

EXERCISE - 1 [A]

- (a)
Isochoric process is constant volume process
- (b)
When ice and water are in equilibrium $\Delta T = 0$. So molar heat capacity is ∞ .
- (c)
 $w = -2.303 nRT \log \frac{V_2}{V_1}$ (for isothermal process)
So $w_{\text{by gas}} = 2.303 nRT \ln \frac{V_1}{V_2}$
- (b)
 $w = nC_v(T_2 - T_1)$ (for adiabatic process)
So $w_{\text{by gas}} = \frac{nR(T_1 - T_2)}{\gamma - 1}$
- (A)
For expansion against vacuum $p_{\text{ext}} = 0$
 $\Rightarrow w = -p_{\text{ext}}(V_f - V_i) = 0$
- (b)
 $W = -2 \times (3.4) = -6.8 \text{ L atm} = -689 \text{ J}$
 $Q = +400 \text{ J}$
 $\Delta U = Q + W = -289 \text{ J}$
- (c)
 $T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$
 $(4T_i) \left(\frac{V_i}{32} \right)^{\gamma-1} = T_i V_i^{\gamma-1}$
 $4 = 32^{\gamma-1}$
 $2^2 = 2^{5(\gamma-1)}$
 $\gamma - 1 = \frac{2}{5} \Rightarrow \gamma = \frac{7}{5} \Rightarrow \text{diatomic}$
- (a)
For irreversible adiabatic process
 $nC_v(T_f - T_i) = -P_{\text{ext}}(V_f - V_i)$
 $\frac{P_f V_f - P_i V_i}{\gamma - 1} = -P_{\text{ext}}(V_f - V_i)$

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

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

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

$$T_f = \frac{1 \times 64}{10 \times 10} \times 273 = 174.72K$$

9. (d)

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

$$T = kV^{1-\gamma}$$

$$\ln T = \ln k + (1-\gamma)\ln V$$

10. (b)

$Q=0$, $W=-ve$ (Since expansion)

So $\Delta U = -ve$

11. (a)

$$W_1 = +15J \quad \Delta U_1 = +30J$$

So $Q_1 = +15J$

$$W_2 = 0 ; \Delta U_2 = -20J$$

So $Q_2 = -20J$

12. (a)

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

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

13. (a)

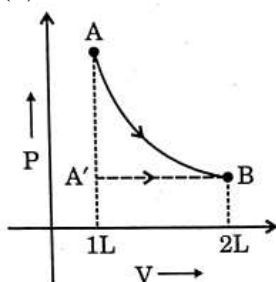
$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}; \gamma = \frac{5}{3}; T_1 = 300K, V_1 = 8L, T_2 = 250K$$

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

14. (b)

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

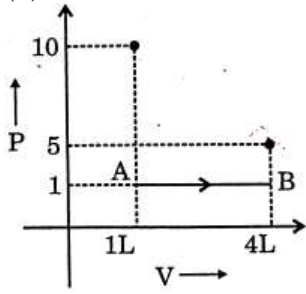
15. (b)



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

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

16. (b)



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

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

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

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

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

$$= 14700 + (20 - 10) \times 100 = 15700 \text{ J}$$

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)

