EXERCISE - 1 [A]

1. (a)
Isochoric process is constant volume process

2. (b)
When ice and water are in equilibrium $\Delta T = 0$. So molar heat capacity is ∞.

3. (c)
$w = -2.303\,nRT\log\frac{V_2}{V_1}$ (for isothermal process)

So $w_{by\,gas} = 2.303\,nRT\,\ell n\frac{V_1}{V_2}$

4. (b)
$w = nCv\left(T_2 - T_1\right)$ (for adiabatic process)

So $w_{by\,gas} = \frac{nR\left(T_1 - T_2\right)}{\gamma - 1}$

5. (A)
For expansion against vaccum $p_{ext} = 0$

$\Rightarrow w = -p_{ext}\left(V_f - V_i\right) = 0$

6. (b)
$W = -2\times(3.4) = -6.8\,L\,atm = -689\,J$

$Q = +400J$

$\Delta U = Q + W = -289\,J$

7. (c)
$T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$

$(4T_i)\left(\frac{V_i}{32}\right)^{\gamma-1} = T_i\,V_i^{\gamma-1}$

$4 = 32^{\gamma-1}$

$2^2 = 2^{5(\gamma-1)}$

$\gamma - 1 = \frac{2}{5} \Rightarrow \gamma = \frac{7}{5} \Rightarrow$ diatomic

8. (a)
For irreversible adiabatic process

$nCv\left(T_f - T_i\right) = -P_{ext}\left(V_f - V_i\right)$

$\frac{P_f V_f - P_i V_i}{\gamma - 1} = -p_{ext}\left(V_f - V_i\right)$

$$\frac{1\times V_f - 10\times 10}{\frac{2}{3}} = -1\left(V_f - 10\right)$$

$$V_f - 100 = -\frac{2}{3}V_f + \frac{20}{3}$$

$$\frac{5}{3}V_f = \frac{320}{3} \Rightarrow V_f = 64\text{L}$$

$$T_f = \frac{1\times 64}{10\times 10}\times 273 = 174.72\,\text{k}$$

9. (d)

$TV^{\gamma-1} = k$

$T = k\,V^{1-\gamma}$

$\ell n\,T = \ell n\,k + (1-\gamma)\,\ell n\,V$

10. (b)

$Q = 0,\ W = -\text{ve}$ (Since expansion)

So $\Delta U = -\text{ve}$

11. (a)

$W_1 = +15\text{J}\ \ \Delta U_1 = +30\,\text{J}$

So $Q_1 = +15\,\text{J}$

$W_2 = 0\ ;\ \Delta U_2 = -20\text{J}$

So $Q_2 = -20\,\text{J}$

12. (a)

$Q = +50\,,\qquad W = -30$

$\Delta U = Q + W = +20$

13. (a)

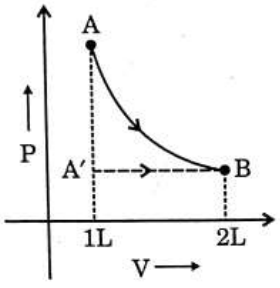
$T_1\,V_1^{\gamma-1} = T_2\,V_2^{\gamma-1};\ \gamma = \frac{5}{3};\ T_1 = 300\,\text{K},\ V_1 = 8\,\text{L}, T_2 = 250\,\text{K}$

$$V_2 = 8\times\left(\frac{300}{250}\right)^{\frac{1}{\gamma-1}} = 10.5\,\text{L}$$

14. (b)

$P_{\text{ext}} = 0 \Rightarrow w = 0,\ q = 0 \Rightarrow \Delta U = 0$ and $T = \text{constant}$

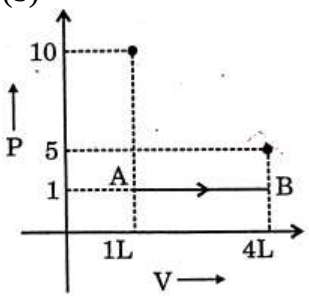
15. (b)



Final temperature in irreversible is more than reversible as ω_{irrev} is less is magnitude.

$\Rightarrow \Delta H_{\text{rev}} > \Delta H_{\text{irrev}}$

16. (b)



$w = -1 \times 3\ \text{L-atm} = -300\ \text{J}$

$\frac{10 \times 1}{300} = \frac{5 \times 4}{T} \Rightarrow T = 600\ \text{K}$

$q = 50 \times 300 = 15000\ \text{J}$

$\Rightarrow\ \Delta U = q + w = 14700\ \text{J}$

$\Delta H = \Delta U + \Delta(PV)$

$= 147000 + (20 - 10) \times 100 = 15700\ \text{J}$

17. (c)

$q_v = x = 5 \times C_v \times 5;$

$q_p = \frac{2x}{5} + 2R \times 5 = \frac{2x}{5} + 2 \times 5 \times \frac{2x}{75} = \frac{10x}{15} = \frac{2x}{3}\ \text{J}$

18. (a)

$T_1 = 600\text{K}$ $\xrightarrow{\text{Iscchoric}}$ $T_2 = 200\text{K}$

$P_1 = 3\text{atm}$ $\xrightarrow{\text{Iscchoric}}$ $P_2 = 1\text{atm}$

$V_1 = 200\text{R}$ $\xrightarrow{\text{Iscchoric}}$ $V_2 = 200\text{R}$

$T_2 = 200\text{K}$

$P_2 = 1\text{atm}$ $\xrightarrow{\text{adiabactic}}$ $P_3 = 3\text{atm}$

$V_2 = 200\text{R}$ $\xrightarrow{\text{adiabactic}}$ $V_3 = 200\text{R} \times \left(\frac{1}{3}\right)^{\frac{1}{\gamma}} = 8.48\,\text{L}$

So $w_3 = -3(16.4 - 8.48)$

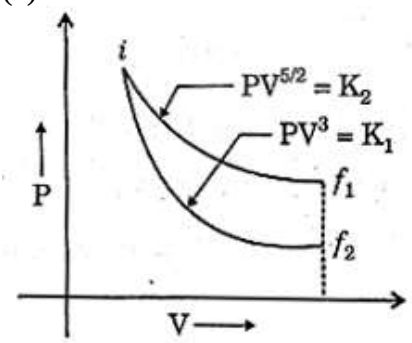
$= -23.76\,\text{L.atm}$

19. (a)

E & H depend only on T if n is constant.

PdV + VdP = nRdT

20. (a)



From the graph, work done in 2nd process is more than 1st process.

21. (d)

In isothermal process, temperature remains constant, while, in adiabatic expansion, temperature $\downarrow$ as work is done at the cost of internal energy. T_{final} of rev. adiabatic expansion is least because more work is done in reversible than irreversible adiabatic expansion.

$\Rightarrow T_a = T_b > T_d > T_c$

22. (d)

$$C_v(mix) = \frac{1\times 3R + 2\times \frac{3}{2}R}{3} = 2R, \Rightarrow C_P = 3R, \gamma = \frac{3}{2}$$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \Rightarrow T = \frac{320}{(4)^{0.5}} = 160\,\text{K}$$

$$\Delta U = \frac{-3\times R\times 160}{\frac{1}{2}} = -960\ R$$

23. (b)

$$w = -nR\Delta T = -2\times 8.314\times(300-400)$$
$$= +1662.8\ \text{J}$$

24. (c)

Rate can not be predicted by thermodynamics.

25. (c)

$$W = -\int_{10}^{100} \frac{10}{V}\,dV$$

$$W = \left(-10\times 2.303\log\frac{100}{10}\right)\text{bar-lit}$$

$$W = -23.03\times 100 = -2303\ \text{J}$$

$$400 = -2303 + q$$

$$q \approx 2700$$

26. (a)

Work = area under the graph = $\pi\times 2\,\text{L}\times 2\,\text{atm} = 4\pi$

27. (a)

$T_{f,\,adiabatic} < T_{f,\,isothermal}$.

28. (c)

As γ increase graph goes down.

29. (d)

Between same initial & final points there can not be isothermal & adiabatic process.

30. (d)

For formation reaction, reactants should be elements in their most stable allotropic state.

31. (b)

For combustion reaction, substance should be burned with sufficient oxygen.

32. (a)
Kirchoff's equation are
$\Delta H_2 = \Delta H_1 + \Delta C_P \left(T_2 - T_1\right)$
$\Delta E_2 = \Delta E_1 + \Delta C_V \left(T_2 - T_1\right)$

33. (c)
$\Delta H = \Delta E + \Delta n_g \left(RT\right)$, Δn_g for the reaction is positive
So $\Delta H < \Delta E$

34. (a)
$\Delta H_f^\circ = -\frac{22}{2} = -11 \text{kcal / mole}$

35. (a)
Calorific values
$CH_4 \rightarrow \frac{890}{16} = 55.625 \text{kJ / g}$
$C_2H_4 \Rightarrow \frac{1411}{28} = 50.393 \text{kJ / g}$
$C_2H_6 \Rightarrow \frac{1560}{30} = 52 \text{kJ / g}$

36. (b)
$\Delta E = \Delta H - \Delta n_g \left(RT\right)$
$= 176 - 1 \times \frac{8.314}{1000} \times 1240 = 165.6 \text{kJ}$

37. (b)
(ii)- (i)
$\Delta H = -393.5 + 395 = 1.5 \text{kJ}$

38. (a)
$\text{Energy} = \frac{1560}{2} = 44 \times n_{H_2O}$
$\Rightarrow n_{H_2O} = 17.727$
$\Rightarrow w_{H_2O} = 319 \text{g}$

39. (b)
$K + H_2O \rightarrow KOH\left(aq\right) + \frac{1}{2}H_2 - 48$
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad -69.39$
$KOH\left(aq\right) \rightarrow KOH\left(s\right) + aq \quad 14$
$K + \frac{1}{2}O_2 + \frac{1}{2}H_2 \rightarrow KOH\left(s\right)$
$\Delta H = -48 - 68.39 + 14 = -102.39$

40. (a)

$\Delta H - \Delta U = \left(\Delta n_g\right) RT$

$= -3 \times \frac{8.314}{1000} \times 298 =$

$= -7.43$

41. (a)

$\Delta H = \Delta E + \left(\Delta n_g\right) RT$

$\Delta H = \Delta E - (5.5) \times \frac{8.314 \times 298}{1000}$

$C_8H_{18(g)} + \frac{25}{2} O_2(g) \rightarrow 8CO_2(g) + 9H_2(\ell)$

$\Delta n_g = 8 - 1 - 12.5 = -5.5$

42. (a)

It is not a formation or combustion reaction

43. (b)

$n_{AL} = \frac{250 \times 4.18}{837.8} = 1.247$

$\Rightarrow n_{Al_2O_3} = \frac{1.247}{2} = 0.624$

44. (a)

$\Delta_g H_{H_2SO_4} = -298.2 - 98.7 - 130.2 - 287.3$

$= -814.4$

45. (b)

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

$n_{C_2H_4} = \frac{6226}{1411}$

$n_{O_2} = \frac{6226}{1411} \times 3 \Rightarrow V_{O_2} = \frac{6226}{1411} \times 3 \times 22.4L$

$= 296.5L$

46. (b)

(i) – (ii)

$N_2O_4(g) \rightarrow 2NO_2(g)$

$\Delta H = 16.18 - 2.31 = +ve$

$\Rightarrow$ endothermic reaction

47. (d)

$\frac{1}{2} H_2(g) + \frac{1}{2} Br_2(g) \rightarrow HBr(g) \quad \frac{\Delta H_1}{2}$

$\frac{1}{2} Br_2(\ell) \rightarrow \frac{1}{2} Br_2(g) \quad \frac{-\Delta H_2}{2}$

$\frac{1}{2} H_2(g) + \frac{1}{2} Br_2(\ell) \rightarrow HBr(g) \quad \frac{\Delta H_1 - \Delta H_2}{2}$

48. (b)

$\Delta H_T < \Delta H_C$

So $C \rightarrow T \quad \Delta H_R = \Delta H_T - \Delta H_C = -ve$

$\Rightarrow$ Exothermic

49. (d)

$= 265 = 4x + 2 \times 3x = -26$

$10x = -265 + 26 = -239$

$x = -23.9$

$3x = -71.7$

50. (b)

$\underset{x\,mole}{C} + \underset{x\,mole}{O_2} \rightarrow CO_2$

$\underset{(1-x)mole}{C} + \underset{\left(\frac{1-x}{2}\right)mole}{\frac{1}{2}O_2} \rightarrow CO$

$94.05x + 26.41(1-x) = 75$

$67.64x = 75 - 26.41$

$x = 0.718$

$m_{O_2} = 32 \times \left(\frac{1}{2} + \frac{x}{2}\right) = 27.49g$

51. (b)

For $\Delta H = \in E \Rightarrow \Delta n_g = 0$

52. (c)

$C + O_2 \rightarrow CO_2 \qquad \Delta H = -390 \ (1)$

$CO + \frac{1}{2}O_2 \rightarrow CO_2 \qquad \Delta H = -278 \ (2)$

(1)- (2)

$\Delta H = -390 + 278 = -112$

53. (d)

For formation reaction, reactants should be in most stable allotropic for m

54. (d)

$\Delta H_n = -\frac{y}{2}$

55. (a)

$\theta = m \,\&\, \Delta T$

θ is doubled & m is also doubled.

56. (a)

$\Delta H_{atomisation} = \frac{104}{2} = 52$

57. (c)

For maximum heat, acid and base reacting should be maximum.

58. (b)

$$H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(\ell)$$

$$-298=433+\frac{492}{2}-42-2B_{O-4}$$

$$B_{O-4}=\frac{1}{2}\left(433+\frac{492}{2}-42+298\right)$$

$$=467.5$$

59. (d)

$$H_2O(\ell)\rightarrow H_2O(g)$$

$$\Delta H=+9.7=\Delta_f H_{H_2O(g)}-\Delta_f H_{H_2O(\ell)}$$

$$\Rightarrow \Delta_f H_{H_2O(g)}=-68+9.7=-58.3\,kcal$$

60. (b)

$$-100=600-2B_{C-C}$$

$$\Rightarrow BE_{C-C}=350$$

61. (b)

$$\Delta H_n=-13700+(366\times 0.86)=-13385$$

62. (b)

$$\frac{1}{2}H_2+\frac{1}{2}Cl_2\rightarrow HCl$$

$$\Delta H=\frac{435}{2}+\frac{243}{2}-431=-92$$

63. (b)

$$\Delta H_n=-13.7\times 2$$

$$=-27.4kcal$$

64. (d)

For max heat $n_{H^+}=n_{OH^-}$

$$1\times V_1=0.5\times 2\times V_2$$

$$\Rightarrow V_1=V_2$$

65. (d)

$$S\rightarrow \ell\rightarrow g$$

$$\Delta H_{fusion}+\Delta H_{vaporisation}$$

$$-100=\frac{x}{2}+\frac{x}{4}-x=-\frac{x}{4}$$

66. (a)

$$-10=\frac{x}{2}+\frac{x}{4}-x=-\frac{x}{4}$$

$$\Rightarrow x=400$$

67. (a)

$$\Delta S = \frac{\theta_{rev}}{T} = \frac{\Delta H_V}{T}$$

68. (a)

$$\Delta S_{sys} = nR\ell n\frac{V_f}{V_i}$$

$$= 1 \times 8.314 \times \ell n10 = 19.15 JJ / K - mol$$

69. (b)

$$\Delta S_{sys} = nR\ell n\frac{V_f}{V_i}$$

70. (b)

Endothermic $\Rightarrow \Delta H = +ve$

$\Rightarrow \Delta S_{sys} > 0 \Rightarrow \Delta S_{surr} = -ve$

71. (c)

Exothermic $\Rightarrow H = -ve$

$\Rightarrow \Delta S_{sys} < 0 \Rightarrow \Delta S_{surr} = +ve$

72. (b)

