

**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  $\infty$ .
- (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)

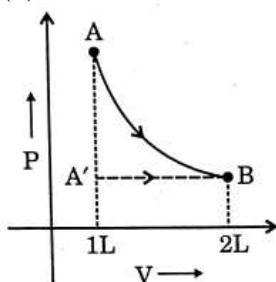
$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}; \gamma = \frac{5}{3}; T_1 = 300K, V_1 = 8L, T_2 = 250K$$

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

14. (b)

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

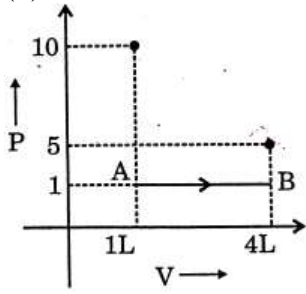
15. (b)



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

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

16. (b)



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

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

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

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

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

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

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)

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

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

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

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

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

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

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  $\rightarrow$

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

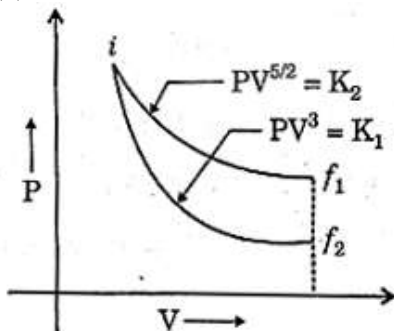
$$= -23.76 \text{ L} \cdot \text{atm}$$

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.  $T_{\text{final}}$  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  $\gamma$  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)  

$$\Delta H = \Delta E + \Delta n_g (RT)$$
,  $\Delta n_g$  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)  

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

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

$$\Rightarrow \text{endothermic reaction}$$
47. (d)  

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

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


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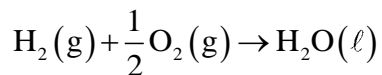

$$\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(\ell) \rightarrow HBr(g) \quad \frac{\Delta H_1 - \Delta H_2}{2}$$

48. (b)  
 $\Delta H_T < \Delta H_C$   
 So  $C \rightarrow T$   $\Delta H_R = \Delta H_T - \Delta H_C = -ve$   
 $\Rightarrow$  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)  
 $C + O_2 \rightarrow CO_2 \quad \Delta H = -390$  (1)  
 $CO + \frac{1}{2}O_2 \rightarrow CO_2 \quad \Delta H = -278$  (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)  
 $\theta = m \& \Delta T$   
 $\theta$  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.

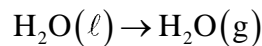
58. (b)



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

$$B_{\text{O}-4} = \frac{1}{2} \left( 433 + \frac{492}{2} - 42 + 298 \right)$$
$$= 467.5$$

59. (d)



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

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

60. (b)

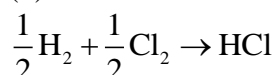
$$-100 = 600 - 2B_{\text{C}-\text{C}}$$

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

61. (b)

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

62. (b)



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

63. (b)

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

$$= -27.4 \text{ kcal}$$

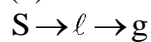
64. (d)

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)



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

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

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)

$$\Delta H_R = 9.7 - 2 \times 90.5$$
$$= -171.3$$
$$\Delta S_R = 304 - 2 \times 210 - 205$$
$$= -321$$
$$\Delta G_R = -171.3 - \frac{298}{1000} \times (-321)$$
$$= -75.64$$

82. (a)

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

83. (c)

For  $\text{C}_2\text{H}_6(\text{g})$ , 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)  
 $(\Delta C_p)_{\text{Reaction}} = 2 \times 4 - 3.5 - 3 \times 3.5 = -6$   
 $\Delta H_{300} = \Delta H_{1000} + \Delta C_p (300 - 1000)$   

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

$$= -88.91 \text{ for 2 moles of NH}_3$$
  
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)  
 $P_4(s) \longrightarrow P_4(g)$   
 $P_4(s) \longrightarrow 4P(g)$   
 $\Rightarrow P_4(g) \longrightarrow 4P(g)$   
 $\Delta H = 1321 - 61 = 6x$   
 $\Rightarrow x = 210 \text{ kJ/mol.}$