$$T_1 = 600 \text{ K}$$

$$P_1 = 3 \text{ atm}$$

$$V_1 = 200 \text{ R}$$

$$T_2 = 200 \text{ K}$$

$$P_2 = 1 \text{ atm}$$

$$V_2 = 200 \text{ R}$$

Ischoric \rightarrow

$$T_2 = 200 \text{ K}$$

$$P_2 = 1 \text{ atm}$$

$$V_2 = 200 \text{ R}$$

$$P_3 = 3 \text{ atm}$$

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

adiabatic \rightarrow

$$\text{So } w_3 = -3(16.4 - 8.48)$$

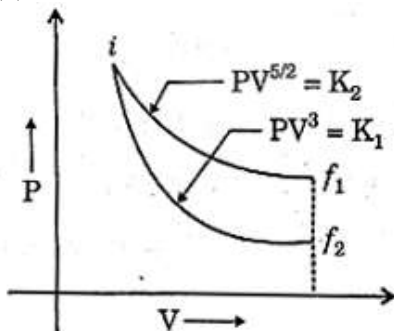
$$= -23.76 \text{ L} \cdot \text{atm}$$

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

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

$$\Delta U = \frac{-3 \times R \times 160}{\frac{1}{2}} = -960 R$$
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)
 $T_{f, \text{adiabatic}} < T_{f, \text{isothermal}}$
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

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

$$\Delta E_2 = \Delta E_1 + \Delta C_v (T_2 - T_1)$$
33. (c)

$$\Delta H = \Delta E + \Delta n_g (RT), \Delta n_g \text{ for the reaction is positive}$$

 So $\Delta H < \Delta E$
34. (a)

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

$$\text{CH}_4 \rightarrow \frac{890}{16} = 55.625 \text{ kJ / g}$$

$$\text{C}_2\text{H}_4 \Rightarrow \frac{1411}{28} = 50.393 \text{ kJ / g}$$

$$\text{C}_2\text{H}_6 \Rightarrow \frac{1560}{30} = 52 \text{ kJ / g}$$
36. (b)

$$\Delta E = \Delta H - \Delta n_g (RT)$$

$$= 176 - 1 \times \frac{8.314}{1000} \times 1240 = 165.6 \text{ kJ}$$
37. (b)
(ii)- (i)

$$\Delta H = -393.5 + 395 = 1.5 \text{ kJ}$$
38. (a)

$$\text{Energy} = \frac{1560}{2} = 44 \times n_{\text{H}_2\text{O}}$$

$$\Rightarrow n_{\text{H}_2\text{O}} = 17.727$$

$$\Rightarrow w_{\text{H}_2\text{O}} = 319 \text{ g}$$
39. (b)

$$\text{K} + \text{H}_2\text{O} \rightarrow \text{KOH}(\text{aq}) + \frac{1}{2} \text{H}_2 - 48$$

$$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \quad -69.39$$

$$\text{KOH}(\text{aq}) \rightarrow \text{KOH}(\text{s}) + \text{aq} \quad 14$$

$$\text{K} + \frac{1}{2} \text{O}_2 + \frac{1}{2} \text{H}_2 \rightarrow \text{KOH}(\text{s})$$

$$\Delta H = -48 - 69.39 + 14 = -102.39$$

40. (a)
 $\Delta H - \Delta U = (\Delta n_g)RT$
 $= -3 \times \frac{8.314}{1000} \times 298 =$
 $= -7.43$
41. (a)
 $\Delta H = \Delta E + (\Delta n_g)RT$
 $\Delta H = \Delta E - (5.5) \times \frac{8.314 \times 298}{1000}$
 $C_8H_{18(g)} + \frac{25}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2(\ell)$
 $\Delta n_g = 8 - 1 - 12.5 = -5.5$
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)

$$\begin{array}{c} C + O_2 \rightarrow CO_2 \\ \text{x mole} \quad \text{x mole} \end{array}$$

$$\begin{array}{c} C + \frac{1}{2} O_2 \rightarrow CO \\ \text{(1-x) mole} \quad \left(\frac{1-x}{2}\right) \text{ mole} \end{array}$$

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

$$67.64x = 75 - 26.41$$

$$x = 0.718$$

$$m_{O_2} = 32 \times \left(\frac{1}{2} + \frac{x}{2}\right) = 27.49g$$
51. (b)
 For $\Delta H = \Delta E \Rightarrow \Delta n_g = 0$
52. (c)
 $C + O_2 \rightarrow CO_2 \quad \Delta H = -390 \text{ (1)}$
 $CO + \frac{1}{2} O_2 \rightarrow CO_2 \quad \Delta H = -278 \text{ (2)}$
 (1) - (2)
 $\Delta H = -390 + 278 = -112$
53. (d)
 For formation reaction, reactants should be in most stable allotropic form
54. (d)
 $\Delta H_n = -\frac{y}{2}$
55. (a)
 $\theta = m \& \Delta T$
 θ is doubled & m is also doubled.
56. (a)
 $\Delta H_{\text{atomisation}} = \frac{104}{2} = 52$
57. (c)
 For maximum heat, acid and base reacting should be maximum.