$\Delta H > 0 \Rightarrow$ since bond are broken

$\Delta S > 0 \Rightarrow \Delta n_g > 0$

73. (d)

$$S_{sys} = 1 \times C_V \ell n2 + 1 \times R\ell n\frac{1}{2}$$

$$= \left(C_{V-R}\right)\ell n\, 2$$

74. (a)

Zeroth law is for thermal equilibrium between bodies

75. (d)

$$\Delta S_{surr} = \frac{64000}{300} = 213$$

76. (a)

$$\Delta S_{Rxn} = 2 \times 68 - 2 \times 126.6 - 201.2$$

$$= -318.4$$

77. (a)

At equilibrium $\Delta G = 0$

78. (a)

For spontaneous $\Delta G < 0$

79. (d)

$$T > \frac{178.3 \times 1000}{160}$$

$\Rightarrow T > 1114$

80. (c)

$T < \frac{49 \times 1000}{40.2}$

$\Rightarrow T < 1219K$

81. (b)

$\Delta H_R = 9.7 - 2 \times 90.5$

$= -171.3$

$\Delta S_R = 304 - 2 \times 210 - 205$

$= -321$

$\Delta G_R = -171.3 - \frac{298}{1000} \times (-321)$

$= -75.64$

82. (a)

$\Delta n < 0. \Delta S > 0$ always spontaneous

$\Delta H > 0, \Delta S < 0$ never spontaneous

83. (c)

For $C_2H_6(g), C$ will be higher

84. (c)

$T > \frac{85 \times 1000}{1.98}$

$\Rightarrow T > 429.3K$

85. (d)

$\Delta H^\circ > 0 \Rightarrow$ opposes

$\Delta S > 0 \Rightarrow$ favours

EXERCISE - 1 [B]

1. (d)
$41 + 463 + 348 - 352 - 415 = 85$ kJ/mol

2. (a)
$\left[n\times 942 + n\times 436 - n\times\left(163\times 2 + 2\times 390\right)\right]\times\frac{1}{n} = 272 \text{ kJ/mole}$

3. (b)
$\Delta H° = -167.1\times 5 - 1284.4 + 285.8\times 4 + 443.5$
$= -533.2$

4. (b)
$\Delta H° = \frac{507}{2} - \frac{427}{2} + \frac{43}{2} + \frac{34}{2} = 78.5 \text{ kJ}$

5. (c)

6. (c)

7. (a)

8. (b)
$\Delta H_1 = x + \frac{3}{2}\Delta H_3 - \frac{\Delta H_2}{2}$
$\Rightarrow\ x = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

9. (b)
$\Delta H° = -537\times 2 - 680\times 2 + 52 = -2382$

10. (b)
$\frac{1}{2}\mathrm{I}_2(s) + \frac{1}{2}\mathrm{Cl}_2(g) \longrightarrow \mathrm{ICl}(g)$
$\Delta H_f = \frac{1}{2}\times\left[62.76 + 151 + 242.3\right] - 211.3$
$= +16.8 \text{ kJ/mol}$

11. (c)

12. (b)
$\Delta H - T\Delta S > 0$ (For non-spontaneous process)
$\Rightarrow\ T > \frac{-\Delta H}{-\Delta S}$ or $T > \frac{1648\times 10^3}{560} = 2943 \text{ K}$

13. (d)

14. (b)

15. (b)

16. (b)

Ice $\rightarrow$ water $\rightarrow$ water $\rightarrow$ steam

(0^oC) (0^oC) (100^oC) (100^oC)

$$\Delta S_{\text{Total}} = 18\times\frac{80}{273}+18\times1\times\ln\left(\frac{373}{273}\right)+18\times\frac{540}{373}$$

17. (b)

$$T=\frac{25\times10^3}{50}\text{K}$$

18. (b)

19. (d)

A(s) $\rightarrow$ B(s)

400 mL 600 mL

$$\int d\left(\Delta G\right)=\int\left(\Delta G\right)dP$$

$$\Delta G-\Delta G^\circ=\left(200\right)\left[P-10^5\right]$$

$$\frac{2\times10^3}{200\times10^{-6}}=P-10^5$$

$$\Rightarrow\quad P=101\times10^5\ \text{N/m}^2$$

$$=101\text{ bar}$$

20. (a)

$$\Delta S_{sys}=nC_v\ln\left(\frac{T_2}{T_1}\right)+nR\ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S=2\times\frac{3}{2}\times2\ln\left(\frac{10}{10}\right)+2\times2\ln\left(\frac{5}{10}\right)$$

21. (b)

22. (a)

$$W=-\frac{7}{28}\times8.3\times300\ln\left(\frac{0.5}{0.1}\right)=-996\text{ J}$$

23. (b)

$\Delta E=\Delta H-\Delta n_gRT$; $\Delta n_g>0$ and $\Delta H<0$

CO formation is exothermic and $\Delta n_g=+1$

24. (c)

$q=0$; $\Delta U=-4\left(30-40\right)=+40$

$$\Delta H = \Delta U + \Delta(PV) = 40 + (120 - 80) = 80 \text{ L-bar}$$

$$\Delta H = 8000 \text{ J}$$

25. (d)

$$q = 10 \times 1 \ln 10 = 23.03 \text{ atm-L}$$

EXERCISE - 1 [C]

1. (189)

$Zn + 2HCl \longrightarrow ZnCl_2 + H_2(g)$;

$w = -\Delta n_g RT$

$= -1 \times 8.3 \times 296 \times \frac{5}{65} \simeq -189$

2. (22)

$\frac{57.4}{2^{1.4}} = P_2 \qquad \Rightarrow P_2 = 22$

3. (6)

Open systems : b, f, g, i, j

Closed systems : a, c, h

Isolated systems : d, e

4. (5200)

$W = -\int PdV = -\int_1^3 6V^2\, dV = 2 \times [27 - 1]$

$= 52 \text{ bar-m}^3$ or 5200 kJ

5. (182)

[23 + 45 + 81 + 33 = 182]

6. (44)

$(\Delta C_P)_{\text{Reaction}} = 2 \times 4 - 3.5 - 3 \times 3.5 = -6$

$\Delta H_{300} = \Delta H_{1000} + \Delta C_P (300 - 1000)$

$= -123.77 + \frac{6 \times 700 \times 8.3}{1000}$

$= -88.91$ for 2 moles of NH_3

7. (5)

Pressure, molar entropy, density, boiling point, molality are intensive properties.

8. (1488)

$\Delta_r H^\circ = 2 \times 414 + 2 \times 330 = 1488 \text{ kJ/mol}$

9. (210)

$P_4(s) \longrightarrow P_4(g)$

$P_4(s) \longrightarrow 4P(g)$

$\Rightarrow P_4(g) \longrightarrow 4P(g)$

$\Delta H = 1321 - 61 = 6x$

$\Rightarrow x = 210 \text{ kJ/mol}.$

10. (4)
Intensive : a, c, d, f, g, h, i, k
Extensive : b, e, j, *l*

11. (3125)
$300\times(0.5)^{\gamma-1}=T_2\times(3)^{\gamma-1}$
$\Rightarrow\ T_2=\dfrac{300}{(6)^{2/5}}=150\text{ K}$
$w=1\times\dfrac{25}{3}\times\dfrac{150}{0.4}=3125\text{ J}$

12. (1700)
$N_2O_5 + O_2 \longrightarrow 2NO_2 + O_3$
10 30 – –
– 20 – –
$NO_2 + O_2 \longrightarrow NO + O_3$
20 20 – –
$20-x$ $20-x$ x x

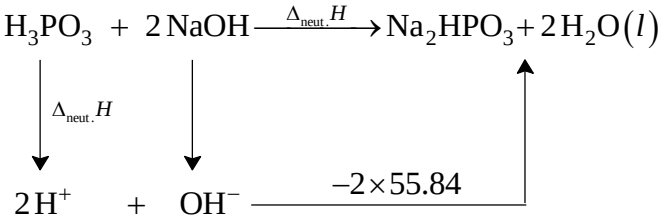
$$\frac{(10+x)}{\left[(20-x)+(20-x)+x+(10+x)\right]}\times100=50$$
$\Rightarrow\ x=15$
$\Delta H=10\times200-15\times20=1700\text{ kJ}$

13. (2)
$29\times2-56=2$

14. (7700)
$T\propto V^3$, T = 300 K
$\Rightarrow\ PV^{-2}=K$ n = 1 mole
$\gamma=\dfrac{5}{3}$
$C=\dfrac{3R}{2}+\dfrac{R}{3}=\dfrac{11R}{6};\ T_f=2400\text{ K}$
$q=1\times\dfrac{11}{6}\times2\times2100=7700\text{ cal}$

15. (8)
$\dfrac{1}{5}=1-\dfrac{T_2}{T_1}$ ...(i)
$\dfrac{2}{5}=1-\dfrac{(T_2-80)}{T_1}$ ...(ii)
$\Rightarrow\ T_1-T_2=80$

16. (5)



$\Delta_{neut.}H = \Delta_{ion}H - 2\times55.84$

$\Delta_{ion}H = 5\,kJ$

17. (3)

State functions : a, b, c, d, g, h, j

Path functions : e, f, i, k

SECTION-I

1. (a)

$$N_2(g)+\frac{1}{2}O_2 \rightarrow N_2O(g)$$

$$N\equiv N(g)+\frac{1}{2}(O=O)\rightarrow \overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}=\overset{+}{N}=\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}(g)$$

$\Delta_f H^\circ$ = [Energy required for breaking of bonds] – [Energy released for forming of bonds]

$$=\left(\Delta H_{N\equiv N}+\frac{1}{2}\Delta H_{O=O}\right)-\left(\Delta H_{N=N}+\Delta H_{N=O}\right)$$

$$=\left(946+\frac{1}{2}\times 498\right)-(418+607)=170\,kJ\,mol^{-1}$$

Resonance energy =observed $\Delta_f H^0$ – calculated $\Delta_f H^\circ$

$82-170=-88\,kJ\,mol^{-1}$.

2. (c)

For isothermal reversible expansion.

$$w=-nRT\ln\frac{V_2}{V_1}$$

3. (a)

Process is isothermal reversible expansion, hence $\Delta U=0$, therefore $q=-w$,

Since $q=+208J, w=-208J$

4. (b)

$$\Delta S^\circ=S^\circ_{CO_2}+2\times S^\circ_{H_2O}-\left(S^\circ_{CH_4}+2\times S^\circ_{O_2}\right)$$

$$=(213.6+2\times 69.9)-(186.2+2\times 205.2)$$

$$=-242.8JK^{-1}mol^{-1}$$

5. (a)

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

Bomb calorimeter gives ΔU of the reaction.

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

$\Delta n_g=-1$

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

$$=-1364.47-\frac{1\times 8.314\times 298}{1000}=-1366.95\,kJ\,mol^{-1}$$

6. (c)

Given $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$; $\Delta_f H = -46.0\,kJ/mol$

$H + H \rightleftharpoons H_2; \Delta_f H = -436\,kJ/mol$

$N + N \rightleftharpoons N_2; \Delta_f H = -712\,kJ/mol$

$\Delta_f H(NH_3) = \frac{1}{2}\Delta H_{N-N} + \frac{3}{2}\Delta H_{H-H} - 3\Delta H_{N-H} \; -46 = \frac{1}{2}(712) + \frac{3}{2}(436) - 3\Delta H_{N-H}$

$\Delta H_{N-H} = 352\,kJ/mol$

7. (b)

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

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

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

$\therefore BE_{(C-C)} = 620 - (6 \times 90) = 80\,kJ/mol$

$\therefore BE_{(C-C)} = \frac{80 \times 10^3}{6.023 \times 10^{23}}\,J/mol$

Now, $E = \frac{hc}{\lambda}$

$\lambda = \frac{6.626 \times 10^{-34} \times 3 \times 10^8 \times 6.023 \times 10^{23}}{80 \times 10^3}$

$\lambda = 1.49 \times 10^{-6}\,m \qquad (\because 1nm = 10^{-9}\,m)$

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

8. (a)

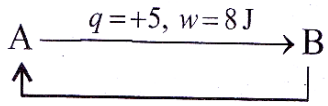
$2H_2O_2 \rightleftharpoons 2H_2O(l) + O_2(g)$

$w = -P_{ext}(\Delta V) = -n_{O_2}RT$

$\because 100$ mole of H_2O_2 on decomposition give 50 mole O_2.

$\therefore w = -(50)(8.3)(300) = -124500J = -124.5kJ$

9. (d)



$\Delta U_{AB} = q + w = 5 + (-8) = -3J$

$q = -3, \Delta U_{BA} = +3$

$\Delta U_{BA} = q + w$

$\Rightarrow 3 = -3 + w \Rightarrow w = +6$ (work done on the system).

10. (c)

$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g); \Delta_r H^\circ_1 = -393.5\,kJ/mol^{-1}$ .....(i)

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\ \Delta_r H^\circ_2 = -285.8 kJ/mol^{-1}$ .....(ii)

$CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g);\ \Delta_r H^\circ_3 = +890.3\,kJ/mol^{-1}$ .....(iii)

$C(\text{graphite}) + 2H_2(g) \longrightarrow CH_4(g); \Delta_r H = ?$ .....(iv)

[Eq. (i)+ Eq. (iii)] + $\left[2 \times \text{Eq.(ii)}\right] = \text{Eq(iv)}$

$\therefore \left[\Delta H_1 + \Delta H_3\right] + \left[2 \times \Delta H_2\right] = \Delta H$

$\left[(-393.5) + (890.3)\right] + \left[2(-285.8)\right] = -74.8 kJ/mol$

11. (d)

$C_6H_6(1) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$

$\Delta n_g = 6 - \frac{15}{2} = -\frac{3}{2}$

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

$= -3263.9 + \left(-\frac{3}{2}\right) \times 8.314 \times 10^{-3} \times 298$

$= -3263.9 - (3.71) = -3267.6\,kJ\,mol^{-1}$

12. (b)

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

$2HI(g) \rightarrow H_2(g) + I_2(g); \Delta n_g = (1+1) - 2 = 0$

$\therefore \Delta H = \Delta U$

13. (a)

$C_7H_{16}(1) + 11O_2(g) \xrightarrow{\Delta} 7CO_2(g) + 8H_2O(l)$

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

$\because \Delta n_g = 7 - 11 = -4 \qquad \therefore \Delta H - \Delta U = -4RT$

14. (a)

We know that heat and work are not state functions but $q + w = \Delta U$ is a state function. $H - TS = G$ is also a state function.

15. (c)

$\Delta U = nC_v\Delta T = 5 \times 28 \times 100 = 14 kJ$

$\Delta(PV) = nR(T_2 - T_1) = 5 \times 8 \times 100 = 4 kJ$

16. (a)

Given: $n = 3$

$T_1 = 300; T_2 = 1000$

$C_p = 23 + 0.01T$

The relation between ΔH and C_p

$$\Delta H = \int_{T_1}^{T_2} nC_p dT \qquad \ldots\ldots(i)$$

After purring all variable values in equation (i), we get

$$\Delta H = n\int_{300}^{1000}(23+0.01T)dT = 3\left[23T + \frac{0.01T^2}{2}\right]_{300}^{1000}$$

$$= 3\left[23(1000-300)\right] + 3\left[\frac{0.01}{2}\left(1000^2 - 300^2\right)\right]$$

$$= 61950\,J = 61.95\,kJ \approx 62\,kJ$$

17. (d)

In expansion against vacuum,

$P_{ext} = 0 \Rightarrow w = -P_{ext}\Delta V = 0$

18. (c)

$\Delta_{sol}.H^{\circ} = \Delta_{lattice}H^{\circ} + \Delta_{Hyd}H^{\circ}$

$4 = 788 + \Delta_{Hyd.}H^{\circ}$

$\Delta_{Hyd}.H^{\circ} = -784\,kJ\,mol^{-1}$

19. (c)

$\Delta H_{atomisation} = \Delta H_{vap} + \text{Bond energy}$

Hence, $x > y$.