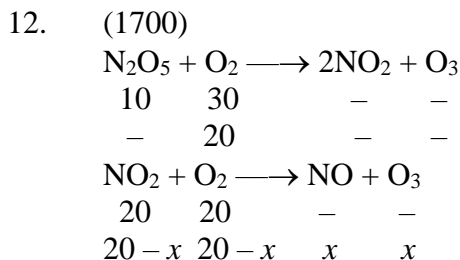
10. (4)  
Intensive : a, c, d, f, g, h, i, k  
Extensive : b, e, j, l

11. (3125)

$$300 \times (0.5)^{\gamma-1} = T_2 \times (3)^{\gamma-1}$$

$$\Rightarrow T_2 = \frac{300}{(6)^{2/5}} = 150 \text{ K}$$

$$w = 1 \times \frac{25}{3} \times \frac{150}{0.4} = 3125 \text{ J}$$



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

$$\Rightarrow x = 15$$

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

13. (2)

$$29 \times 2 - 56 = 2$$

14. (7700)

$$T \propto V^3, \quad T = 300 \text{ K}$$

$$\Rightarrow PV^{-2} = K \quad n = 1 \text{ mole}$$

$$\gamma = \frac{5}{3}$$

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

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

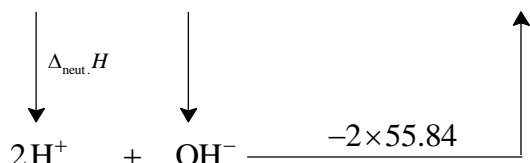
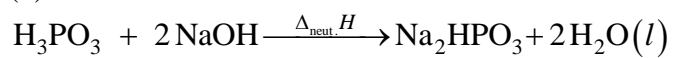
15. (8)

$$\frac{1}{5} = 1 - \frac{T_2}{T_1} \quad \dots \text{(i)}$$

$$\frac{2}{5} = 1 - \frac{(T_2 - 80)}{T_1} \quad \dots \text{(ii)}$$

$$\Rightarrow T_1 - T_2 = 80$$

16. (5)



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

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

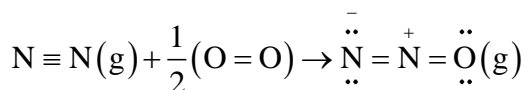
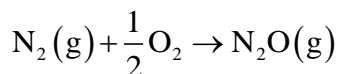
17. (3)

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)

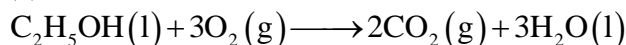
Process is isothermal reversible expansion, hence  $\Delta U = 0$ , therefore  $q = -w$ ,

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  $\Delta U$  of the reaction.

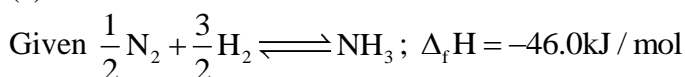
Given,  $\Delta U = -1364.47 \text{ kJ mol}^{-1}$

$$\Delta n_g = -1$$

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

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

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)

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

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

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

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

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

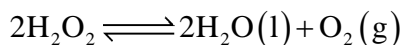
$$\text{Now, } E = \frac{hc}{\lambda}$$

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

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

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

8. (a)

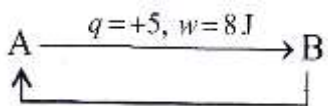


$$w = -P_{\text{ext}}(\Delta V) = -n_{\text{O}_2}RT$$

$\therefore$  100 mole of  $\text{H}_2\text{O}_2$  on decomposition give 50 mole  $\text{O}_2$ .

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

9. (d)



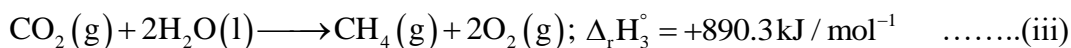
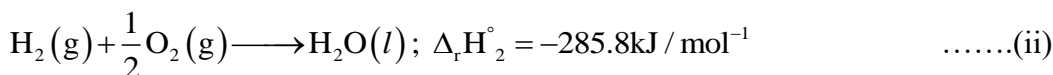
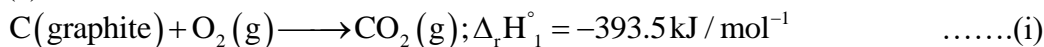
$$\Delta U_{\text{AB}} = q + w = 5 + (-8) = -3 \text{ J}$$

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

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

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

10. (c)