58. (b)

$$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\ell)$$

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

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

$$= 467.5$$
59. (d)

$$\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O}(\text{g})$$

$$\Delta H = +9.7 = \Delta_f H_{\text{H}_2\text{O}(\text{g})} - \Delta_f H_{\text{H}_2\text{O}(\ell)}$$

$$\Rightarrow \Delta_f H_{\text{H}_2\text{O}(\text{g})} = -68 + 9.7 = -58.3 \text{ kcal}$$
60. (b)

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

$$\Rightarrow BE_{\text{C}-\text{C}} = 350$$
61. (b)

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

$$\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2 \rightarrow \text{HCl}$$

$$\Delta H = \frac{435}{2} + \frac{243}{2} - 431 = -92$$
63. (b)

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

$$= -27.4 \text{ kcal}$$
64. (d)
 For max heat $n_{\text{H}^+} = n_{\text{OH}^-}$

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

$$\Rightarrow V_1 = V_2$$
65. (d)

$$\text{S} \rightarrow \ell \rightarrow \text{g}$$

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

$$-100 = \frac{x}{2} + \frac{x}{4} - x = -\frac{x}{4}$$
66. (a)

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

$$\Rightarrow x = 400$$

67. (a)

$$\Delta S = \frac{\theta_{\text{rev}}}{T} = \frac{\Delta H_v}{T}$$
68. (a)

$$\Delta S_{\text{sys}} = nR \ln \frac{V_f}{V_i}$$

$$= 1 \times 8.314 \times \ln 10 = 19.15 \text{ J / K - mol}$$
69. (b)

$$\Delta S_{\text{sys}} = nR \ln \frac{V_f}{V_i}$$
70. (b)
 Endothermic $\Rightarrow \Delta H = +ve$
 $\Rightarrow \Delta S_{\text{sys}} > 0 \Rightarrow \Delta S_{\text{surr}} = -ve$
71. (c)
 Exothermic $\Rightarrow H = -ve$
 $\Rightarrow \Delta S_{\text{sys}} < 0 \Rightarrow \Delta S_{\text{surr}} = +ve$
72. (b)
 $\Delta H > 0 \Rightarrow$ since bond are broken
 $\Delta S > 0 \Rightarrow \Delta n_g > 0$
73. (d)

$$S_{\text{sys}} = 1 \times C_v \ln 2 + 1 \times R \ln \frac{1}{2}$$

$$= (C_{v-R}) \ln 2$$
74. (a)
 Zeroth law is for thermal equilibrium between bodies
75. (d)

$$\Delta S_{\text{surr}} = \frac{64000}{300} = 213$$
76. (a)

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

$$= -318.4$$
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)

$$T < \frac{49 \times 1000}{40.2}$$
$$\Rightarrow T < 1219\text{K}$$

81. (b)

$$\Delta H_{\text{R}} = 9.7 - 2 \times 90.5$$
$$= -171.3$$
$$\Delta S_{\text{R}} = 304 - 2 \times 210 - 205$$
$$= -321$$
$$\Delta G_{\text{R}} = -171.3 - \frac{298}{1000} \times (-321)$$
$$= -75.64$$

82. (a)

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

83. (c)

For $\text{C}_2\text{H}_6(\text{g})$, C will be higher

84. (c)

$$T > \frac{85 \times 1000}{1.98}$$
$$\Rightarrow T > 429.3\text{K}$$

85. (d)

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

EXERCISE - 1 [B]