20. (a)

A system at higher temperature has greater entropy (randomness). S and ΔS are related with T as:

$S_T = \int_0^T \frac{nC.dT}{T}$ and $\Delta S = \int \frac{dq}{T}$

Thus, both S and ΔS are function of temperature.

21. (a)

$H = U + PV(\text{By definition})$

$\Delta H = \Delta U + \Delta(PV)$ at constant pressure

$\Delta H = \Delta U + P\Delta V$

22. (b)

For a spontaneous process Gibb's free energy value is negative at constant temperature and pressure i.e, $\Delta G_{T,P} < 0$.

(B) In isobaric pressure, pressure remains constant i.e., $\Delta P = 0$ while in isothermal process, temperature remains constant i.e., $\Delta T = 0$.

(C) $\Delta H_{reaction} = (\sum \text{bond energies of reactants}) - (\sum \text{bond energies of products})$

(D) In exothermic process , energy is released. So, the value of enthalpy is negative i.e., $\Delta H < 0$.

23. (a)

$\Delta G = \Delta H - T\Delta S \qquad \because \Delta S_g > \Delta S_1 > \Delta S_s$

$\therefore$ On melting the entropy increases and ΔG becomes more negative and hence it becomes easier to reduce metal.

24. (c)

$\Delta_f H = \sum \Delta_c H(\text{Reactant}) - \sum \Delta_c H(\text{Product})$

$= 3\times(-1300) - (-3268) = -632\,\text{kJ mol}^{-1}$

25. (c)

$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

Heat of combustion

$= \sum \Delta_f H_{(\text{products})} - \sum \Delta_f H_{(\text{reactants})}$

$\Delta_c H(C_2H_6, g) = 2\Delta cH(C, \text{graphite}) + 3\Delta_c H(H_2, g) - \Delta_f H(O_2, g) - \Delta_f H(C_2H_6, g)$

$= -1560 = 2(-394) + 3(-286) - 0 - \Delta_f H(C_2H_6, g)$

$\Rightarrow \Delta_f H(C_2H_6, g) = -86\ \text{KJmol}^{-1}$

26. (d)

Since in adiabatic system, no heat exchange between system and surrounding, hence when methane undergoes combustion, due to endothermic reaction, the temperature rises in container (A)

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{Heat}$

In diathermic container, heat can change between system and surrounding, hence heat release into the surrounding, hence heat releases into the surrounding and temperature of system (B) remains same.

27. (c)

The most appropriate relations are given in B and C only.

28. (b)

Given equation

(A) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g),\ \Delta H_1^\circ = -x\ \text{kJ mol}^{-1}$

(B) $C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g),\ \Delta H_2^\circ = -y\ \text{kJ mol}^{-1}$

We have to find ΔH° for the reaction,

$C(\text{graphite}) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \quad ...(i)$

$CO_2(g) \longrightarrow CO(g) + \frac{1}{2}O_2(g) \quad ...(ii)$

$\Delta H_1 = \frac{x}{2}\ \text{kJ/mole}$

$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) \quad ...(iii)$

$\Delta H_2 = -y\ \text{kJ/mol}^{-1}$

Eq. (i) = Eq. (ii) + Eq. (iii)

$$\Delta H = \frac{x}{2} - y$$

$$\Rightarrow \quad \Delta H = \frac{x - 2y}{2}$$

29. (a)

For free expansion, $p_{external} = 0$

$\therefore$ Work done, $W = -p_{ext}\Delta V = 0$

$\because$ Adiabatic process, $q = 0$

Also from 1st laws of thermodynamics.

$$\Delta U = q + W$$

$$\Delta U = 0$$

Internal energy is a function of temperature.

If internal energy is constant

$$\Delta T = 0$$

So, for free expansion, $q = 0, \Delta T = 0, W = 0$

Hence, option (a) is correct.

30. (b)

Both A and R are true and R is the correct explanation of A. The enthalpy of neutralization of strong acid and strong base is always –57 kJ/mol. The reason for that is, strong monoacid gives one mole of H^+ and strong mono base gives on mole of OH^- which form one mole of water.

31. (a)

Among the given options (a) is incorrect. Its correct form is :

$(\Delta G)k$ is positive for non-spontaneous reaction.

SECTION-II

1. (557)

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

Or $\Delta U = \Delta H - V\Delta P = -560 - \left[1(40-70)\times 0.1\right]$

$= -560 + 3 = -557\,kJ\,mol^{-1}$

So, the magnitude is $557\,kJ\,mol^{-1}$

2. (–13538)

From $\Delta H^\circ = \Delta U^\circ + \Delta n_g RT$

$\Delta H^\circ = -20\times 1000 - 1\times 8.314 J/mol.K \times 298K$

$= -22477.57J$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -22477.57 - \left(298\times(-30)\right)$

$= -13538J$

3. (189494)

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

$n = \frac{90}{18} = 5\text{mol}$

$H_2O(l) \rightleftharpoons H_2O(g)$

$\Delta n = 1$

$41000 = \Delta U + 1 \times 8.314 \times 373 \Rightarrow \Delta U = 37898.875\,J$

For 5 moles, $\Delta U = 37898.87 \times 5 = 189494\,J$

4. (–326400)

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

$\Delta H_C = -327\,\text{kcal}$

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

$\Rightarrow -327 \times 10^3 = \Delta U + (-1) \times 2 \times 300$

$\Rightarrow \Delta U = -327 \times 10^3 + 600$

$\therefore \Delta U = -326400\,\text{cal}$

5. (5)

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

$\Delta G = -57.8 - 298 \times \left(-176 \times 10^{-3}\right) = -5\,\text{kJ mol}^{-1}$

6. (50)

$q = 150$ joules

$w = -200$ Joules

$\Delta E = q + w$ (First law of thermodynamics)

$\Rightarrow \Delta E = 150 + (-200) = -50$ Joules

7. (2218)

$Fe + 2HCl \longrightarrow FeCl_2 + H_2$

No. of moles $Fe = \frac{50}{55.85}$ moles

No. of moles of H_2 produced $= \frac{50}{55.85}$ moles

Word done $= -P_{ext}; \Delta V = -\Delta n_g RT$

$= \frac{50}{55.85} \times 8.314 \times 298 \approx 2218J$

8. (718)

$\Delta_f H^\circ_{KCl} = \Delta_{sub} H^\circ_{(K)} + \Delta_{ionization} H^\circ_{(K)} + \frac{1}{2}\Delta_{bond} H^\circ_{(Cl_2)} + \Delta_{electron\,gain} H^\circ_{(Cl)} + \Delta_{lattice} H^\circ_{(KCl)}$

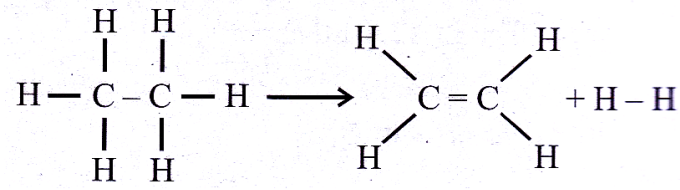
$\Rightarrow -436.7 = 89.2 + 419 + \frac{1}{2}(243.0) + \{-348.6\} + \Delta_{lattice} H^\circ_{(KCl)}$

$\Rightarrow \Delta_{lattice} H^\circ_{(KCl)} = -717.8\,\text{kJ mol}^{-1} \simeq 718\,\text{kJ mol}^{-1}$

9. (101)

$\Delta H_{sub} = \Delta H_{fus.} + \Delta H_{vap.} = 2.8 + 98.2 = 101\,kJ/mol$

10. (128)



$\Delta_r H = \sum B.E_{Reactant} - \sum B.E_{Products}$

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

$= \left[347 + 6\times 414\right] - \left[611 + 4\times 414 + 436\right] = 128\,kJ\,mol^{-1}$

11. (309)

$SF_6(g) \rightarrow S(g) + 6F(g)$

$\Delta H^{\circ} = \Delta H_f^{\circ}(S) + 6\Delta H_f^{\circ}(F) - \Delta H_f^{\circ}(SF_6)$

$= 275 + 6\times 80 - (-1100) = 1855\,kJ\,mol^{-1}$

Also, $\Delta H^{\circ} = 6\Delta H_{S-F}$

$\therefore \Delta H_{S-F} = \dfrac{1855}{6} = 309.17 \simeq 309\,kJ\,mol^{-1}$

12. (3)

State Variable is an independent variable of a state function.

13. (2)

$C_{m.p} - C_{m.v.} = R \Rightarrow 20.785 - C_{m,v} = 8.314$

$\Rightarrow C_{m.v} = 12.471\,J\,K^{-1}mol^{-1}$

$\Delta U = nC_{m,v}\Delta T$

$\Rightarrow n = \dfrac{5000}{12.471\times(500-300)} \Rightarrow n = 2$

14. (200)

Moles of coal $= \dfrac{2.4}{12} = 0.2$

$q = C_v dT$

$q = 20\times(300-298) = 40kJ$

0,2 moles evolved $= 40kJ$

1 moles evolved $= \dfrac{40}{0.2} = 200\,kJ/mol$

$\Delta H = -200\,kJ/mol$

15. (1718)

$$w = -2.303nRT\log\frac{V_2}{V_1}$$

$$P_1V_1 = P_2V_2 \Rightarrow \frac{V_2}{V_1} = \frac{P_1}{P_2} = \frac{6}{3} = 2$$

$$w = -2.303\times1\times300\times\log(2)$$

$$\Rightarrow w = -1718.1J$$

16. (117)

Molar mass of $NH_3 = 17\,g/mol$

Moles of NH_3 given $= \frac{17}{17} = 1\,mole$

For 1 mole enthalpy change $= 23.4\,kJ$

5 moles enthalpy change $= 23.4\times5 = 117\,kJ$

17. (0)

For free expansion : $w = -P_{ext}dV$

$P_{ext} = 0; w = 0$

Isothermal expansion , $\Delta U = 0$

$\Delta U = q + w = q = -w = 0$

18. (8630)

$n = 5\,mol; T = 300K; V_1 = 10L; V_2 = 20L$

Work done in isothermal condition.

$$w_{rev} = -nRT\ln\frac{V_2}{V_1}$$

$$= -5\times8.3\times300\ln\frac{20}{10} = -8630.38J$$

19. (300)

$\Delta G = \Delta H - T\Delta S = 0$ at equilibrium

$\Rightarrow -165\times10^3 - T\times(-550) = 0 \Rightarrow T = 300K$

20. (103.7)

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$ ….. (1)

$\Delta H_1 = -2220\ kJ/mol$

$C + O_2 \rightarrow CO_2$ ….. (2)

$\Delta H_2 = -393.5kJ/mol$

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ ….. (3)

$\Delta H_3 = -285.8kJ/mol$

Formation of $C_3H_8(1mole)$:

$3C + 4H_2 \rightarrow C_3H_8$ ….. (4)

Equation (4) obtained by

$3\times Eq(2)+4\times Eq.(3)-Eq.(1)$

$=3\times(-393.5)+4\times(-285.8)-(-2220.0)$

$=-1180.5-1143.2+2220.0=-103.7\,kJ/mol$

21. (2)

$\Delta H_{neutralization}=-57.3\,kJ/mol$

In case of acetic acid

$\Delta H=\Delta H_{ioni}+\Delta H_{neitralization}$

$-55.3=\Delta H_{ioni}-57.3$

$\Delta H_{ion_i}=2kJ/mol$

22. (727)

$\Delta U=-726\,kJ/mol$

$\Delta n_g=1-3/2=-1/2$

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

$=-726-\frac{1}{2}\times\frac{8.3\times300}{1000}=-727.245$

23. (38)

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

$\Delta n_g=\sum np-\sum nR=1-0=1$

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

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

$=41.1-\frac{1\times8.31\times373}{1000}kJ/mol=38kJ/mol$

24. (54)

HNO_3	NaOH
$=120mmol$	$400mL\times0.1M$

$HNO_3+NaOH\rightarrow NaNO_3+H_2O$

Start	120	40
End	80	0 40mmol

$\Delta_f H=40mmol\times(57\times10^3)\,J\,mol^{-1}$

$=40\times10^{-3}mol\times57\times10^3\,J\,mol^{-1}=2280\,J$

$mS\Delta T=2280\Rightarrow1000g\times4.2\times\Delta T=2280$

$\Delta T=\frac{2280}{4.2}\times10^{-3}=\frac{22800}{42}\times10^{-3}=542.86\times10^{-3}$

$= 54.286 \times 10^{-2}\,K = 54.286 \times 10^{-2}\,^{\circ}C$

25. (4)

Extensive properties Mole, volume, Gibbs free energy

Intensive properties Mole mass, molar heat capacity, molarity, E°_{cell}

Thus, total number of intensive properties are 4.

26. (1200)

Power of heater = 60 W

= 60 J/s

Total energy emitted $= 60 \times 100$

= 6000 J

Heat capacity × temperature difference = total energy emitted

Heat capacity × 5°C = 6000

Heat capacity $= \frac{6000}{5} = 1200\ J/K$

27. (150)

Given, Number of moles = 1 mole

Temperature (T_i) = $27°C = 300\ K$

Since, the processes is adiabatic, hence,

$q = 0$

$\Rightarrow \quad W = \Delta U$

On substituting values, we will get

$W = nC_V\Delta T$

$-3 \times 10^3 = 1 \times 20\left[T_2 - 300\right]$

$T_2 - 300 = -150$ or $T_2 = 150\ K$

28. (0)

For in isothermal processes, the temperature remains constant.

So, the change in internal energy is zero.

29. (620)

$1 \rightarrow 2 \Rightarrow$ Isobaric processes

$2 \rightarrow 3 \Rightarrow$ Isochoric processes

$3 \rightarrow 1 \Rightarrow$ Isothermal processes

Work done

$(W) = W_{1\rightarrow 2} + W_{2\rightarrow 3} + W_{3\rightarrow 1}$

$= \left(-p\left(V_2 - V_1\right) + 0 + \left[-p_1 V_1 \ln\left(\frac{V_2}{V_1}\right)\right]\right)$

$= \left[-1 \times \left(40 - 20\right) + 0 + 0\left[-1 \times 20 \ln\left(\frac{20}{40}\right)\right]\right]$

= – 6.2 bar L

$\left|W\right| = 6.2\ \text{bar L} = 620\ L$

30. (3)

Given $n = 1, R = 8.314\ JK^{-1}mol^{-1}$

$V_2 = 3L, V_1 = 2L$

$$\Rightarrow \quad \Delta S_{system} = nR\ln\left(\frac{V_2}{V_1}\right)$$

$$= 1\times 8.314\ln\left(\frac{3}{2}\right)$$

$$= 3.37\ JK^{-1}$$

$$\Delta S_{surroundings} = 3.37 \approx 3\ JK^{-1}$$

31. (10)

Reaction, $A \rightleftharpoons B$ at 298 K

Given, $\Delta H° = -54.07\ kJ/mol$

$\Delta S° = 10\ J/K/mol$

We know that,

$\Delta G° = \Delta H° - T\Delta S°$

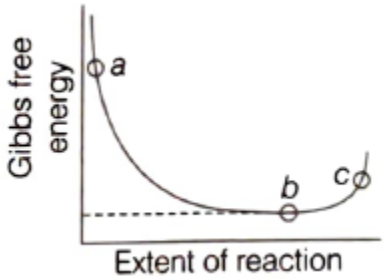
or $-2.303RT\log K = -54070 - 298\times 10$

$-5705\times kigK = -57050$

So, $\log K = 10$

32. (2)

Graph between Bibbs free energy *vs* extent of reaction.



- At a point we observe $\Delta_r G < 0$
  So, reaction is spontaneous.
- At b point $\Delta G = 0$ (equilibrium)
- At c point Gibbs free energy $\Delta_r G > 0$
  So, reaction is non-spontaneous
- Two statements B and C are correct (2).