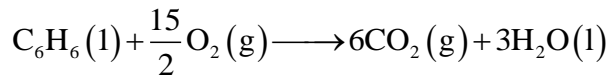


$$[\text{Eq. (i)} + \text{Eq. (iii)}] + [2 \times \text{Eq. (ii)}] = \text{Eq (iv)}$$

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

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

11. (d)



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

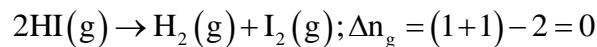
$$\Delta H = \Delta U + \Delta n_g RT$$

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

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

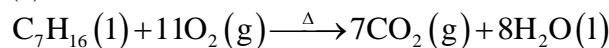
12. (b)

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



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

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)

Given:  $n = 3$

$$T_1 = 300; T_2 = 1000$$

$$C_p = 23 + 0.01T$$

The relation between  $\Delta H$  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

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

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

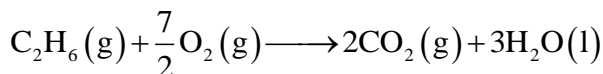
$$= 61950 \text{ J} = 61.95 \text{ kJ} \approx 62 \text{ kJ}$$

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  $\Delta S$  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  $\Delta S$  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  $\Delta G$  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  $557 \text{ kJ mol}^{-1}$

27. (-13538)

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

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

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

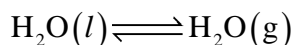
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -22477.57 - (298 \times (-30))$$

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

28. (189494)

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

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

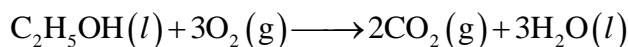


$$\Delta n = 1$$

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

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)

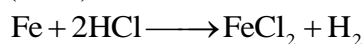
$$q = 150 \text{ joules}$$

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

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

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

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)

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

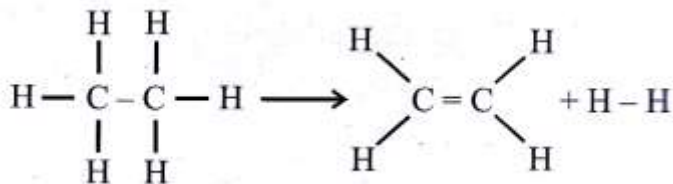
$$\Rightarrow -436.7 = 89.2 + 419 + \frac{1}{2}(243.0) + \{-348.6\} + \Delta_{\text{lattice}} H_{(\text{KCl})}^\circ$$

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

34. (101)

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

35. (128)

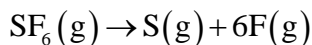


$$\Delta_r H = \sum \text{B.E}_{\text{Reactant}} - \sum \text{B.E}_{\text{Products}}$$

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

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

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.

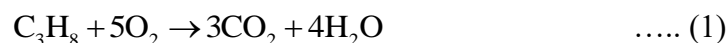
$$\begin{aligned} w_{\text{rev}} &= -nRT \ln \frac{V_2}{V_1} \\ &= -5 \times 8.3 \times 300 \ln \frac{20}{10} = -8630.38 \text{ J} \end{aligned}$$

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  $\text{C}_3\text{H}_8$  (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)

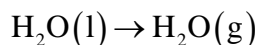
$$\Delta U = -726\text{kJ/mol}$$

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

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

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

48. (38)



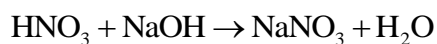
$$\Delta n_g = \sum n_p - \sum n_R = 1 - 0 = 1$$

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

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

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

49. (54)



Start 120 40

End 80 0 40mmol

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

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

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

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

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

## EXERCISE - 2 [A]

1. (a)

$$\Delta S = nC_v \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

$$= 2R \ln 2 = 11.5$$

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)

$$w = nRT \ln \frac{V_f}{V_i}$$

$$= 2.5 \times 8.314 \times 310 \ln \frac{2.5 \times 8.314 \times 310}{58 \times 10^3}$$

$$= 44665$$

5. (c)

At  $0^\circ\text{C}$  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)

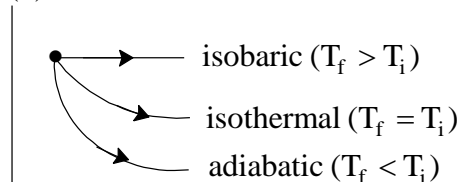
For bath  $\Delta S = \frac{Q}{T_{\text{Bath}}}$