1. (d)
 $41 + 463 + 348 - 352 - 415 = 85 \text{ kJ/mol}$
2. (a)

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

$$\Delta H^\circ = -167.1 \times 5 - 1284.4 + 285.8 \times 4 + 443.5$$

$$= -533.2$$
4. (b)

$$\Delta H^\circ = \frac{507}{2} - \frac{427}{2} + \frac{43}{2} + \frac{34}{2} = 78.5 \text{ kJ}$$
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)

$$\Delta H^\circ = -537 \times 2 - 680 \times 2 + 52 = -2382$$
10. (b)

$$\frac{1}{2} \text{I}_2(s) + \frac{1}{2} \text{Cl}_2(g) \longrightarrow \text{ICl}(g)$$

$$\Delta H_f = \frac{1}{2} \times [62.76 + 151 + 242.3] - 211.3$$

$$= +16.8 \text{ kJ/mol}$$
11. (c)
12. (b)
 $\Delta H - T\Delta S > 0$ (For non-spontaneous process)

$$\Rightarrow T > \frac{-\Delta H}{-\Delta S} \text{ or } T > \frac{1648 \times 10^3}{560} = 2943 \text{ K}$$
13. (d)

14. (b)

15. (b)

16. (b)

Ice \rightarrow water \rightarrow water \rightarrow steam
(0°C) (0°C) (100°C) (100°C)

$$\Delta S_{\text{Total}} = 18 \times \frac{80}{273} + 18 \times 1 \times \ln\left(\frac{373}{273}\right) + 18 \times \frac{540}{373}$$

17. (b)

$$T = \frac{25 \times 10^3}{50} \text{ K}$$

18. (b)

19. (d)

A(s) \rightarrow B(s)
400 mL 600 mL

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

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

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

$$\Rightarrow P = 101 \times 10^5 \text{ N/m}^2 \\ = 101 \text{ bar}$$

20. (a)

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

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

21. (b)

22. (a)

$$W = -\frac{7}{28} \times 8.3 \times 300 \ln\left(\frac{0.5}{0.1}\right) = -996 \text{ J}$$

23. (b)

$$\Delta E = \Delta H - \Delta n_g RT ; \Delta n_g > 0 \text{ and } \Delta H < 0$$

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

24. (c)

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

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

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

25. (d)

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

EXERCISE - 1 [C]

1. (189)
 $\text{Zn} + 2\text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2(\text{g});$
 $w = -\Delta n_g RT$

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

2. (22)

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

3. (6)
 Open systems : b, f, g, i, j
 Closed systems : a, c, h
 Isolated systems : d, e

4. (5200)

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

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

5. (182)
 $[23 + 45 + 81 + 33 = 182]$

6. (44)
 $(\Delta C_p)_{\text{Reaction}} = 2 \times 4 - 3.5 - 3 \times 3.5 = -6$
 $\Delta H_{300} = \Delta H_{1000} + \Delta C_p (300 - 1000)$

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

 $= -88.91 \text{ for } 2 \text{ moles of } \text{NH}_3$

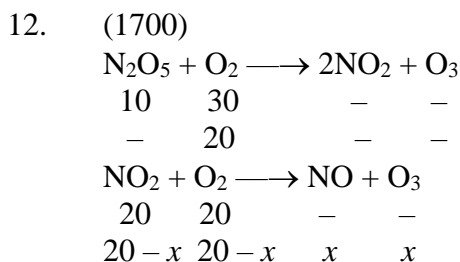
7. (5)
 Pressure, molar entropy, density, boiling point, molality are intensive properties.