33. (6)

$$A + B \underset{K_b=10^2}{\overset{K_f=10^{-3}}{\rightleftharpoons}} C + D$$

Sine, equilibrium constant can be calculated as

$$K_{eq} = \frac{K_f}{K_b} \text{ or , } k_{eq} = \frac{10^3}{10^2} = 10$$

Again, the relation between ΔG° and K_{eq} can be calculated from the formula

$$\Delta G^\circ = -RT \ln K$$

So, $\Delta G^\circ = -8.3 \times 300 \times \ln(10)$

or $\Delta G^\circ = -5.7 \text{ kJ/mol} \approx -6 \text{ kJ/mol}$

34. (800)

$A_2 + B_2 \longrightarrow 2AB$

$\Delta H_f^\circ (AB) = -200 \text{ kJ mol}^{-1}$

$\therefore$ ΔH_f° for reaction

$A_2 + B_2 \longrightarrow 2AB$ is -400 kJ mol^{-1}

Given that, bond enthalpy of A_2, B_2 and AB is 1 : 0.5 : 1.

Assume that bond enthalpy of A_2 is $x \text{ kJ mol}^{-1}$

$\therefore$ Bond enthalpy of $B_2 = 0.5x$ kJ mol

$\therefore$ Bond enthalpy AB = x kJ/mol

$$= (BE)_{A_2} + (BE)_{B_2} - 2(BE)_{AB}$$

$\Rightarrow \quad \Delta H_r^\circ = -400 \text{ kJ mol}$

$\Rightarrow \quad -400 = x + 0.5x - 2x$

$x = 800 \text{ kJ mol}$

35. (4)

A $\rightarrow$ Endothermic (atomisation)

B $\rightarrow$ Endothermic (atomisation)

C $\rightarrow$ Endothermic (vaporisation)

D $\rightarrow$ Exothermic (combustion)

E $\rightarrow$ Endothermic (dissolution)

36. (1411)

Consider the following reaction

$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(\ell)$

$\Delta U = -1406 \text{ kJ mol}^{-1}$

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

$$= -1406 + \frac{(-2) \times 8.314 \times 300}{1000}$$

$$= -1406 - 4.98$$

$$\approx -1411 \text{ kJ mol}^{-1}$$

The minimum value of $T\Delta S$ at equilibrium, $T\Delta S = -1411 \text{ kJ}$

$[\because \Delta G = \Delta H - T\Delta S \Rightarrow$ at equilibrium $\Delta G = 0 \Rightarrow T\Delta S = \Delta H]$

37. (278)

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$

$\Delta H = -241.8\ kJ/mol \quad ...(i)$

$C + O_2 \longrightarrow CO_2$

$\Delta H = -393.5\ kJ/mol \quad ...(ii)$

$C_2H_5OH + 3O_2 \longrightarrow 3H_2O + 2COl2$

$\Delta H = -1234.7\ kJ/mol \quad ...(iii)$

Formation of C_5H_5OH will be

$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(\ell)$

Heat of formation of $C_2H_5OH(\ell) = Eq.(ii) + 3 \times Eq.(i) - Eq.(iii)$

$2 \times (-393.5) + 3 \times (-241.8) - (0 - 1234.7)$

$= -787 - 725.4 + 1234.7$

$= -277.7$

$\approx -278\ kJ/mol$

38. (1006)

Heat released by combustion of 1 mole of

$C_2H_6 = \Delta U = \frac{-20 \times 0.5}{0.3} \times 30$

$= -1000\ kJ$

$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(\ell)$

$\Delta n = 2 - \left(1 + \frac{7}{2}\right) = -\frac{5}{2}$

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

$= -1000 - \frac{5}{2} \times 8.3 \times 10^{-3} \times 300\ K$

$= -1000 - 6.225$

$= -1006\ kJ$

Thus, heat released = 1006 kJ/mol

39. (499)

$2H_2O(g) \longrightarrow H_2(g) + \frac{1}{2}O_2(g),\ \Delta H_1 = 242 \times 2\ kJ/mol$

$H_2(g) + O_2(g) \longrightarrow 2OH,\ \Delta H_2 = 78\ kJ/mol$

$H_2(g) \longrightarrow 2H(g),\ \Delta H_3 = 436\ kJ/mol$

$2H_2O \longrightarrow 2H + 2OH,\ \Delta H = 998\ kJ/mol\ (= \Delta H_1 + \Delta H_2 + \Delta H_3)$

$\Rightarrow$ For 1 mole H_2O,

$\Delta H = \frac{998}{2} = 499\ kJ/mol$

40. (173)

$$CCl_4(g) + 2H_2O(g) \longrightarrow CO_2(g) + 4HCl(g)$$

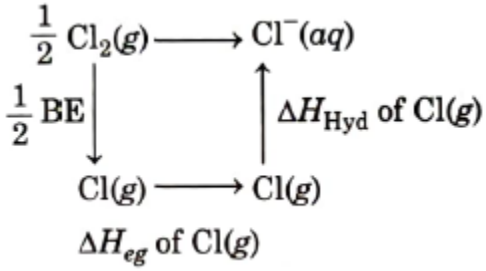
$$\Delta H_r = (\Delta H_f CO_2 + 4\Delta H_f HCl) - (\Delta H_f CCl_4 + 2\Delta H_f H_2O)$$

$$= [-394 + 4\times(-92)] - [-105 + 2\times(-242)]$$

$$= -173 \text{ kJ/mol}$$

41. (610)

From Born Haber cycle,



From Hess's heat sumation law

$$\Delta H^\circ = \frac{1}{2}\times BE + \Delta H_{eg} + \Delta H_{Hyd}$$

$$= \frac{1}{2}\times 240 + (-350) + (-380)$$

$$= 120 - 350 - 380 = -610 \text{ kJ mol}^{-1}$$

42. (925)

Let volume of C_2H_4 is x litre,

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

Initial	x	–	–
Final	–	2x	2x

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

Initial	(16.8 – x)	–
Final	–	(16.8 – x)

Total volume of $CO_2 = 2x + 16.8 - x$

$\Rightarrow$ $28 = 16.8 + x$ or $x = 11.2$ L

Volume of $C_2H_4 = 11.2$ L

Volume of $CH_4 = (16.8 - 11.2)\text{L} = 5.6$ L

No. of moles of $CH_4 = \frac{5.6}{22.47} = 0.25$ mol

No. of moles of $C_2H_4 = \frac{11.2}{22.4} = 0.5$ mol

So, the heat evolved will be

$\Rightarrow$ $0.25(-900) + 0.5(-1400) = -925$ kJ

43. (360)

Energy utilised by the athlete

= 50% of 1800 kJ

$= \frac{50}{100} \times 1800 = 900 \text{ kJ}$

Utilised energy of athlete $= n_{H_2O} \times 45$

$900 = n_{H_2O} \times 45$

$\Rightarrow \quad n_{H_2O} = 20 \text{ mol}$

$W_{H_2O} = 20 \times 18 = 360 \text{ g}$

44. (38)

Given,

$\Delta H^{\circ}_{vapour} = +40.79 \text{ kJ/mol}$

$T = 100°C = 373 K$

Using enthalpy equation,

$\Delta H^{\circ}_{vapour} = \Delta U° + \Delta n_g RT$

$\Delta U° = 40.79 - \frac{8.3 \times 373}{1000}$

$= 37.67 \text{ kJ/mol} \approx 38 \text{ kJ/mol}$

45. (55)

Given, $V_1 = 100 \text{ L}$ and $V_2 = 10 \text{ L}$

Work done is given,

$W = -nRT \ln \frac{V_2}{V_1}$

$= -1 \times 0.08206 \times 291.15 \times 2.303 \log \frac{10}{100}$

$= 55 \text{ L atm}$

Hence, final answer is 55 L atm.

46. (274)

In adiabatic condition, q = 0

Then, equation for change in internal energy will be given by

$\Delta U = q + W \quad (q = 0)$

$nC_V \Delta T = -p_{ext}(V_2 - V_1) \qquad ...(i)$

as $(W = p\Delta V)$

$V_2 = 2V_1 \qquad$ (given)

$\frac{nRT_2}{p_2} = \frac{2nRT_1}{p_1} \qquad ...(ii)$

$p_1 = 5 \text{ atm}, T_1 = 298 \text{ K}$

p_2 from Eq. (ii) will be

$p_2 = \frac{5T_2}{2 \times 298}$

Now from Eq. (i)

(Put $p_{ext} = 1\,atm$)

$$n\frac{5}{2}R\left(T_2 - T_1\right) = -1\left[\frac{nRT_2}{p_2} - \frac{2nRT_1}{p_1}\right]$$

Put, $T_1 = 298$ and $p_2 = \frac{5T_2}{2\times 298}$

$$\frac{5n}{2}R\left[T_2 - 298\right] = nR\left[\frac{T_1}{5} - \frac{T_2}{\left(\frac{5T_2}{2\times 298}\right)}\right] \qquad ...(iii)$$

On solving Eq. (iii)

$T_2 = 274.16\,K$

Hence, nearest integer value of temperature is 274 K.

47. (200)

For isothermal process, $\Delta U = 0$

So, $Q = -W$

$$= -\left[-p_{ext}\left(V_2 - V_1\right)\right]$$

$$Q = 5\left[20 - 60\right]$$

$$= -200\,atm\,L$$

48. (28721)

It is isothermal reversible expansion, so work done in negative.

Work done is given by

$$W = -2.303nRT\log\left(\frac{V_2}{V_1}\right)$$

$$= -2.303\times 5\times 8.314\times 300\log\left(\frac{100}{10}\right)$$

$$= -28720.713\,J$$

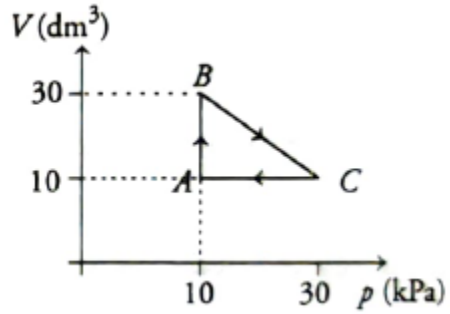
$$\approx -28721\,J$$

Hence, the value of x is 28721.

49. (200)

Work done is given by area enclosed in the p *vs* V cyclic graph.

Sign is +ve fro clockwise cyclic process for V *vs* p graph.



Work done = Area of triangle

$$= \frac{1}{2} \times \text{base} \times \text{height}$$

$$= \frac{1}{2} \times 20 \times 20$$

$$= 200 \text{ J}$$

Hence, work done is 200 J.

50. (1200)

For isothermal expansion at constant pressure, heat is given by

$$Q = -p_{ext}\left(V_2 - V_1\right)$$

$$= -80 \times 1000 \times \left(45 - 30\right) \times 10^{-3}$$

$$= -15 \times 80 = -1200 \text{ J}$$

Negative sign indicates heat is lost.

Hence, among of heat transfer is 1200 J.

51. (400)

Given,

$$\Delta H_{vap} = 30 \text{ kJ/mol}$$

$$\Delta S_{vap} = 75 \text{ J mol}^{-1}\text{K}^{-1}$$

$$T = ?$$

At equilibrium, $\Delta G = 0$

$$\Delta H_{vap} = T\Delta S_{vap}$$

So, $30 \times 1000 = T \times 75$

$T = 400$ K

52. (2000)

From Gibb's free energy equation,

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

For reaction to be spontaneous

$$\Delta G = -\text{ve}$$

For limiting case $\Delta G = 0$

$$\Delta H = T\Delta S$$

$$T = \frac{\Delta H}{\Delta S} = \frac{400 \text{ kJ/mol}}{0.2 \text{ kJ/mol-K}} = 2000 \text{ K}$$

Hence, reaction will become spontaneous above 200 K.

53. (57)

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$= -2.303RT \log K_{eq}$$

$$= -2.303 \times 8.314 \times 300 \times \log 10$$

$$= -5744.14 \text{ J/mol}$$

$$= -5.744 \text{ kJ/mol}$$

$$= -57.44 \times 10^{-1} \text{ kJ/mol}$$

Thus, the value is 57.

54. (37)

Given, T = 400 K

$\Delta H^{\Theta} = 77.2\ \text{kJ/mol}$

$\Delta S = 122\ \text{JK}^{-1}$

Free energy is given by

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

$= 77.2 \times 10^3 - 400 \times 122$

$= 28400\ \text{J}$

$\Delta G^\circ = -2.303\ RT \log K$

$28400 = -2.303 \times 8.314 \times 400 \times \log K$

$\log K = -3.708$

or $\log K = -37.08 \times 10^{-1}$

Hence, the missing value is 37.

55. (2)

According to question

$H^+ + OH^- \longrightarrow H_2O \Rightarrow x$ (for HCl)

$2H^+ + 2OH^- \longrightarrow 2H_2O$

$\Rightarrow \quad 2x = y$ (for H_2SO_4)

$\Rightarrow \quad \frac{y}{x} = 2$

56. (82)

$CuSO_4(s) + H_2O(\ell) \longrightarrow CuSO_4(aq);\ \Delta H = -70\ \text{kJ} \quad \ldots(i)$

$CuSO_4 \cdot 5H_2O(s) + H_2O(\ell) \longrightarrow CuSO_4(aq);\ \Delta H = 12\ \text{kJ} \quad \ldots(ii)$

Subtracting Eqs. (i) and (ii)

$CuSO_4 + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O;\ \Delta H = -70 - 12 = -82\ \text{kJ}$

57. (150)

The complete reaction is as follow,

$C_6H_5COOH(s) + \frac{15}{2}O_2(g) \longrightarrow 7CO_2(g) + 3H_2O(\ell)$

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

$= -321.30 - \frac{1}{2}\frac{R}{100} \times 300$

$= (-321.30 - 150R)\ \text{kJ}$

Matching with equation given in question the value of x is 150.

58. (6535)

Given,

$$6C(\text{graphite}) + 3H_2(g) \longrightarrow C_6H_6(\ell);\ \Delta H = 48.5\ \text{kJ/mol} \quad \ldots(\text{i})$$

$$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -393.5\ \text{kJ/mol} \quad \ldots(\text{ii})$$

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

Eq. $(\text{i}) \times 1 + (\text{ii}) \times 6 + (\text{iii}) \times 3$

$= -48.5 - 6 \times 393.5 - 3 \times 286$

$= -3267.5\ \text{kJ 1 mol}$

$= -6535\ \text{kJ for 2 mol}$

59. (125)

Given, Bond enthalpies of

C–H = 414 kJ; C–C = 347 kJ

H–H = 435 kJ; C=C = 615 kJ

Now, the formation of ethane takes place as follows

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

$$\Delta H = \text{B.E.}(C=C) + 4\text{B.E.}(C-H) + \text{B.E.}(H-H) - \text{B.E.}(C-C) - 6\text{B.E.}(C-H)$$

$$\Delta H = \text{B.E.}(C=C) + \text{B.E.}(H-H) - \text{B.E.}(C-C) - 2\text{B.E.}(C-H)$$

$$\Rightarrow \quad \Delta H = 615 + 435 - 347 - 2(414)$$

$$\Delta H = -125\ \text{kJ}$$

60. (492)

Two given reactions are

$$2Fe(s) + \frac{3}{2}O_2(s) \longrightarrow Fe_2O_3(s);\ \Delta H^\circ = -822\ \text{kJ/mol} \quad \ldots(\text{i})$$

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g);\ \Delta H^\circ = -110\ \text{kJ/mol} \quad \ldots(\text{ii})$$

Multiply Eq. (ii) by 3 and then subtract Eq. (i) from this equation to get the required equation.

$$3C(s) + Fe_2O_3(s) \longrightarrow 2Fe(s) + 3CO(g) \quad \ldots(\text{iii})$$

Then, $\Delta H_3 = 3 \times \Delta H_2 - \Delta H_1$

$= 3(-110) - (-822)$

$= 492\ \text{kJ/mol}$

Hence, enthalpy change is 492 kJ/mol

61. (56)

Given,

$$\Delta H^\circ_{\text{vapour}} CCl_4 = 30.5\ \text{kJ/mol}$$

Mass of $CCl_4 = 284\ \text{g}$

Molar mass of $CCl_4 = 154\ \text{g/mol}$

Moles of $CCl_4 = \frac{284}{154} = 1.844\ \text{mol}$

$\Delta H^{\circ}_{vapour}$ for 1 mole = 30.5 kJ/mole

$\Delta H^{\circ}_{vapour}$ for 1.844 mole

$= 30.5 \times 1.844$

$= 56.242$ kJ

Hence, final answer is 56 kJ (nearest integer).