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

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

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

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)  
 $\Delta U_R = -723 - 8.314 \times 0.3 \times (-1) = -69.8 \text{ kJ/mole}$   
 $n_{C_2H_4} = 3.5, n_{HCl} = 3$   
 So  $\Delta U = -69.8 \times 3 \text{ kJ} = -209.4$
17. (a)  
 $w = -600R \ln \frac{1}{2} - 2R(400 - 300) - 800R \ln 2 - 2R(300 - 400)$   
 $= -200R \ln 2 = -100R \ln 4$
18. (c)  
 $-3000 = 1 \times 20 \times (T_f - 300)$   
 $T_f = 150K$

19. (d)

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

$$\Rightarrow \frac{5}{2} T_f - \frac{5}{2} \times 350 = -T_f + 700$$

$$\Rightarrow \frac{7}{2} T_f = \frac{9}{2} \times 350 \Rightarrow T_f = 450 \text{K}$$

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

20. (b)

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

21. (b)

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

22. (c)

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

$$\Rightarrow T_2 = 600$$

23. (a)

$$\Delta H = -3 + (-1) \frac{2 \times 300}{1000} = -3.6 \text{ kcal}$$

$$\Delta G = -3.6 + \frac{10 \times 300}{1000} = -0.6 \text{ kcal}$$

24. (c)

$$\Delta S = n C_v \ln \frac{T_f}{T_i} = 2 \times \frac{3}{2} R \ln \frac{573}{473}$$

25. (d)

At phase equation  $\Delta G = 0$

26. (c)

$$\text{H}_2\text{O}(\ell, 1 \text{atm}, 373 \text{K}) \longrightarrow \text{H}_2\text{O}(g, 1 \text{atm}, 373 \text{K})$$

$$\Delta G = 0$$

$$\text{H}_2\text{O}(g, 1 \text{atm}, 373 \text{K}) \longrightarrow \text{H}_2\text{O}(g, 2 \text{atm}, 373 \text{K})$$

$$\Delta G = \int V dp = nRT \ln \frac{P_f}{P_i}$$

$$= 373 R \ln 2$$

27. (d)

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

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

$$= C_v \ln \frac{T_f}{T_H} + C_v \ln \frac{T_f}{T_C}$$

$$= C_v \ln \frac{T_f^2}{T_H T_C} = C_v \ln \frac{(T_H + T_C)^2}{4T_H T_C}$$

28. (c)  
 $S^\circ$  of  $H_2 > 0$  at 298 K

29. (a)  
 $\Delta H > 0$ ,  $\Delta S > 0$   
 (+ve y intercept) (-ve slope)

30. (a)  
 In adiabatic reversible process only  
 $T^\gamma P^{1-\gamma} = k$

31. (a)

$$\Delta S = 2090 \ln \frac{273}{200} + \frac{3.34 \times 10^5}{273} + 4180 \ln \frac{373}{273} + \frac{22.6 \times 10^5}{373} + 2090 \ln \frac{400}{373}$$

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

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)

$$150 \times 50 \times t = \frac{1 \times 150 \times 10^3}{293 \times 0.0821} \times \frac{7}{2} R \times 17$$

$$\Rightarrow t = 6.86 \text{ min}$$

37. (a)

$$\begin{aligned} \Delta E &= 2.25 \times 10^6 - \frac{1000}{18} \times 8.314 \times 373 \\ &= 2.08 \times 10^6 \end{aligned}$$

38. (b)

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

$$\Delta U \approx 25 \text{ J}$$

$$Q = 42 \text{ J}$$

$$\Rightarrow W = -17 \text{ J}$$

$$-17 = -10^5 \times 8.5 \times 10^{-4} \times h$$

$$h = 20 \text{ cm.}$$

39. (c)

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

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

$$h = \frac{(\sqrt{3} - 1) \times 1000}{16\pi}$$

$$h = 14.5 \text{ cm}$$

## 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.

$$P_1 V_1 = P_2 V_2, \Delta E = 0, \Delta H_1 = H_2$$

6. (a, b, c)

$$P_i = 2 \text{ bar}, T_i = 273 \text{ K}, P_f = 4 \text{ bar}$$

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

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

$$\Rightarrow T_f = 4 \times 273 = 1092 \text{ K}$$

$$\Delta E = 1 \times 12.5 \times (1092 - 273) \\ = 10.24 \text{ kJ}$$

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

$$Q = 1 \times 16.657 \times (1092 - 273) = 13.64 \text{ kJ}$$

$$W = \Delta E - Q \\ = -3.4 \text{ kJ}$$

7. (a, b, d)