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



$$\frac{(10+x)}{[(20-x) + (20-x) + x + (10+x)]} \times 100 = 50$$

$$\Rightarrow x = 15$$

$$\Delta H = 10 \times 200 - 15 \times 20 = 1700 \text{ kJ}$$

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

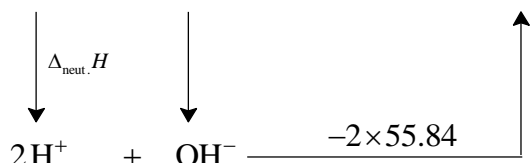
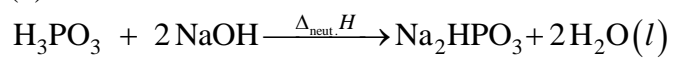
14. (7700)
 $T \propto V^3, \quad T = 300 \text{ K}$
 $\Rightarrow PV^{-2} = K \quad n = 1 \text{ mole}$
 $\gamma = \frac{5}{3}$

$$C = \frac{3R}{2} + \frac{R}{3} = \frac{11R}{6}; T_f = 2400 \text{ K}$$

$$q = 1 \times \frac{11}{6} \times 2 \times 2100 = 7700 \text{ cal}$$

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

16. (5)



$$\Delta_{\text{neut.}}H = \Delta_{\text{ion}}H - 2 \times 55.84$$

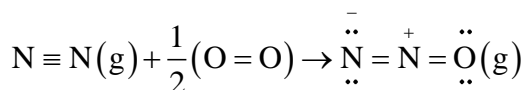
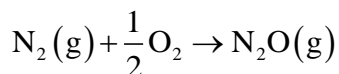
$$\Delta_{\text{ion}}H = 5 \text{ kJ}$$

17. (3)

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

Path functions : e, f, i, k

1. (a)



$\Delta_f H^\circ = [\text{Energy required for breaking of bonds}] - [\text{Energy released for forming of bonds}]$

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

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

Resonance energy = observed $\Delta_f H^\circ$ - calculated $\Delta_f H^\circ$

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

2. (c)

For isothermal reversible expansion.

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

3. (a)

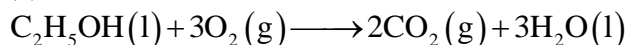
Process is isothermal reversible expansion, hence $\Delta U = 0$, therefore $q = -w$,

Since $q = +208\text{J}$, $w = -208\text{J}$

4. (b)

$$\begin{aligned} \Delta S^\circ &= S^\circ_{\text{CO}_2} + 2 \times S^\circ_{\text{H}_2\text{O}} - (S^\circ_{\text{CH}_4} + 2 \times S^\circ_{\text{O}_2}) \\ &= (213.6 + 2 \times 69.9) - (186.2 + 2 \times 205.2) \\ &= -242.8 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

5. (a)



Bomb calorimeter gives ΔU of the reaction.

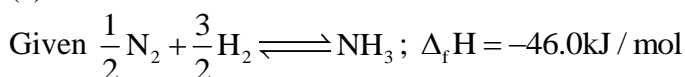
Given, $\Delta U = -1364.47 \text{ kJ mol}^{-1}$

$$\Delta n_g = -1$$

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

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

6. (c)





$$\Delta_f H(\text{NH}_3) = \frac{1}{2} \Delta H_{\text{N-N}} + \frac{3}{2} \Delta H_{\text{H-H}} - 3 \Delta H_{\text{N-H}} - 46 = \frac{1}{2}(712) + \frac{3}{2}(436) - 3 \Delta H_{\text{N-H}}$$

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

7. (b)

$$\text{In } \text{CH}_4, 4 \times \text{BE}_{(\text{C-H})} = 360 \text{ kJ/mol}$$

$$\therefore \text{BE}_{(\text{C-H})} = 90 \text{ kJ/mol}$$

$$\text{In } \text{C}_2\text{H}_6, \text{BE}_{(\text{C-C})} + 6 \times \text{BE}_{(\text{C-H})} = 620 \text{ kJ/mol}$$

$$\therefore \text{BE}_{(\text{C-C})} = 620 - (6 \times 90) = 80 \text{ kJ/mol}$$

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

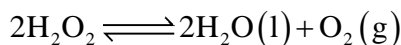
$$\text{Now, } E = \frac{hc}{\lambda}$$

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

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

$$\therefore \lambda = 1.49 \times 10^3 \text{ nm}$$

8. (a)

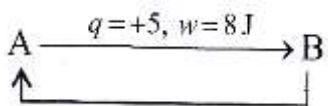


$$w = -P_{\text{ext}}(\Delta V) = -n_{\text{O}_2}RT$$

\therefore 100 mole of H_2O_2 on decomposition give 50 mole O_2 .