EXERCISE - 2 [A]

1. (a)

$$\Delta S = nC_V \ell n \frac{T_f}{T_i} + nR\ell_n \frac{V_f}{V_i}$$

$$= 2R\ell n2 = 11.5$$

2. (a)

$$\int \frac{C_P}{T} dT = \int \frac{dQ}{T} = \Delta S$$

3. (c)

Entropy change of universe is always positive

4. (a)

$$w = nRT\ell n \frac{V_f}{V_i}$$

$$= 2.5 \times 8.314 \times 310\, \ell n \frac{\frac{2.5 \times 8.314 \times 310}{58 \times 10^3}}{55 \times 10^{-3}}$$

$$= 44665$$

5. (c)

At $0^\circ C$ ice & water have same G.

6. (d)

(a) In melting $\Delta V > 0 \Rightarrow W < 0$

(b) In melting of ice $\Delta V < 0 \Rightarrow W > 0$

(c) In expansion $\Delta V > 0 \Rightarrow W < 0$

(d) In expansion against vacuum

$W = 0, Q = 0, \Delta U = \Delta H = 0$

7. (a)

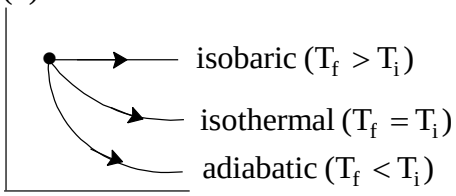
For bath $\Delta S = \frac{Q}{T_{Bath}}$

For glass $\Delta S = \frac{Q}{T_{glass}}$

Since $T_{bath} < T_{glass}$

So, $|\Delta S_{bath}| > |\Delta S_{glass}|$

8. (b)



9. (d)

(1) $\Delta n_g = 0$

(2) $\Delta n_g = -1$

(3) $\Delta n_g = +1$

So, $3 > 1 > 2$

10. (a)

Combustion reaction $\Rightarrow \Delta H = -ve$

$\Delta n_g < 0 \Rightarrow \Delta S = -ve$

11. (c)

At equilibrium

$\Delta G = 0$, So $G_A = G_B$

12. (a)

$\Delta H_R = -74.9$

$\Delta S_R = 186.3 - 5.6 - 2 \times 130.7$

$\Delta G_R = \Delta H_R - T\Delta S_R = -50.8$

13. (d)

$$\Delta G = nRT \ln \frac{P_f}{P_i} = 8.314 \times 293 \ln \frac{1}{2}$$

$$= -1.7 \text{ kJ/mole}$$

14. (c)

Entropy depends on moles.

15. (c)

O_3 has highest C_V

16. (c)

$\Delta U_R = -723 - 8.314 \times 0.3 \times (-1) = -69.8 kJ / mole$

$n_{C_2H_4} = 3.5, n_{HCl} = 3$

So $\Delta U = -69.8 \times 3 kJ = -209.4$

17. (a)

$$w = -600R \ell n \frac{1}{2} - 2R(400 - 300) - 800R \ell n 2 - 2R(300 - 400)$$

$$= -200R \ell n 2 = -100R \ell n 4$$

18. (c)

$-3000 = 1 \times 20 \times (T_f - 300)$

$T_f = 150K$

19. (d)

$$2\times\frac{5}{2}R\times\left(T_f-350\right)=-2\left(\frac{2RT_f}{2}-\frac{2R\times350}{1}\right)$$

$$\Rightarrow\frac{5}{2}T_f-\frac{5}{2}\times350=-T_f+700$$

$$\Rightarrow\frac{7}{2}T_f=\frac{9}{2}\times350\Rightarrow T_f=450K$$

$$w=2\times\frac{5}{2}R\times\left(450-350\right)=500R$$

20. (b)

$$\eta=1-\frac{298}{373}=22.2$$

21. (b)

$$1-\frac{300}{500}=\frac{w}{2}\Rightarrow w=0.8k\,cal$$

22. (c)

$$1-\frac{T_2}{1000}=1-\frac{360}{T_2}$$

$$\Rightarrow T_2=600$$

23. (a)

$$\Delta H=-3+\left(-1\right)\frac{2\times300}{1000}=-3.6\,kcal$$

$$\Delta G=-3.6+\frac{10\times300}{1000}=-0.6\,kcal$$

24. (c)

$$\Delta S=nC_v\ell n\frac{T_f}{T_i}=2\times\frac{3}{2}R\,\ell n\frac{573}{473}$$

25. (d)

At phase equation $\Delta G=0$

26. (c)

$$H_2O\left(\ell,1atm,373K\right)\longrightarrow H_2Olg,1atm,373K$$

$$\Delta G=0$$

$$H_2O(g,1atm\,373K)\longrightarrow H_2O\left(g,2atm,373K\right)$$

$$\Delta G=\int Vdp=nRT\,\ell n\frac{P_f}{P_i}$$

$$=373\,R\ln2$$

27. (d)

$$T_f = \frac{T_H + T_C}{2}$$

$$\Delta S = \int_{T_H}^{T_f} ms\frac{dT}{T} + \int_{T_C}^{T_f} ms\frac{dT}{T}$$

$$= C_v \ell n \frac{T_f}{T_H} + C_v \ell n \frac{T_f}{T_C}$$

$$= C_v \ell n \frac{T_f^{\,2}}{T_H T_C} = C_V \ell n \frac{(T_H + T_C)^2}{4T_H T_C}$$

28. (c)

$S°$ of $H_2 > 0$ at 298 K

29. (a)

$\Delta H > 0, \qquad \Delta S > 0$

$(+\text{ve y intercept})(-\text{ve slope})$

30. (a)

In adiabatic reversible process only

$T^{\gamma}\ P^{1-\gamma} = k$

31. (a)

$$\Delta S = 2090 \ln \frac{273}{200} + \frac{3.34\times10^5}{273} + 4180 \ln \frac{373}{273} + \frac{22.6\times10^5}{373} + 2090 \ln \frac{400}{373}$$

$$= 9390\ \text{J/kg}$$

32. (c)

$RE = 3X_1 - X_2$

33. (b)

$\Delta_f H_{H_2O(g)} = x_2 + x_1 T_1$

So, $\Delta H_{\text{reaction}} = 2x_3 + 3x_2 + 3x_1 T_1 - x_4$

34. (a)

Q is halved and m is also halved.

35. (b)

$$\frac{d}{dT}\left(\frac{\Delta G}{T}\right) = \frac{a}{T^2} + \frac{b}{T} = \frac{-\Delta H}{T^2}$$

$$\Rightarrow \Delta H = -a - bT$$

36. (c)

$$150\times50\times t = \frac{1\times150\times10^3}{293\times0.0821}\times\frac{7}{2}R\times17 \qquad \Rightarrow \quad t = 6.86\ \text{min}$$

37. (a)

$$\Delta E = 2.25\times10^6 - \frac{1000}{18}\times8.314\times373$$

$$= 2.08\times10^6$$

38. (b)

$\Delta U = 1.5nR\Delta T = 3R$

$\Delta U \simeq 25\ J$

$Q = 42\ J$

$\Rightarrow W = -17\ J$

$-17 = -10^5\times8.5\times10^{-4}\times h$

$h = 20\ cm\ .$

39. (c)

$$-2nRT\ln\frac{V}{1} = \frac{1}{2}\left(-nRT\ln\frac{3}{1}\right)$$

$\Rightarrow\ V = \sqrt{3}\,L$

$$h = \frac{\left(\sqrt{3}-1\right)\times1000}{16\pi}$$

$h = 14.5\ cm$

EXERCISE - 2 [B]

One or More Than One Option Correct

1. (c, d)
Volume & Kinetic energy depend on amount of substance.

2. (a, d)
Internal Energy is a state function so it does not depend on path.
It does changes during isothermal change.

3. (b, c, d)
For reversible adiabatic process.
$PV^{\gamma} = k,\ TV^{\gamma-1} = k,\ T^{\gamma}P^{1-\gamma} = k$

4. (a, b)
E is a state function, which depends on T

5. (a, b, d)
For isothermal process, T is constant.
$P_1V_1 = P_2V_2,\ \Delta E = 0,\ \Delta H_1 = H_2$

6. (a, b, c)
$P_i = 2\ bar,\ T_i = 273\,k,\ \ P_f = 4\ bar$

$$\frac{P}{V}=R \Rightarrow \frac{P_i}{V_i}=\frac{P_f}{V_f} \Rightarrow V_f=2V_i$$

$$\Rightarrow T_f=\frac{P_f V_f}{P_i V_i}T_i \Rightarrow T_f=4T_i$$

$$\Rightarrow T_f=4\times 273=1092\,K$$

$$\Delta E=1\times 12.5\times(1092-273)$$

$$=10.24\,kJ$$

$$C_{process}=C_V+\frac{R}{1-(-1)}=12.5+\frac{8.314}{2}=16.657$$

$$Q=1\times 16.657\times(1092-273)=13.64\,kJ$$

$$W=\Delta E-Q$$

$$=-3.4\,kJ$$

7. (a, b, d)

$$2\times\frac{3}{2}R\times(T_f-T_i)=-1\times(10-1)$$

$$T_f-T_i=\frac{-9}{3R} \Rightarrow T_f=T_i-\frac{3}{R}$$

$$\Rightarrow T_f=400-\frac{3}{0.0821}=363\,K$$

$$T_{f,\,rev,\,adiabatic}<T_{f,\,irr.,\,adiabatic}$$

$\Delta S_{sys}=0$ for adiabatic process.

8. (b, c, d)

For ideal gas

$$dE=dQ+dW=dQ-PdV$$

$$dH=dE+PdV+VdP=dQ+VdP$$

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

$$dG=VdP-SdT$$

9. (c, d)

Heat & work done path functions.

10. (a, b, c)

For adiabatic process Q = 0

$$W=\Delta U=nC_V\Delta T=\frac{nR(T_2-T_1)}{\gamma-1}$$

$$W=-Pext(V_f-V_i)$$

$$=-P_{ext}\left(\frac{nRT_f}{P_f}-\frac{nRT_i}{P_i}\right)$$

11. (a, b, c)

$$\Delta H=\Delta U+\Delta(PV)=\Delta U+P\Delta V+V\Delta P+\Delta P\Delta V$$

12. (a, b, c)

At 400K & 1 atm $X(\ell)$ is in equilibrium with $X(g)$

i.e. $\Delta G = 0$

at constant T

$$\Delta G = nRT \ln \frac{P_2}{P_1}$$

If $P_2 > P_1$ then $\Delta G = +ve$

If $P_2 < P_1$, then $\Delta G = -ve$

$$\Delta G = nRT \ln \frac{2}{1} > 0$$

$$\Delta G = nRT \ln \frac{0.1}{1} < 0$$

Correct option a,b,c

13. (a, c, d)

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

$T_2 > T_1$

$\Delta S = +ve$

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

$T_2 > T_1$

$\Delta H_2 > \Delta H_1$

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

$T\Delta S > \Delta H$

$\Delta G < 0$

i.e. process is spontaneous correct option a,c,d

14. (a, b, c, d)

For adiabatic irreversible

$\Delta S_{sys} \neq 0$

For isoentropic process

$\Delta S_{sys} = 0$

$\Delta G_{sys} = \Delta H - T\Delta S < 0$

If ΔH is positive & ΔS is positive at high T.

$dG = VdP - SdT$ is applicable for PV only

$$\Delta S_{system} = -\frac{n\Delta H_{vap}}{T} = -\frac{0.5 \times 40600}{373} = -54.42\, JK^{-1}$$

Comprehension Type

Passage - I

1. (b)

$$W = -nRT \ln \frac{P_i}{P_f}$$

$$W = -P_i V_i \ln \frac{P_i}{P_f}$$

$$W = -2 \times 8 \ln \frac{2}{20} = 36.848 \text{ bar L}$$

2. (c)

$$W = -20\left(\frac{16}{20} - 8\right) = -16 + 160 = 144 \text{ L bar}$$

3. (b)

$$W = -10\left(\frac{16}{10} - 8\right) - 20\left(\frac{16}{20} - \frac{16}{10}\right)$$
$$= -16 + 80 - 16 + 32$$
$$= 80 \text{ L Bar}$$

Passage - II

4. (a)

$$\Delta H_{\text{neutralisation}} = q - 55.84$$
$$-49.86 = q - 55.84$$
$$q = 5.98 \text{kJ / mol}$$

5. (b)

$$Ca(OH)_2 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + 2H_2O$$
$$\Delta H = 2 \times \Delta H_{\text{neutralisation}}$$
$$= 2 \times (-55.84)$$
$$= -111.68 \text{kJ}$$

6. (b)

$$H_2SO_4 + 2NaOH \rightarrow N_2SO_4 + 2H_2O$$
$$V_{H_2SO_4} = V_1$$
$$V_{NaOH} = V_2$$
$$V_1 + V_2 = 100$$

For max temp rise

$$0.05V_1 \times 2 = 0.1V_2$$
$$V_1 = V_2 = 50 \text{ ml}$$

Passage - III

7. (c)

$\Delta G < 0$ for spontaneous $r \times n$

$$\Delta H - T\Delta S < 0$$
$$\Delta S > \frac{\Delta H}{T}$$

$$\Delta S > \frac{15000}{300} = 50 J\,mole^{-1}K^{-1}$$

8. (a)

$$\Delta G = \Delta H - T\Delta S$$
$$\Delta G = -T\Delta S$$
$$\Delta G = -T\left[-n_1 R \ln x_1 - n_2 R \ln x_2\right]$$
$$= 8.314 \times 298\left[4 \ln \frac{4}{5} + 1 \ln \frac{1}{5}\right]$$
$$\Delta G = -6.19\,kJ$$

9. (a)

$$2CoCl_4(aq) + Zn(s) \rightarrow 2CeCl_3(aq) + ZnCl_2(aq)$$
$$E = 0.4108 + 0.003T$$
$$\Delta S = -\frac{\partial(\Delta G)}{\partial T}$$
$$\Delta S = -\frac{\partial(-nFE)}{\partial T}$$
$$\Delta S = nF\frac{\partial E}{\partial T}$$
$$\Delta S = nF \times 0.003$$
$$\Delta S = 2 \times 96500 \times 0.003 = 579\,JK^{-1}$$

Passage - IV

10. (b)
11. (c)
12. (a)
13. (c)

Passage - V

14. (b)
15. (d)
16. (a)

Matching Type

1. (A) – P; (B) – S; (C) – R; (D) - Q

(A) Reversible cooling at constant volume

$\Delta V = 0$

$w = 0$

$T_2 < T_1$

$\Delta U < 0$

$\Delta U = q < 0$ (P)

(B) Reversible isothermal expansion

$\Delta T = 0 \Rightarrow \Delta U = 0$

$V_2 > V_1 \Rightarrow w < 0 \Rightarrow q > 0$ (S)

(C) Adiabatic expansion in vaccum $q = 0$

$q = 0$

$P_{ext} = 0$

$V_2 > V_1$, $w = 0 \Rightarrow \Delta U = 0$ (R)

(D) Reversible melting of sulphur at normal melting points heat required $\Rightarrow q > 0$

$v_2 > v_1 \Rightarrow w < 0$

$\Delta U = q + w$

$q > w$

$\Delta V > 0$

(Q)

2. (A) – PS; (B) – QR; (C) – R; (D) - S

(A) Reversible isothermal expansion

$$W = -nRT \ln \frac{V_2}{V_1} = -2.303 nRT \log \frac{V_2}{V_1}$$ (only for isothermal reversible)

(P, S)

(B) Reversible adiabatic expansion

$PV^{\gamma} =$ constant (only for reversible adiabatic)

$$W = \frac{nR}{\gamma - 1}\left(T_2 - T_1\right)$$

(Q,R)

(C) Irreversible adiabatic expansion

$$W = \Delta U = \frac{nR}{\gamma - 1}\left(T_2 - T_1\right)$$ (R)

(D) Irreversible isothermal compression $\Delta T = 0 \Rightarrow \Delta H = 0$

3. (A) – PS; (B) – R; (C) – Q; (D) - Q

(A) $\left(\Delta G_{sus}\right)_{T,P} = 0$ equilibrium ΔG is useful work & here it is zero.