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

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

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

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

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

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  $Q = 0$

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

$$W = -P_{\text{ext}}(V_f - V_i)$$

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

11. (a, b, c)

$$\begin{aligned}\Delta H &= \Delta U + \Delta(PV) \\ &= \Delta U + P\Delta V + V\Delta P + \Delta P\Delta V\end{aligned}$$

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)

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

$$T_2 > T_1$$

$$\Delta S = +ve$$

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

$$T_2 > T_1$$

$$\Delta H_2 > \Delta H_1$$

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

$$T\Delta S > \Delta H$$

$$\Delta G < 0$$

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

14. (a, b, c, d)

For adiabatic irreversible

$$\Delta S_{\text{sys}} \neq 0$$

For isentropic process

$$\Delta S_{\text{sys}} = 0$$

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

If  $\Delta H$  is positive &  $\Delta S$  is positive at high T.

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

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



## 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)

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

### Passage - II

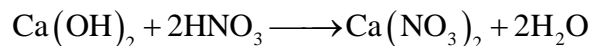
4. (a)

$$\Delta H_{\text{neutralisation}} = q - 55.84$$

$$-49.86 = q - 55.84$$

$$q = 5.98 \text{ kJ/mol}$$

5. (b)

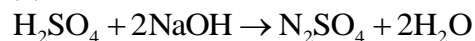


$$\Delta H = 2 \times \Delta H_{\text{neutralisation}}$$

$$= 2 \times (-55.84)$$

$$= -111.68 \text{ kJ}$$

6. (b)



$$V_{\text{H}_2\text{SO}_4} = V_1$$

$$V_{\text{NaOH}} = V_2$$

$$V_1 + V_2 = 100$$

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  $r \times n$   
 $\Delta H - T\Delta S < 0$

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

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

8. (a)  
 $\Delta G = \Delta H - T\Delta S$   
 $\Delta G = -T\Delta S$   
 $\Delta G = -T[-n_1R \ln x_1 - n_2R \ln x_2]$   
 $= 8.314 \times 298 \left[ 4 \ln \frac{4}{5} + 1 \ln \frac{1}{5} \right]$   
 $\Delta G = -6.19 \text{ kJ}$

9. (a)  
 $2\text{CoCl}_4(\text{aq}) + \text{Zn}(\text{s}) \rightarrow 2\text{CeCl}_3(\text{aq}) + \text{ZnCl}_2(\text{aq})$   
 $E = 0.4108 + 0.003T$   
 $\Delta S = -\frac{\partial(\Delta G)}{\partial T}$   
 $\Delta S = -\frac{\partial(-nFE)}{\partial T}$   
 $\Delta S = nF \frac{\partial E}{\partial T}$   
 $\Delta S = nF \times 0.003$   
 $\Delta S = 2 \times 96500 \times 0.003 = 579 \text{ JK}^{-1}$

### 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 vacuum  $q = 0$   
 $q = 0$   
 $P_{\text{ext}} = 0$   
 $V_2 > V_1$ ,  $w = 0 \Rightarrow \Delta U = 0$  (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  
 $PV^\gamma = \text{constant}$  (only for reversible adiabatic)  
 $W = \frac{nR}{\gamma - 1} (T_2 - T_1)$   
(Q,R)
- (C) Irreversible adiabatic expansion  
 $W = \Delta U = \frac{nR}{\gamma - 1} (T_2 - T_1)$  (R)
- (D) Irreversible isothermal compression  $\Delta T = 0 \Rightarrow \Delta H = 0$
3. (A) – PS; (B) – R; (C) – Q; (D) - Q
- (A)  $(\Delta G_{\text{sus}})_{T,P} = 0$  equilibrium  $\Delta G$  is useful work & here it is zero.  
(P,S)