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

9. (d)



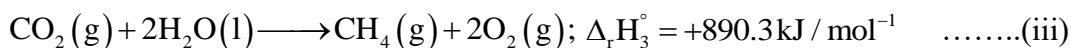
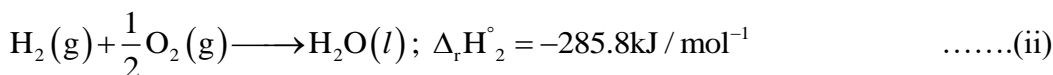
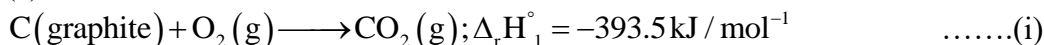
$$\Delta U_{\text{AB}} = q + w = 5 + (-8) = -3 \text{ J}$$

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

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

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

10. (c)

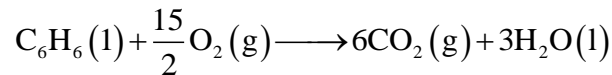


$$[\text{Eq. (i)} + \text{Eq. (iii)}] + [2 \times \text{Eq. (ii)}] = \text{Eq (iv)}$$

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

$$[(-393.5) + (890.3)] + [2(-285.8)] = -74.8 \text{ kJ / mol}$$

11. (d)



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

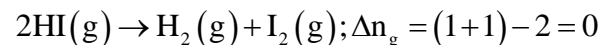
$$\Delta H = \Delta U + \Delta n_g RT$$

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

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

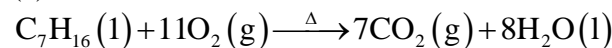
12. (b)

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



$$\therefore \Delta H = \Delta U$$

13. (a)



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

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

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)

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

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

16. (a)

$$\text{Given: } n = 3$$

$$T_1 = 300; T_2 = 1000$$

$$C_p = 23 + 0.01T$$

The relation between ΔH and C_p

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

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

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

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

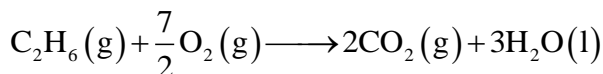
$$= 61950 \text{ J} = 61.95 \text{ kJ} \approx 62 \text{ kJ}$$

17. (d)
In expansion against vacuum,
 $P_{\text{ext}} = 0 \Rightarrow w = -P_{\text{ext}} \Delta V = 0$
18. (c)
 $\Delta_{\text{sol}} H^\circ = \Delta_{\text{lattice}} H^\circ + \Delta_{\text{Hyd}} H^\circ$
 $4 = 788 + \Delta_{\text{Hyd}} H^\circ$
 $\Delta_{\text{Hyd}} H^\circ = -784 \text{ kJ mol}^{-1}$
19. (c)
 $\Delta H_{\text{atomisation}} = \Delta H_{\text{vap}} + \text{Bond energy}$
Hence, $x > y$.
20. (a)
A system at higher temperature has greater entropy (randomness). S and ΔS are related with T as:
 $S_T = \int_0^T \frac{nC_v dT}{T}$ and $\Delta S = \int \frac{dq}{T}$
Thus, both S and ΔS are function of temperature.
21. (a)
 $H = U + PV$ (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) $\Delta H_{\text{reaction}} = (\sum \text{bond energies of reactants}) - (\sum \text{bond energies of products})$
(D) In exothermic process, energy is released. So, the value of enthalpy is negative i.e., $\Delta H < 0$.
23. (a)
 $\Delta G = \Delta H - T\Delta S \quad \because \Delta S_g > \Delta S_l > \Delta S_s$
 \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)