$\left(P, S\right)$

(B) $\Delta S_{total} > 0$

Spontaneous

(R)

(C) $\Delta S_{total} < 0$

Non-spontaneous

(Q)

(D) $\left(\Delta G_{sus}\right)_{T,P} > 0$ non-spontaneous

(Q)

4. (A) – P; (B) – R, C – QS; (D) – Q

(A) Heating of an ideal gas at constant pressure

$\Delta T \neq 0 \Rightarrow \Delta H = nc_p\Delta T$

(P)

(B) Compression of liquid at constant temperature

$\Delta U \neq nc\Delta T$ $\Delta G = V\Delta P + s\Delta T$

(R)

(C) Reversible process for an ideal gas at constant T

$\Delta T = 0 \Rightarrow \Delta U = nq\Delta T = 0$

$\Delta G = nRT\ln\frac{P_2}{P_1}$

(Q,S)

(D) Adiabatic free expansion of an ideal gas

$w = -p_{ext}\Delta V = 0$

$q = 0$

$\Delta U = 0$

(Q)

5. (A) – Q; (B) – P; (C) – R; (D) – S

(A) $\Delta U = nc_v\Delta T$

$\left(\frac{\partial U}{\partial T}\right)_v = C_v$ for 1 mole

(Q)

(B) $\Delta H = ncp\Delta T$

$\left(\frac{\partial H}{\partial T}\right)_p = C_p$ for 1 mole

(C) $G = VdP - SdT$ at constant p

$\left(\frac{\partial G}{\partial T}\right)_p = -S$

(R)

(D) $\partial G = vdp = sdT$ at constant T

$\left(\frac{\partial G}{\partial p}\right)_T = V$

EXERCISE - 2 [C]

1. $W = -nRT\ell n\frac{V_f}{V_i}$

$= 1\times 8.314\times 298\,\ell n\left(\frac{1}{5}\right) = -3.988\,kJ$

2. $V = 0.5\,\ell t \longrightarrow 4\,\ell t$

T = 298 K

$TV^{\gamma-1} = constant$

$298\times(0.5)^{1/3}=T\times4^{1/3}$

So, $T=149K$

3. $\Delta E=q+W=(-65)+(+20)=-45J$

4. $CaCO_3\rightarrow CaO+CO_2$

$q=\Delta H=177.9kJ$

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

$$\Delta U=177.9-\left(24.4+\frac{16.9}{1000}-\frac{34.2}{1000}\right)\times0.101325=175.4\text{ kJ}$$

5. n=1, 300 K, 10 atm, V_1 $\xrightarrow[\gamma=1.33]{}$ n=1, T, 1 atm, V_2

$q=0$

$\Delta E=W$

$$\Rightarrow-1\times\left(\frac{1\times R\times T}{1}-\frac{1\times R\times300}{10}\right)=1\times3R\times(T-300)$$

$=-(T-30)=3(T-300)$

$=4T=930$

$\Rightarrow T=232.5$

$\Rightarrow\Delta E=W=nC_V\Delta T=1\times3\times8.314\times(232.5-300)$

$\Rightarrow\boxed{W=-1.683kJ}$

6. $TV^{\gamma-1}=k$

$300\,V^{1/3}=T\times(27V)^{1/3}$

$\Rightarrow\boxed{100K=T}$

$\Delta E=W=1\times25.08\times(100-300)=5016$

7. $TV^{\gamma-1}=k$

$298.15\times V^{\gamma-1}=248.44\times(2V)^{\gamma-1}$

$$\frac{298.15}{248.44}=(2)^{\gamma-1}$$

$$\log\left(\frac{298.15}{248.44}\right)=(\gamma-1)\log2$$

$\gamma-1=0.263$

$C_V=31.61$

8. $$W=-1\times\left(\frac{298R}{1}-\frac{298R}{5}\right)=-19.57\text{ L-atm}$$

9. $T_A = \dfrac{1\times 22.4}{0.082} = 273\,K$

$T_B = \dfrac{1\times 44.8}{0.082} = 546\,K$

$T_C = \dfrac{0.5\times 44.8}{0.082} = 273K$

For process $\vec{A}$

$\Delta E = 1\times\dfrac{3}{2}\times R\times 273 = 3.4\text{ kJ}$

$q = \Delta H = 1\times\dfrac{5}{2}\times R\times 273 = 5.67\text{ kJ}$

$W = \Delta E - q = -R\times 273 = -2.27\text{ kJ}$

For process $\vec{B}$

$W = 0$

$q = \Delta E = 1\times\dfrac{3}{2}R\times(-273) = -3.4\text{ kJ}$

For process $\vec{C}$

$\Delta E = \Delta H = 0$

$W = (-q) = -1\times 8.314\times 273\,\ell n\dfrac{22.4}{44.8}$

$= -8.314\times 273\,\ell n\dfrac{1}{2}$

$= +8.314\times 273\times \ell n 2$

$= 1572.9\text{ J}$

10. $q = \Delta H$ (constant pressure process)

$\Rightarrow \Delta H = +1\,kcal$

$\because \Delta H = \Delta E + P\Delta V$

$\Rightarrow \Delta E = 1\,kcal - \dfrac{(1\times 0.3)\times 0.101325}{4.2} = 0.993\,kcal$

11. $\Delta H = 1440\,cal$

$\therefore \Delta H = \Delta E + P\Delta V$

$\therefore \Delta H = \Delta E + 1\times(0.018 - 0.0196)$

$\Rightarrow \Delta E = 1440\,cal - 101.325\times\dfrac{-0.0016\times 1}{4.2}$

$= 1440 + 0.0386\,cal$

≈ 1440

12. $W = -1\times(1.1-1)$

$\Rightarrow -0.1\text{L-atm} = -10.1325\text{ J}$

13. $q = \Delta H = -36.5\,kJ$

$W = \dfrac{-1\times 500cm^2\times 50cm}{1000} = -25\text{ L-atm} = -2.53\text{ kJ}$

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

$\Delta E = -36.5\,kJ - 2.53\,kJ$

$\approx -39.03\,kJ$

14. $-P_{ext}\left(V_f - V_i\right) = nC_V\left(T_f - T_i\right)$

$-1\left(\dfrac{nRT_f}{2} - \dfrac{nRT_i}{5}\right) = n \times \dfrac{5}{2}R\left(T_f - T_i\right)$

$3T_f = 2.7\,T_i$

$T_f = 0.9 \times 300 = 270\,K$

$\Rightarrow \Delta E = W = 2 \times \dfrac{5}{2}R \times (270 - 300) = -1247.1$

$\Delta H = 2 \times \dfrac{7}{2}R \times (270 - 300) = -1745.9J$

15. $P_{ent} = 1atm$

$V_i = \dfrac{5 \times 0.082 \times 300}{4} = 30.75\,L$

$V_f = \dfrac{5 \times 0.082 \times 300}{1} = 123\,L$

$\therefore W = -1 \times (123 - 30.75) \times 101.325\,J$

$W = -9347\,J$

Reversible

$W = -5 \times 8.314 \times 300\,\ell n\left(\dfrac{4}{1}\right)$

$W = -17.288\,kJ$

16. $n = 3$

$T = 200K \xrightarrow[\text{adiabatic}]{\text{reversible}} T = 250K$

$P = 2atm \qquad P$

$V_1 \qquad V_2$

$C_V = 27.5$

$\Rightarrow 2 \times V_1 = 3 \times 0.082 \times 200$

$V_1 = 3 \times 0.082 \times 100$

$V_1 = 0.246 \times 100 = 24.6\,\ell$

$q = 0 \qquad W = \Delta E = nC_V\Delta T = 3 \times 27.5 \times (250 - 200) = 4.125\,kJ$

$\Delta H = 3 \times (27.5 + 8.314) \times 50 = 5.372\,kJ$

$TV^{\gamma - 1} = C$

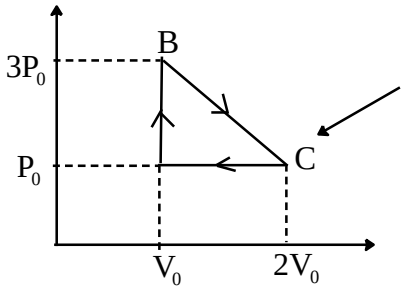
$\gamma = \dfrac{C_P}{C_V} = \dfrac{35.814}{27.5} = 1.3$

$\Rightarrow 200 \times (24.6)^{0.3} = 250 \times (V_2)^{0.3}$

$$\left(\frac{200}{250}\right)^{\frac{10}{3}} \times 24.6 = V_2 \Rightarrow V_2 = 11.7\,L$$

$$P = \frac{3 \times 0.082 \times 250}{11.7} = 5.256\,atm$$

17. (a)



$n = 1$

$$W = \frac{-1}{2} \times V_0 \times 2P_0$$

$$W = -P_0V_0$$

Workdone by the gas $= P_0V_0$

(b) $\overrightarrow{CA}$

$$W = P_0 \times V_0$$

$$\Delta E = 1 \times \frac{3}{2} R \times \left[\frac{P_0V_0}{R} - \frac{2P_0V_0}{R}\right]$$

$$\Delta E = \frac{3}{2} \times -P_0V_0 = -\frac{3}{2}P_0V_0 \qquad \Delta E = q + W$$

$$\Rightarrow q = -\frac{3}{2}P_0V_0 - P_0V_0$$

$$q = -\frac{5}{2}P_0V_0$$

$\overrightarrow{AB}$

$W = 0$

$$\Delta W = 1 \times \frac{3R}{2} \times \left(\frac{3P_0V_0}{R} - \frac{P_0V_0}{R}\right)$$

$$\Delta E = 3P_0V_0$$

(c) $\Delta U_{total} = q_{total} + W_{total}$

$$0 = \left(3P_0V_0 + Q_{BC} - 2.5P_0V_0\right) - P_0V_0$$

$$Q_{BC} = 0.5P_0V_0$$

(d) $$\frac{y - 3P_0}{x - V_0} = \frac{3P_0 - P_0}{V_0 - 2V_0}$$

$$\frac{P - 3P_0}{V - V_0} = \frac{2P_0}{-V_0}$$

$$P = 5P_0 - \frac{2P_0}{V_0}V$$

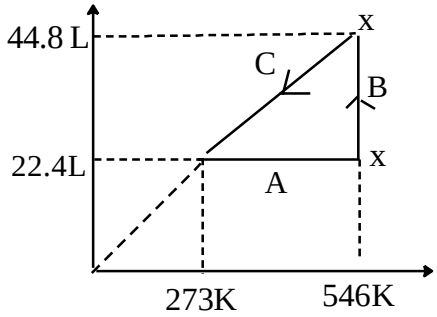
$$T = \frac{5P_0}{R}V - \frac{2P_0}{RV_0}V^2$$

$$\frac{dT}{dV} = \frac{5P_0}{R} - \frac{4P_0}{RV_0}V = 0$$

$$\Rightarrow\ V = \frac{5V_0}{4}$$

$$T_{max} = \frac{5P_0}{R}\left(\frac{5V_0}{4}\right) - \frac{2P_0}{RV_0}\left(\frac{5V_0}{4}\right)^2 = \frac{25}{8}P_0V_0/R$$

18.



$$P_1 = 1\times\frac{0.082\times273}{22.4} = 1\,\text{atm}$$

$$P_2 = 1\times\frac{0.0082\times546}{22.4} = 2\,\text{atm}$$

$$P_3 = 1\times\frac{0.082\times546}{44.8} = 1\,\text{atm}$$

A is isochoric

$W = 0$

$$q = \Delta E = 1\times\frac{3}{2}\times8.314\times(546-273) = 3404.583\text{J}$$

$$\Delta H = 1\times\frac{5}{2}\times8.314\times(546-273)$$

B is isothermal

$\Rightarrow \Delta E = \Delta H = 0$ $\qquad \Delta E = q + W$

$$W = -q = -1\times R\times546\,\text{K}\left(\frac{44.8}{22.4}\right) = -R\ln2\times546$$

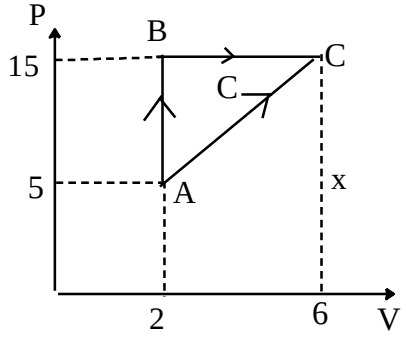
C is isobaric

$$\Delta E = 1\times\frac{3}{2}\times R\times(-273) \qquad \Delta E = q + W$$

$$\Delta H = 1\times\frac{5}{2}\times R\times(-273) \qquad -\frac{3}{2}R273 = -\frac{5}{2}R\times273 + W$$

$$Q = \Delta H = 1\times\frac{5}{2}\times R\times273 \qquad W = R\times273$$

19. Area under the curve AC is less thus W is less for process AC.



(b) $q_{AC} = +200J$

$$W = \frac{1}{2} \times (5+15) \times 4$$

$$= \frac{1}{2} \times 20 \times 4 = 40J$$

$$W = -40J$$

$\because \Delta E = q + W$

$\Rightarrow E_c - E_A = +200 - 40$

$\Rightarrow E_C = 160 + 10 = 170J$

(c) $\omega_{AB} = 0$

$q = \Delta E$

$\Rightarrow q = 10J$

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

$$= -14.2 kcal/mol + \frac{1 \times 2 \times 298}{1000}$$

$$= (-14.2 + 0.6) kcal$$

$$= -13.6 kcal$$

21. $q = nc\Delta T$

$$= \frac{213.5}{18} \times 18 \times 75$$

$$= 16.012 kcal$$

22. $V_1 = 3 dm^3 \longrightarrow 5.0 dm^3$

$P_{net} = 3atm$

$\Rightarrow \omega = -3 \times 2atm \approx -6 \times 100J$

$q = \omega \because q = mc\Delta T (\because C \text{ in } g^{-1})$

$\Rightarrow 6 \times 100 = 180 \times 4.18(\Delta T)$

$0.8 \sim \Delta T$

$\Rightarrow T - 290 = 0.8$

$\Rightarrow T = 290.8K$

23. P is constant

(a) So, $Q = \Delta H = 22.2\ \text{kJ}$

(b) $\Delta H_V = \dfrac{22.2}{10/18} = 39.96\ \text{kJ / mole}$

(c) $W = -\left(n_g\right)RT$

$= -\dfrac{10}{18} \times 8.314 \times 373$

$= -1722.85\ \text{J}$

$= -1.72\ \text{kJ}$

(d) $\Delta E = Q + W$

$= 22.2 - 1.72$

$= 20.48\ \text{kJ}$

24. $0.4 = 1 - \dfrac{T_C}{T_H}$

$0.55 = 1 - \dfrac{T_C - 60}{T_H}$

$0.55 = 1 - \dfrac{T_C}{T_H} + \dfrac{60}{T_H}$

$0.15 = \dfrac{60}{T_H}$

$T_H = \dfrac{60}{0.15} = 400$

$T_C = 240$

25. $\Delta S = \dfrac{\Delta H}{T} \Rightarrow 29.4 = \dfrac{4.60 \times 10^3}{T}$

$\Rightarrow T \approx 156.5\text{K}$

26. $\sum \dfrac{dq_{rev}}{T} = \sum ds$

Since S is a state function cycle integral will be Zero.