- (B)  $\Delta S_{\text{total}} > 0$   
Spontaneous  
(R)
- (C)  $\Delta S_{\text{total}} < 0$   
Non-spontaneous  
(Q)
- (D)  $(\Delta G_{\text{sus}})_{T,P} > 0$  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  
 $w = -p_{\text{ext}} \Delta V = 0$   
 $q = 0$   
 $\Delta U = 0$   
(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. 
$$W = -nRT \ln \frac{V_f}{V_i}$$

$$= 1 \times 8.314 \times 298 \ln \left( \frac{1}{5} \right) = -3.988 \text{ kJ}$$
  
2.  $V = 0.5 \ell \text{t} \longrightarrow 4 \ell \text{t}$   
 $T = 298 \text{ K}$   
 $TV^{\gamma-1} = \text{constant}$   
 $298 \times (0.5)^{1/3} = T \times 4^{1/3}$   
 So,  $T = 149 \text{ K}$
  
3.  $\Delta E = q + W = (-65) + (+20) = -45 \text{ J}$
  
4.  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$   
 $q = \Delta H = 177.9 \text{ kJ}$   
 $\Delta H = \Delta E + P\Delta V$   
 $\Delta U = 177.9 - \left( 24.4 + \frac{16.9}{1000} - \frac{34.2}{1000} \right) \times 0.101325 = 175.4 \text{ kJ}$
  
5. 
$$\begin{array}{ccc} n=1 & & n=1 \\ 300 \text{ K} & & T \\ 10 \text{ atm} & \xrightarrow{\gamma=1.33} & 1 \text{ atm} \\ V_1 & & V_2 \\ q = 0 & & \\ \Delta E = W & & \\ \Rightarrow -1 \times \left( \frac{1 \times R \times T}{1} - \frac{1 \times R \times 300}{10} \right) = 1 \times 3R \times (T - 300) & & \\ = -(T - 300) = 3(T - 300) & & \\ = 4T = 930 & & \\ \Rightarrow T = 232.5 & & \\ \Rightarrow \Delta E = W = nC_v \Delta T = 1 \times 3 \times 8.314 \times (232.5 - 300) & & \\ \Rightarrow \boxed{W = -1.683 \text{ kJ}} & & \end{array}$$
  
6.  $TV^{\gamma-1} = k$   
 $300 \text{ V}^{1/3} = T \times (27 \text{ V})^{1/3}$   
 $\Rightarrow \boxed{100 \text{ K} = T}$   
 $\Delta E = W = 1 \times 25.08 \times (100 - 300) = 5016$

$$\begin{aligned}
7. \quad TV^{\gamma-1} &= k \\
298.15 \times V^{\gamma-1} &= 248.44 \times (2V)^{\gamma-1} \\
\frac{298.15}{248.44} &= (2)^{\gamma-1} \\
\log\left(\frac{298.15}{248.44}\right) &= (\gamma-1)\log 2 \\
\gamma-1 &= 0.263 \\
C_V &= 31.61
\end{aligned}$$

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

$$\begin{aligned}
9. \quad T_A &= \frac{1 \times 22.4}{0.082} = 273 \text{ K} \\
T_B &= \frac{1 \times 44.8}{0.082} = 546 \text{ K} \\
T_C &= \frac{0.5 \times 44.8}{0.082} = 273 \text{ K}
\end{aligned}$$

For process  $\vec{A}$

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

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

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

For process  $\vec{B}$

$$W = 0$$

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

For process  $\vec{C}$

$$\Delta E = \Delta H = 0$$

$$W = (-q) = -1 \times 8.314 \times 273 \ln \frac{22.4}{44.8}$$

$$= -8.314 \times 273 \ln \frac{1}{2}$$

$$= +8.314 \times 273 \times \ln 2$$

$$= 1572.9 \text{ J}$$

$$\begin{aligned}
10. \quad q &= \Delta H \text{ (constant pressure process)} \\
&\Rightarrow \Delta H = +1 \text{ kcal} \\
&\because \Delta H = \Delta E + P\Delta V \\
&\Rightarrow \Delta E = 1 \text{ kcal} - \frac{(1 \times 0.3) \times 0.101325}{4.2} = 0.993 \text{ kcal}
\end{aligned}$$