Heat of combustion

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

$$\Delta_c H(\text{C}_2\text{H}_6, \text{g}) = 2\Delta_c H(\text{C, graphite}) + 3\Delta_c H(\text{H}_2, \text{g}) - \Delta_f H(\text{O}_2, \text{g}) - \Delta_f H(\text{C}_2\text{H}_6, \text{g})$$

$$= -1560 = 2(-394) + 3(-286) - 0 - \Delta_f H(\text{C}_2\text{H}_6, \text{g})$$

$$\Rightarrow \Delta_f H(\text{C}_2\text{H}_6, \text{g}) = -86 \text{ kJ mol}^{-1}$$

26. (557)

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

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

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

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

27. (-13538)

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

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

$$= -22477.57 \text{ J}$$

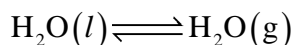
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -22477.57 - (298 \times (-30))$$

$$= -13538 \text{ J}$$

28. (189494)

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

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

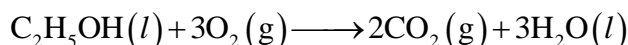


$$\Delta n = 1$$

$$41000 = \Delta U + 1 \times 8.314 \times 373 \Rightarrow \Delta U = 37898.875 \text{ J}$$

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

29. (-326400)



$$\Delta H_c = -327 \text{ kcal}$$

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

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

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

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

30. (5)

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

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

31. (50)

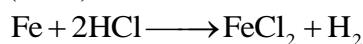
$$q = 150 \text{ joules}$$

$$w = -200 \text{ Joules}$$

$$\Delta E = q + w \quad (\text{First law of thermodynamics})$$

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

32. (2218)



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

$$\text{No. of moles of H}_2 \text{ produced} = \frac{50}{55.85} \text{ moles}$$

$$\text{Work done} = -P_{\text{ext}} \Delta V = -\Delta n_g RT$$

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

33. (718)

$$\Delta_f H_{\text{KCl}}^\circ = \Delta_{\text{sub}} H_{(\text{K})}^\circ + \Delta_{\text{ionization}} H_{(\text{K})}^\circ + \frac{1}{2} \Delta_{\text{bond}} H_{(\text{Cl}_2)}^\circ + \Delta_{\text{electron gain}} H_{(\text{Cl})}^\circ + \Delta_{\text{lattice}} H_{(\text{KCl})}^\circ$$

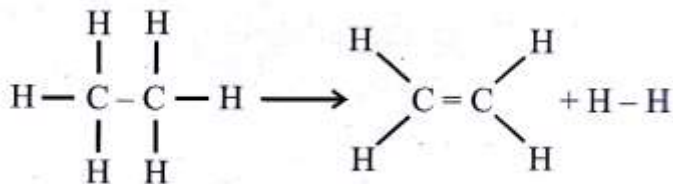
$$\Rightarrow -436.7 = 89.2 + 419 + \frac{1}{2}(243.0) + \{-348.6\} + \Delta_{\text{lattice}} H_{(\text{KCl})}^\circ$$

$$\Rightarrow \Delta_{\text{lattice}} H_{(\text{KCl})}^\circ = -717.8 \text{ kJ mol}^{-1} \approx 718 \text{ kJ mol}^{-1}$$

34. (101)

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

35. (128)

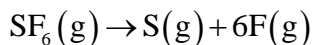


$$\Delta_r H = \sum \text{B.E}_{\text{Reactant}} - \sum \text{B.E}_{\text{Products}}$$

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

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

36. (309)



$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\text{S}) + 6\Delta H_f^\circ(\text{F}) - \Delta H_f^\circ(\text{SF}_6) \\ &= 275 + 6 \times 80 - (-1100) = 1855 \text{ kJ mol}^{-1}\end{aligned}$$

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

$$\therefore \Delta H_{\text{S-F}} = \frac{1855}{6} = 309.17 \approx 309 \text{ kJ mol}^{-1}$$

37. (3)

State Variable is an independent variable of a state function.

