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)

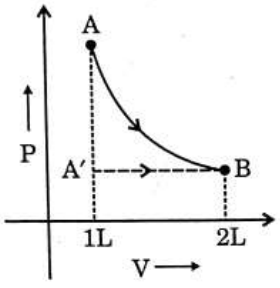
$T_1\,V_1^{\gamma-1} = T_2\,V_2^{\gamma-1};\ \gamma = \frac{5}{3};\ T_1 = 300\,\text{K},\ V_1 = 8\,\text{L}, T_2 = 250\,\text{K}$

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

14. (b)

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

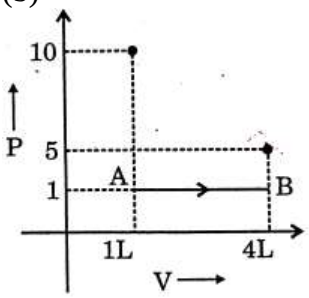
15. (b)



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 $w_3 = -3(16.4 - 8.48)$

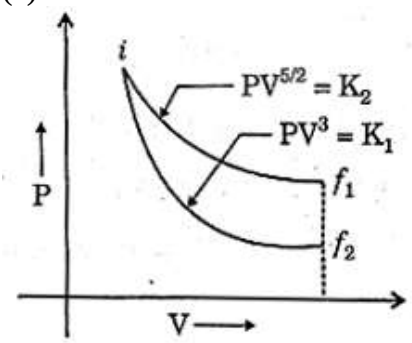
$= -23.76\,\text{L.atm}$

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

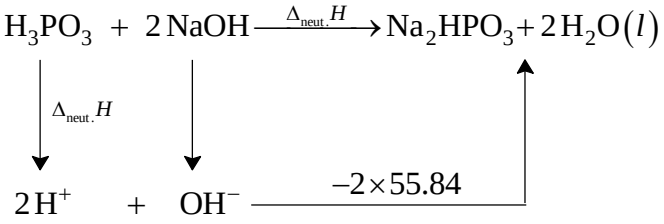
$$\frac{(10+x)}{\left[(20-x)+(20-x)+x+(10+x)\right]}\times100=50$$
$\Rightarrow\ x=15$
$\Delta H=10\times200-15\times20=1700\text{ kJ}$

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)

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

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

$\Delta_f H^\circ$ = [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)

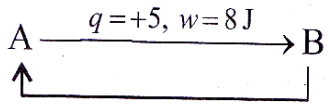
$2H_2O_2 \rightleftharpoons 2H_2O(l) + O_2(g)$

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

$\because 100$ 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)

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

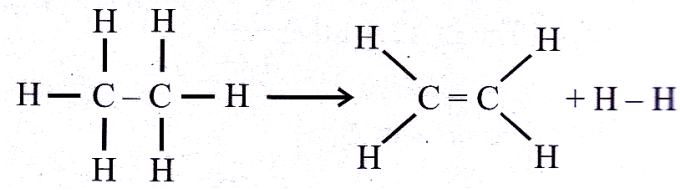
$\Rightarrow -436.7 = 89.2 + 419 + \frac{1}{2}(243.0) + \{-348.6\} + \Delta_{lattice} H^\circ_{(KCl)}$

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

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,

$\Delta G° = \Delta H° - T\Delta S°$

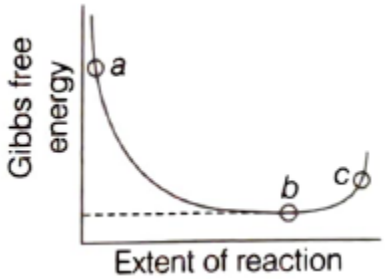
or $-2.303RT\log K = -54070 - 298\times 10$

$-5705\times kigK = -57050$

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

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

$\Rightarrow$ $\Delta H_r^\circ = -400$ kJ mol

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

$x = 800$ 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, $T\Delta S = -1411$ 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)

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

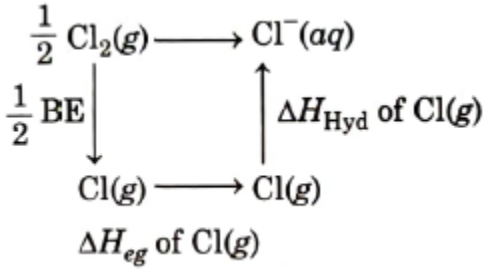
$$\Delta H_r = (\Delta H_f CO_2 + 4\Delta H_f HCl) - (\Delta H_f CCl_4 + 2\Delta H_f H_2O)$$

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

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

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

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

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

$$= -28720.713\,J$$

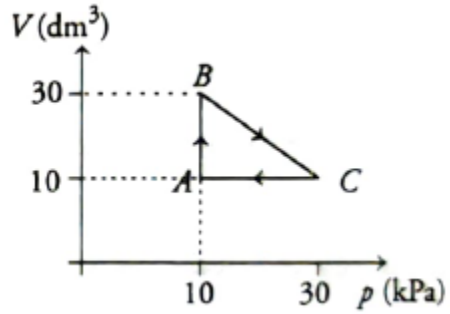
$$\approx -28721\,J$$

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).