27. $28.8 = \dfrac{30.5 \times 10^3}{T}$

$\Rightarrow T = 1059\text{K}$

28. $dS = \int \dfrac{dQ}{T}$

$dS = \int \dfrac{C_p dT}{T}$

$= \int \dfrac{25.5}{T} dT + \int 13.6 \times 10^{-3} dT - \int 42.5 \times 10^{-7} T dT$

$= 25.5\left[\ell nT\right]_{300}^{600} + 13.6 \times 10^{-3}\left(600 - 300\right)$

$$-42.5\times10^{-7}\times\left[\frac{T^2}{2}\right]_{300}^{600}$$

$$=25.5\,\ell n\,2+13.6\times10^{-3}\times300-\frac{42.5\times10^{-7}}{2}\times\left(600^2-360^2\right)$$

$$=17.67+4.08-\frac{42.5}{2}\times10^{-7}\times6^2-3^2\times10^4$$

$$=17.67+4.08-573-75\times10^{-3}$$

$$=21.177\,JK^{-1}mol^{-1}$$

29. $\Delta S=2\times239.7-(152.3+223)$

$=479.4-375.3$

$=104.1\,J/mol^{-1}K$

$\Delta G=29300-298\times104.1$

$=-1721.8$

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

$=-2808\times10^3-310\times182.4$

$=-2864.5kJ$

31. $Na(s)+\frac{1}{2}Cl_2(g)\rightarrow NaCl(s)$

$\Delta S=72-\left[51+\frac{223}{2}\right]=-90.5\,JK^{-1}mol^{-1}$

$\frac{1}{2}N_2-2H_2+\frac{1}{2}Cl_2\longrightarrow NH_4Cl(s)$

$\Delta S=95-\left[\frac{1}{2}\times192+2\times131+\frac{1}{2}\times223\right]$

$=95-(96+262+111.5)$

$=95-419.5$

$=-374.5\,JK^{-1}mol^{-1}$

Graphite $\rightarrow$ Diamond

$\Rightarrow\Delta S=-[5.19-2.43]=-3.26\,JK^{-1}mol^{-1}$

32. $\Delta H=-106.7-(-139.3)=32.6\,kJ/mol$

$\Delta G=32.6\times10^3-298\times94.98$

$=32600-28304$

$=+ve$

33. $CO(g)+\frac{1}{2}O_2(g)\longrightarrow CO_2(g)$

$\Delta H^\circ=-393.5-[-110.5+0]$

$\Delta H^\circ=-283\,kJ/mol$

$$\Delta S^{\circ} = 213.7 - \left[197.6 + \frac{205}{2}\right]$$

$$\Delta S^{\circ} = -86.4\,JK^{-1}mol$$

$$\Delta G^{\circ} = -283000 - 298 \times (-86.4)$$

$$\Delta G^{\circ} = -257.25\,kJ$$

34. $\Delta H = \Delta E + (-1) \times 8.314 \times 298$

$$\Delta H = -10.46 - \frac{2477.5}{1000}$$

$$= -12.9375$$

$$\Delta G = -12.94 \times 10^3 - 298 \times (-43.93)$$

$$= 151J$$

$$= +0.151\,kJ\,mol^{-1}$$

Not feasible.

35. $H_2O + CO \longrightarrow H_2 + CO_2$

(I) $\Delta H = -94.05 - [-57.8 - 26.42] = -9.83\,kcal$

(II) $\Delta G = 0 + (-94.24) - [-54.64 - 32.79]$

$= -6.81 kcal / mol$

(III) $-6.81 \times 10^3 = -9.83 \times 10^3 - 298 \times \Delta S$

$\Rightarrow \Delta S = -10.13\,cal$

(IV) $\Delta H = \Delta E (\because \Delta n = 0)$

$\Delta E = -9.83\,kcal / mol$

(V) $\Delta S = 31.2 + 81.1 - [x + 47.3] = -10.13 \ = +45.13\,cal\,mol^{-1}K^{-1}$

36. $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow HCl \quad \Delta H = -22.1 kcal$

$$\frac{\Delta H_{350} - \Delta H_{300}}{350 - 300} = 1 \times 6.8 - \left[\frac{6.82}{2} + \frac{7.7}{2}\right]$$

$$\frac{\Delta H_{350} - 22.1\,kcal}{50} = \frac{6.8 - 7.26}{1000} = -\frac{0.46}{1000}$$

$$\Delta H_{350} + 22.1\,kcal = -\frac{23}{1000}$$

$$\Rightarrow \Delta H_{350} = -22.123\,kcal$$

37. $1m^3 = 1000\,\ell$

$$\Rightarrow 1000\ell = \frac{1000}{22.7}\,mole$$

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

$$\Delta H = -2 \times 241.6 - 398.8 - (-76.2)$$

$$= -805.8\,kJ / mol$$

$\therefore$ Heat evolved $= \dfrac{1000}{22.7} \times 805.8 \text{ kJ / mol}$

$= 35.498 \text{ MJ}$

38. $C_2H_6 + \dfrac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$

$\Delta H = -\dfrac{3120}{2}$

$\Rightarrow -\dfrac{3120}{2} = \left[2 \times -395 + 3 \times -286\right] - \Delta H_f^{\circ}\left(C_2H_6\right)$

$\Delta H_f^{\circ}\left(C_2H_6\right) = -\left(790 + 858\right) + \dfrac{3120}{2}$

$= -1648 + 1560$

$= -88 \text{ kJ / mol}$

39. $C(s) + 2S(\text{standard}) \longrightarrow CS_2$

$\Rightarrow \Delta H_f = +108.76 + \left[-393.3 + 2 \times -293.72\right]$

$= +1108.76 - \left[393.3 + 2 \times 293.72\right]$

$= +128.02 \text{ kJ}$

40. $HgO(s) \longrightarrow Hg(s) + \dfrac{1}{2}O_2(g)$

$\Delta H_R = 0 - \left(-90.8 \text{ kJ mol}^{-1}\right)$

$= +90.8 \text{ kJ / mol}$

$1 \text{mole HgO} \longrightarrow 90.8 \text{ kJ}$

$n_{Hg} = \dfrac{41.84}{90.8} = 0.461$

$m_{Hg} = 0.465 \times 200.6 = 92.44$

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

$90.8 = \Delta E + \dfrac{1}{2} \times \dfrac{8.314 \times 298}{1000}$

$90.8 \text{ kJ} = \Delta E + 1.24 \text{kJ}$

$89.56 \text{kJ} = \Delta E \qquad \Rightarrow 89.56 \text{kJ} \longrightarrow 1 \text{mole Hg}$

$n_{Hg} = \dfrac{41.84}{89.56} = 0.4672$

$m_{Hg} = 0.4672 \times 200.6 = 93.72$

41. $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6$

$\Rightarrow \Delta H = -1410.8 - 285.9 + 1558.8$

$\Delta H = -136.9 \text{kJ}$

42. 14kg of butane

1 mole butane $\longrightarrow 2658 \text{kJ}$ heat

$1\,\text{day} \longrightarrow 20\times10^{6}\,\text{J}$

$26\,\text{day} \longrightarrow 26\times2\times10^{7}\,\text{J} = 52\times10^{7}\,\text{J}$

$520,000\,\text{kJ}$

$\Rightarrow 58\text{g} \longrightarrow 2658\,\text{kJ}$

$14000\text{g} \longrightarrow \dfrac{2658}{58}\times14000\,\text{kJ}$

$641,586.2\,\text{kJ}$

$\Delta = 121586$

$= \% = \dfrac{121586}{641586}\times100$

$=18.95\%$

43. $NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(\ell)$

$\Rightarrow \Delta H_{\text{reaction}} = 81.46 + 2(-285.78) - (-367.5)$

$= -122.6\,\text{kJ}$

$\Delta E = -122.6 - 1\times\dfrac{8.314}{1000}\times298 = -125.08\ \text{kJ}$

44. $\Delta H = -337 - 68.4 - (-373)$

$= -32.4\ \text{kcal}$

45. $C + H_2O \rightarrow H_2 + CO$

$\Delta H_R = -110.53 - (-241.70)$

$= 131.17\ \text{kJ/mol}$

So, total heat required $= 131.17\times\dfrac{100}{12}$

$C + O_2 \rightarrow CO_2$

$\Delta H_R = -393.51\,\text{kJ / mole}$

$131.17\times\dfrac{100}{12} = 393.51\times\dfrac{x}{12}$

$\Rightarrow\ x = \dfrac{100}{3} = 33.33\,\text{g}$

46. $C_6H_{12}O_6(g) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$

$\Delta n_g = 6$

$\Delta U = -651000 - 6\times2\times290$

$= 654,480$

47. $n_{CH_4} = \dfrac{89.03}{890.3} = \dfrac{1}{10} \Rightarrow W_{CH_4} = 1.6\,\text{g}$

$n_{CO_2} = \dfrac{89.03}{890.3} = \dfrac{1}{10} \Rightarrow W_{CO_2} = 4.4\,\text{g}$

48. $C_6H_5COOH(\ell)+\frac{15}{2}O_2(g)\rightarrow 7CO_2(g)+3H_2O(\ell)$

$\Delta U_R=-\frac{23.85\times 0.55}{\frac{0.5}{122}}=-3200.67$

$\Delta H_R=-3200.67+\left(-\frac{1}{2}\times\frac{8.314}{1000}\times 288\right)=-3201.87$

49. $\frac{120}{180}\times 2880\times\frac{1}{4}=100\times x$

$x=4.8$

50. $\Delta_R C_P=2\times 4R-\frac{7}{2}R-3\times\frac{7}{2}R=-6R$

$\Delta H_{323\,K}=\Delta H_{300\,K}+\int_{300}^{323}-6R\,dT$

$=-91.94-\frac{6\times 8.31\times 23}{1000}=-93.09$

51. $\Delta_R C_P=\left(\frac{8}{5}\alpha+4\beta T\right)-3\times(\alpha+\beta T)=-\frac{7}{5}\alpha+\beta T$

$\Delta H_{600\,K}=\Delta H_{300\,K}+\frac{1}{1000}\int_{300}^{600}\left(-\frac{7}{5}\alpha+\beta T\right)dT$

$=-100-\frac{7}{5}\alpha\times\frac{300}{1000}+\frac{\beta}{2000}\left(600^2-300^2\right)$

$=-100-0.42\alpha+135\beta$

52. $\Delta H_{C,\,Propene}=3\times(-393.5-285.8)-20.42=-2058.32$

$\Delta H_{C,\,Cyclopropene}=-2058.32-33=-2091.32$

53. (1) + (2) – (3)

$\Delta H_f=-48-68.4+14=-102.4$

54. $\Delta_R C_P=\left(7.3+\frac{3}{100}T\right)-\left(7.3+\frac{2}{100}T\right)=\frac{T}{100}$

$\Delta H_{1000\,K}=\Delta H_{300K}+\frac{1}{1000}\int_{300}^{1000}\frac{T}{100}\times dT$

$=-41.8+\frac{1}{1000}\times\frac{1000^2-300^2}{200}=-37.25\text{ kJ}$

55. $-105=20.5+96+28.75+x-159.5$

$x=-90.75$ kcal/mole

56. Delong and petit law

$0.0276 \times \text{At.wt} \approx 6.4$

$\Rightarrow \text{At.wt} \approx 232$

$$\frac{\frac{79.34}{232}}{x} = \frac{114.79 - 79.34}{35.5} \Rightarrow x = 2.92$$

So, exact value of x is 3.

$$\frac{\frac{79.34}{\text{AW}}}{3} = \frac{114.79 - 79.34}{35.5} \Rightarrow \text{AW} = 238.36$$

57. $C_2H_2 + \frac{5}{2}O_2 \rightarrow 2CO_2 + H_2O$

$\Delta H = -312 = 2 \times (-94.38) + (-68.38) - \Delta H_{f, C_2H_2}$

$\Delta H_{f, C_2H_2} = 54.86$

$2C + H_2 \rightarrow C_2H_2$

$\Delta H = 54.86 = 2 \times 150 + 2 \times 51.5 - 2 \times 93.6 - BE_{C \equiv C}$

$BE_{C \equiv C} = 160.94$

58. $CuSO_4 + 5H_2O \longrightarrow CuSO_4.5H_2O$

$\Delta H = -15.9 - 2.8 = -18.7$

59. $HAuBr_4 + 4HCl \rightarrow HAuCl_4 + 4HBr$

$\Delta H_R = 36.8 - 28 = 8.8 \text{ kcal/mole}$

$n_{HAuBr_4} = \frac{0.44}{8.8} = \frac{1}{20}$

% conversion = $\frac{1}{20} \times 100 = 5\%$

60. (i) – (ii)

1-Butene $\rightarrow$ trans-2-butene

$\Delta H = \Delta H_1 - \Delta H_2 = -649.8 + 647 = -2.8$

So, $\Delta H_1 = -1, \Delta H_2 = 1.8$

61. $\Delta H_R = (35.5 + 3 \times 414 + 351.5 + 464.5) + \left(\frac{3}{2} \times 494\right) - (2 \times 711 + 143) - (2 \times 40.6 + 4 \times 464.5)$

$= -669.7 \text{ kJ}$

Only One Option Correct

1. (b)

2. (a)

3. (c)

4. (b)

5. (c)

6. (a)

7. (d)

8. (d)

9. (a)

10. (b)

11. (a)

12. (c)
The standard enthalpy of the combustion of glucose can be calculated by the equation
$C_6H_{12}O_6(s)+6O_2(g)\rightarrow 6CO_2(g)+6H_2O(l)$
$\Delta H_C = 6\times\Delta H_f(CO_2)+6\times\Delta H_f(H_2O)-\Delta H_f(C_6H_{12}O_6)$
$\Delta H^\circ = 6(-400)+6(-300)-(-1300) = -2900 kJ/mol$
For one gram of glucose, enthalpy of combustion
$\Delta H^\circ = -\frac{2900}{180} = -16.11 kJ/g$

13. (b)
Given conditions are boiling conditions for water due to which system is in equilibrium .
$H_2O(l)\rightleftharpoons H_2O(g)$
$\Delta S_{total} = 0$
$\Delta S_{system}+\Delta S_{surroudings} = 0$
$\Delta S_{system} = -\Delta S_{surroundings}$
For process , $\Delta S_{system} > 0$
$\Delta S_{surroundings} < 0$

14. (c)
From 1st law of thermodynamics
$q_{sys} = \Delta U - w = 0-[-P_{ext}\Delta V]$
$= 3.0at\times(2.0L-1.0L) = 3.0L-atm$

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

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

15. (a)

$C(\text{graphite}) \rightarrow C(\text{diamond})$ (Isothermally)

$$\Delta_r G^\circ = \Delta G^\circ(\text{diamond}) - \Delta G^\circ(\text{graphite})$$

$$-2.9 \times 10^3 = -\Delta P \times 2 \times 10^{-6}$$

$$\Delta P = \frac{2.9 \times 10^3}{2 \times 10^{-6}} = 1.45 \times 10^9 \text{ Pa} = 1.45 \times 10^9 \times 10^{-5} \text{ bar}$$

$$= 1.45 \times 10^4 \text{ bar} = 14500 \text{ bar}$$

$$P = \Delta P + P_0 = 14500 + 1 = 14501 \text{ bar}$$

One or More than One Option Correct

1. (a, c, d ***or*** a, d)

2. (a, c)

3. (a, b, c)

Since the vessel is thermally insulated, $q = 0$

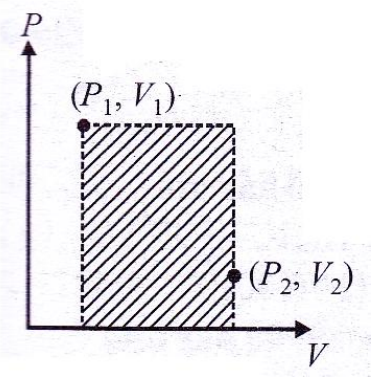
Further since, $P_{ext} = 0$, so $w = 0$, hence $\Delta U = 0$

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

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

4. (a, b, c)

(a)



During irreversible compression, , maximum work is done on the gas (corresponding to shaded area) when $P_1 = P_2$

(d) When $T_1 = T_2 \Rightarrow \Delta U = nC_V\Delta T = 0$

In reversible adiabatic expansion , $T_2 < T_1$

$\therefore \Delta T = -ve$ and also $\Delta U = -ve$

(B) In face expansion , $P_{ext} = 0, \therefore W = 0$

From 1st law of thermodynamics,

$\Delta U = q + W$

$\therefore \Delta U = q$

If expansion is carried out isothermally, $\Delta U = 0$

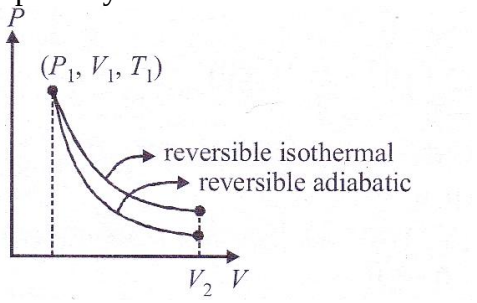
Hence $q = 0$

$\therefore$ It is adiabatic process.