38. (2)

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

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

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

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

39. (200)

$$\text{Moles of coal} = \frac{2.4}{12} = 0.2$$

$$q = C_v dT$$

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

$$0.2 \text{ moles evolved} = 40 \text{ kJ}$$

$$1 \text{ moles evolved} = \frac{40}{0.2} = 200 \text{ kJ / mol}$$

$$\Delta H = -200 \text{ kJ / mol}$$

40. (1718)

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

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

$$w = -2.303 \times 1 \times 300 \times \log(2)$$

$$\Rightarrow w = -1718.1 \text{ J}$$

41. (117)

$$\text{Molar mass of NH}_3 = 17 \text{ g / mol}$$

$$\text{Moles of NH}_3 \text{ given} = \frac{17}{17} = 1 \text{ mole}$$

$$\text{For 1 mole enthalpy change} = 23.4 \text{ kJ}$$

5 moles enthalpy change = $23.4 \times 5 = 117 \text{ kJ}$

42. (0)

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

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

Isothermal expansion , $\Delta U = 0$

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

43. (8630)

$n = 5 \text{ mol}; T = 300 \text{ K}; V_1 = 10 \text{ L}; V_2 = 20 \text{ L}$

Work done in isothermal condition.

$$\begin{aligned} w_{\text{rev}} &= -nRT \ln \frac{V_2}{V_1} \\ &= -5 \times 8.3 \times 300 \ln \frac{20}{10} = -8630.38 \text{ J} \end{aligned}$$

44. (300)

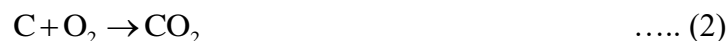
$\Delta G = \Delta H - T\Delta S = 0$ at equilibrium

$$\Rightarrow -165 \times 10^3 - T \times (-550) = 0 \Rightarrow T = 300 \text{ K}$$

45. (103.7)



$$\Delta H_1 = -2220 \text{ kJ / mol}$$



$$\Delta H_2 = -393.5 \text{ kJ / mol}$$



$$\Delta H_3 = -285.8 \text{ kJ / mol}$$

Formation of C_3H_8 (1mole) :



Equation (4) obtained by

$$3 \times \text{Eq}(2) + 4 \times \text{Eq}(3) - \text{Eq}(1)$$

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

$$= -1180.5 - 1143.2 + 2220.0 = -103.7 \text{ kJ / mol}$$

46. (2)

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

In case of acetic acid

$$\Delta H = \Delta H_{\text{ioni}} + \Delta H_{\text{neutralization}}$$

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

$$\Delta H_{\text{ion}_1} = 2\text{kJ/mol}$$

47. (727)

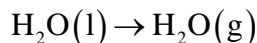
$$\Delta U = -726\text{kJ/mol}$$

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

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

$$= -726 - \frac{1}{2} \times \frac{8.3 \times 300}{1000} = -727.245$$

48. (38)



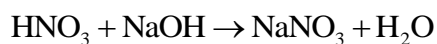
$$\Delta n_g = \sum n_p - \sum n_R = 1 - 0 = 1$$

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

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

$$= 41.1 - \frac{1 \times 8.31 \times 373}{1000} \text{kJ/mol} = 38\text{kJ/mol}$$

49. (54)



Start 120 40

End 80 0 40mmol

$$\Delta_r H = 40\text{mmol} \times (57 \times 10^3) \text{J mol}^{-1}$$

$$= 40 \times 10^{-3} \text{mol} \times 57 \times 10^3 \text{J mol}^{-1} = 2280 \text{J}$$

$$mS\Delta T = 2280 \Rightarrow 1000\text{g} \times 4.2 \times \Delta T = 2280$$

$$\Delta T = \frac{2280}{4.2} \times 10^{-3} = \frac{22800}{42} \times 10^{-3} = 542.86 \times 10^{-3}$$

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