 10^5(1 \times 10^{-2} - 1 \times 10^{-3})$
$= -1 \times 10^5 \times 9 \times 10^{-3} = -900\ \mathrm{J}$

43. (d) :

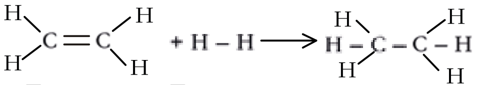


We know that for a cyclic process the net change in internal energy is equal to zero and change in the internal energy does not depend on the path by which the final state is reached.

44. (b) : For spontaneity, change in entropy (dS) must be positive, means it should be greater than zero.
Change in Gibbs free energy (dG) must be negative means that it should be lesser than zero. $(dS)_{V,\,E} > 0$, $(dG)_{T,\,P} < 0$.

45. (c) : This is according to Hess's law.

46. (d) :



$\Delta H_{\mathrm{Reaction}} = \Sigma BE_{\mathrm{reactant}} - \Sigma BE_{\mathrm{product}}$
$= 4 \times 414 + 615 + 435 - (6 \times 414 + 347) = 2706 - 2831 = -125\ \mathrm{kJ}$

47. (d) : It does not violate first law of thermodynamics but violates second law of thermodynamics.

48. (b) : For endothermic reaction, ΔH = +ve
Now, $\Delta G = \Delta H - T\Delta S$
For non-spontaneous reaction, ΔG should be positive
Now ΔG is positive at low temperature if ΔH is positive.
ΔG is negative at high temperature if ΔS is positive.

49. (d) : ΔH = negative shows that the reaction is spontaneous. Higher value for ΔH shows that the reaction is more feasible.