If carried out adiabatically $(q = 0) \therefore \Delta U = 0$

$\therefore$ It is an isothermal process

(c) During adiabatic expansion, the final temperature is less than the initial temperature. Therefore ,the final volume in adiabatic expansion will also be less than the final volume in isothermal expansion. This can be graphically shown as:



The magnitude of work done by the gas is equal to the area under the curve. As seen from the figure, the area under curve in reversible isothermal is more. Hence, the magnitude of work done is lesser in adiabatic reversible expansion as compared to the corresponding work in isothermal expansion.

5. (b, c)

$A - C \Rightarrow$ isochoric process

$A - B \Rightarrow$ isothermal process

$B - C \Rightarrow$ isobaric process

(a) $q_{AC} = \Delta U_{AC} = nC_{V,m}(T_2 - T_1) = \Delta U_{BC}$

$W_{AB} = -nRT\ln\left(\frac{V_2}{V_1}\right)$ (pressure is not constant)

(b) $W_{BC} = -P_2(V_1 - V_2) = P_2(V_2 - V_1)$

$q_{BC} = \Delta H_{BC} = nC_{p,m}(T_2 - T_1) = \Delta H_{AC}$

(c) $\Delta H_{CA} = nC_{P,m}(T_1 - T_2)$

(d) $\Delta U_{CA} = nC_{V,m}(T_1 - T_2)$

$\Delta H_{CA} < \Delta U_{CA}$ since both are negative $(T_1 < T_2)$ and $C_{p,m} > C_{V,m}$

6. (a, c)

Enthalpy of formation is the enthalpy change for formation of 1 mole of substance from its elements present in the most stale natural form.

7. (a, b, c)

P-V work done is applicable for reversible isobaric as well as isothermal and adiabatic process.

$w = -\int P_{ext}.dV$

For van der Waals equation

$P_{ext} = P = \left(\frac{RT}{\nu - b} - \frac{a}{\nu^2}\right)$

$w = -\int d\nu\left(\frac{RT}{\nu - b} - \frac{a}{\nu^2}\right)$ ……(i)

Equation (i) is not applicable to irreversible process. Therefore work don is calculated assuming pressure is constant throughout the process.

8. (a, b, d)

From state I to II(Reversible isothermal expansion):

$T \to \text{constant},\ \Delta V \to +\text{ve}, \Delta S \to +\text{ve}, \Delta H \to 0$

$\Delta P \to -\text{ve}$

From state II to III (Reversible adiabatic expansion):

$q \to 0, \Delta V \to +\text{ve}, \Delta S \to \text{ constant}$

$\Delta H \to -\text{ve}, \Delta P \to -\text{ve}, \Delta T \to -\text{ve}$

$\therefore$ Plots (a), (b), (d) are correct while (c) is wrong as from state II to III, H is decreasing.

Paragraph Type

Passage - I

1. (c)

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

Hence, T increases (Heating)

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

Hence, T decreases (Cooling),

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

Hence, T decreases(Cooling),

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

Hence, T increases (Heating)

2. (b)

L to M and N to K, both are having constant volume therefore, these processes are isochoric.

Numerical Value Answer

1. (935.00)

$$SnO_2(s) + C(s) \longrightarrow Sn(s) + CO_2(g)$$

$$\Delta_f H^\circ = [-394] - [-581] = 187\,\text{kJ/mole} = 187 \times 10^3\,\text{J/mol}$$

$$\Delta_f S^\circ = [52 + 210] - [56 + 6] = 200\,\text{JK}^{-1}\text{mol}^{-1}$$

$$T = \frac{\Delta_f H^\circ}{\Delta_f S^\circ} = \frac{187 \times 10^3}{200} = 935\,\text{K}$$

2. (10)

Process $(I) \Rightarrow$ (Adiabatic reversible)

$$\frac{\Delta U}{R} = 450 - 2250$$

$$\Delta U = -1800R$$

$$W_1 = \Delta U = -1800R$$

Process(II) $\Rightarrow$ (Reversible isothermal process)

$T_1 = 900K$

Calculation of T_2 after reversible adiabatic process

$$\Delta U = nC_v dT$$

$$\Rightarrow -1800R = 1\frac{5}{2}R(T_2 - 900)$$

$$T_2 = 180K$$

$$W_{II} = -nRT_2 \ln \frac{V_3}{V_2} = W_I$$

$$\Rightarrow -1 \times R \times 180 \ln \frac{V_3}{V_2} = -1800R$$

$$\Rightarrow \ln \frac{V_3}{V_2} = 10$$

3. (166.28)

$$\text{Slope} = \frac{dy}{dx} = \frac{d(\ln K)}{d(10^4 / T)}$$

$$\Rightarrow \frac{-\Delta H\phi}{10^4 R} = \frac{-7-(-3)}{12-10}$$

$$\Rightarrow \Delta H^{\phi} = 2 \times 10^4 \times = 2 \times 10^4 \times 8.314 J/mol$$

$$= 166.28 kJ/mol$$

4. (141.34)

From the plot when, $\frac{10^4}{T} = 10 \ [T = 1000K]$

$$\ln\left(\frac{p_2}{1}\right) = -3$$

$$\Delta G^{\circ} = -RT \ln K \Rightarrow \Delta H^{\phi} - T\Delta S^{\phi} = -RT \ln \frac{p_z}{p^{\phi}}$$

Substituting in following equation:

$$\ln\left(\frac{p_z}{1}\right) = -\frac{\Delta H^{\phi}}{RT} + \frac{\Delta S^{\phi}}{R}$$

We get , $-3 = -\frac{2 \times 10^4 \times R}{R \times 1000} + \frac{\Delta S^{\phi}}{R}$

$$\Rightarrow S^{\phi} = 17R \Rightarrow \Delta S^{\phi} = 17 \times 8.314 J/K - mol$$

$$\Rightarrow \Delta S^{\phi} = 141.34 J/K - mol$$

5. (90.39)

$$2Hg(g) + O_2(g) \rightarrow 2HgO(s)$$

$$\Delta_r H^{\circ} = 2\Delta_f H^{\circ}(HgO, s) - 2\Delta_f H^{\circ}(Hg, g) - \Delta_f H^{\circ}(O_2, g)$$

$$= 2\Delta_f H^{\circ}(HgO, s) - 2\Delta_f H^{\circ}(Hg, g) \qquad \text{.....(i)}$$

$$\left[\because \Delta_f H^{\circ}(O_2, g) = 0\right]$$

Now, $\Delta_r H^{\circ}$ is the heat evolved by bomb calorimeter due to the occurrence of the reaction at constant volume.

$$\therefore -(Q_v)_r = \Delta_r U$$

$$\therefore \Delta_r H = \Delta_r U + \Delta n_g R = -C\Delta T + \Delta n_g RT$$

[Where C – the heat capacity of calorimeter $= 20 kJ/K$ at $298K$]

$$= -\left[20(312.8 - 298)\right] - 3RT$$

$= -296 - 3 \times 8.3 \times 10^{-3} \times 298 \text{kJ} = -303.42 \text{kJ}$

Hence, from equation (i)

$-303.42 = 2\Delta_f H^\circ (\text{HgO}, \text{s}) - 2 \times 61.32$

Or, $2\Delta_f H^\circ (\text{HgO}, \text{s}) = -180.78 \text{kJ}$

$\therefore$ Standard Molar Enthalpy of formation of HgO

$= \dfrac{-180.78}{2} = -90.39 \text{kJ}$

$\Rightarrow |\text{X}| = 90.39$

6. (0.31)

S_T and S_0 are entropies of the phases at temperatures T and 0 K, respectively.

$$S = S_0 + \int C_p \frac{dT}{T} \qquad [S_0 = 0 \text{ at } 0\,\text{K}]$$

$$\Rightarrow \quad S_\alpha = S_0 + \int (C_p)_\alpha \frac{dT}{T}$$

$$\Rightarrow \quad S_\beta = S_0 + \int (C_p)_\beta \frac{dT}{T}$$

$$\Rightarrow \quad S_\beta - S_\alpha = \left[(C_p)_\beta - (C_p)_\alpha \right] \int \frac{dT}{T}$$

Given, $C_{p_\beta} - C_{p_\alpha} = 1$

$S_\beta - S_\alpha = \ln T + C$ at any temperature T.

$$\Rightarrow \quad (S_\beta - S_\alpha)_{T_2} - (S_\beta - S_\alpha)_{T_1} = \ln T_2 - \ln T_1$$

$T_2 = 600$ K, $T_1 = 300$ K, from the graph $S_\beta - S_\alpha$ at 600°C = 1

$(1) - (S_\beta - S_\alpha)_{300} = \ln 600 - \ln 300$

$1 - (S_\beta - S_\alpha)_{300} = \ln 2 = 0.69$

$\Rightarrow (S_\beta - S_\alpha)_{300} = 1 - 0.69$

$= 031 \text{ J mol}^{-1}\text{K}^{-1}$

7. (300)

Change in Gibbs free energy transition from α to β phase = 0

Thus, $\Delta H = T\Delta S$

$\Delta H \text{ (at 600 K)} = 600 \times 1 \qquad [\because \Delta S = 1]$

$= 600 \text{ J mol}^{-1}$

According to Kirchhoff's law,

$$\Delta H_f - \Delta H_i = C_p (T_f - T_i) \qquad \ldots(\text{i})$$

Using the Eq. (i),

$\Delta H_{600} - \Delta H_{300} = 1 \times (C_{p,\beta} - C_{p,\alpha})(600 - 300)$

$600 - \Delta H_{300} = 1 \times 1 \times 300$

$\Delta H_{300} = 600 - 300$

$= 300 \text{ J mol}^{-1}$

8. (7)

$A \rightarrow B$ (reversible adiabatic)

$\therefore \quad T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$T_1 = 600,\ V_1 = 10,\ T_2 = 60,\ \gamma = \frac{5}{3}\left(\text{from } C_{p,\,m} = \frac{5}{2}R\right)$

$\therefore \quad (600)(10)^{2/3} = (60)(V_2)^{2/3}$

$(V_2)^{\frac{2}{3}} = (10)^{\frac{5}{3}}$

$\Rightarrow \quad V_2 = (10)^{\frac{5}{2}}$

Also, $q_{AB} = 0$ and $q_{AC} = RT_2 \ln 10$

$\therefore \quad q_{BC} = nRT_2 \ln\left(\frac{V_3}{V_2}\right)$

$= RT_2 \ln\left(\frac{V_3}{V_2}\right) \qquad (\because n = 1)$

$\Rightarrow \quad q_{AC} = q_{BC}$

$\therefore$ Total heat absorbed

$= RT_2 \ln\left(\frac{V_3}{V_2}\right) = RT_2 \ln 10$

$\Rightarrow \quad \ln\left(\frac{V_3}{V_2}\right) = \ln 10$

$V_3 = 10V_2$

$V_3 = 10(10)^{5/2} = (10)^{7/2}$

Now, the value of

$2\log V_3 = 2\log(10)^{7/2}$

$= 2 \times \frac{7}{2}\log 10 = 7$

9. (8120)

Given,

$n = 5$ mol

$C_{V,\,m} = 12\ JK^{-1}mol^{-1}$

$R = 8.3\ JK^{-1}mol^{-1}$

$T_2 = 415\ K$

$T_1 = 335\ K$

$V_2 = 20\ L$

$V_1 = 10\ L$

Now, from the graph it is clear that $X \rightarrow Y$ is an isothermal process ($dT = 0$)

So, $\Delta H_{X \rightarrow Y} = nC_p dT = 0$

Also, $Y \rightarrow Z$ is an isochoric process

$\Delta U_{Y \rightarrow Z} = nC_V dT$

$\Delta U_{Y \rightarrow Z} = 5 \times 12 \times (415 - 335)$

$\Delta U_{Y \rightarrow Z} = 4800\ J$

$$\Delta H_{Y\to Z} = \Delta U_{Y\to Z} + \Delta(pV)$$

or $\Delta H_{Y\to Z} = \Delta U_{Y\to Z} + nR\Delta T$

$$\Delta H_{Y\to Z} = 4800 + (5\times 8.3\times 80)$$

$$\Delta H_{Y\to Z} = 8120\ J$$

Matrix-Match

1. (A) – P, R, S ; (B) – R, S ; (C) – T ; (D) – P, Q, T

(A) $CO_2(s)\to CO_2(g)$

It is phase transition. The process is endothermic (sublimation). Gas is produced, so entropy increases.

(B) On heating $CaCO_2$ deposes. So, process is endothermic.

The energy increases as gaseous product is formed.

(C) $2H\bullet\to H_2(g)$

Entropy decrease as number of gaseous particle decreases.

(D) The transition between different allotropes is considered as phase transition.

White and red P are allotropes.

Due to polymeric nature of red P, its entropy is less than that of white P.

Red P is more stable than white.

So, ΔH is $-ve$

2. (A) – R, T ; (B) – P, Q, S ; (C) – P, Q, S ; (D) – P, Q, S, T

(A) – R, T

$H_2O(l)\rightleftharpoons H_2O(s)$

It is at equilibrium at 273 K and 1 atm

So, ΔS_{sys} is negative.

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

(B) – P, Q, S

Expansion of 1 mole of an ideal in vacuum under isolated condition

Hence, $w = 0$

And $q_p = C_p dT(\because dT = 0)$

$\Rightarrow q = 0$

$\Delta U = C_v dT(\because dT = 0)\ \Delta U = 0$

(C) – P, Q, S

Mixing of two ideal gasses at constant temperature

Hence , $\Delta T == 0$

$\therefore q = 0; \Delta U = 0$

Also $w = 0(\Delta U = q + w)$

(D) – P, Q, S, T

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

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

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

Subjective

1. $\Delta H = -114.52$ J

2. $\Delta H^\circ = -285.4$ kJ/mol, $\Delta G^\circ = -257.2$ kJ/mol

3. (ii) $-W = q = 620.77$ J, (iii) $\Delta H = 0$, $\Delta U = 0$, $\Delta S = 0$

4. $\Delta U = 0.1$ litre atm, $\Delta H = 9.9$ litre atm

5. –557kJ/mol