11.  $\Delta H = 1440 \text{ cal}$   
 $\therefore \Delta H = \Delta E + P\Delta V$   
 $\therefore \Delta H = \Delta E + 1 \times (0.018 - 0.0196)$   
 $\Rightarrow \Delta E = 1440 \text{ cal} - 101.325 \times \frac{-0.0016 \times 1}{4.2}$   
 $= 1440 + 0.0386 \text{ cal}$   
 $\approx 1440$
12.  $W = -1 \times (1.1 - 1)$   
 $\Rightarrow -0.1 \text{ L-atm} = -10.1325 \text{ J}$
13.  $q = \Delta H = -36.5 \text{ kJ}$   
 $W = \frac{-1 \times 500 \text{ cm}^2 \times 50 \text{ cm}}{1000} = -25 \text{ L-atm} = -2.53 \text{ kJ}$   
 $\Delta H = \Delta E + P\Delta V$   
 $\Delta E = -36.5 \text{ kJ} - 2.53 \text{ kJ}$   
 $\approx -39.03 \text{ kJ}$
14.  $-P_{\text{ext}}(V_f - V_i) = nC_V(T_f - T_i)$   
 $-1 \left( \frac{nRT_f}{2} - \frac{nRT_i}{5} \right) = n \times \frac{5}{2} R(T_f - T_i)$   
 $3T_f = 2.7 T_i$   
 $T_f = 0.9 \times 300 = 270 \text{ K}$   
 $\Rightarrow \Delta E = W = 2 \times \frac{5}{2} R \times (270 - 300) = -1247.1$   
 $\Delta H = 2 \times \frac{7}{2} R \times (270 - 300) = -1745.9 \text{ J}$
15.  $P_{\text{ext}} = 1 \text{ atm}$   
 $V_i = \frac{5 \times 0.082 \times 300}{4} = 30.75 \text{ L}$   
 $V_f = \frac{5 \times 0.082 \times 300}{1} = 123 \text{ L}$   
 $\therefore W = -1 \times (123 - 30.75) \times 101.325 \text{ J}$   
 $W = -9347 \text{ J}$   
 Reversible  
 $W = -5 \times 8.314 \times 300 \ln \left( \frac{4}{1} \right)$   
 $W = -17.288 \text{ kJ}$
16.  $n = 3$   
 $T = 200 \text{ K} \xrightarrow[\text{adiabatic}]{\text{reversible}} T = 250 \text{ K}$   
 $P = 2 \text{ atm} \qquad \qquad \qquad P$

$$V_1 \qquad V_2$$

$$C_v = 27.5$$

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

$$V_1 = 3 \times 0.082 \times 100$$

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

$$q = 0 \qquad W = \Delta E = nC_v \Delta T = 3 \times 27.5 \times (250 - 200) = 4.125 \text{ kJ}$$

$$\Delta H = 3 \times (27.5 + 8.314) \times 50 = 5.372 \text{ kJ}$$

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

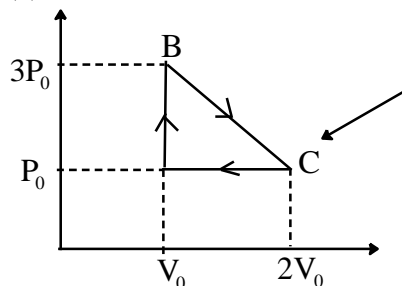
$$\gamma = \frac{C_p}{C_v} = \frac{35.814}{27.5} = 1.3$$

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

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

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

17. (a)



$$n = 1$$

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

$$W = -P_0 V_0$$

$$\text{Work done by the gas} = P_0 V_0$$

(b)  $\overrightarrow{CA}$

$$W = P_0 \times V_0$$

$$\Delta E = 1 \times \frac{3}{2} R \times \left[ \frac{P_0 V_0}{R} - \frac{2P_0 V_0}{R} \right]$$

$$\Delta E = \frac{3}{2} \times -P_0 V_0 = -\frac{3}{2} P_0 V_0 \quad \Delta E = q + W$$

$$\Rightarrow q = -\frac{3}{2} P_0 V_0 - P_0 V_0$$

$$q = -\frac{5}{2} P_0 V_0$$

$\overrightarrow{AB}$

$$W = 0$$



$$\Delta W = 1 \times \frac{3R}{2} \times \left( \frac{3P_0 V_0}{R} - \frac{P_0 V_0}{R} \right)$$

$$\Delta E = 3P_0 V_0$$

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

$$0 = (3P_0 V_0 + Q_{BC} - 2.5P_0 V_0) - P_0 V_0$$

$$Q_{BC} = 0.5P_0 V_0$$

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

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

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

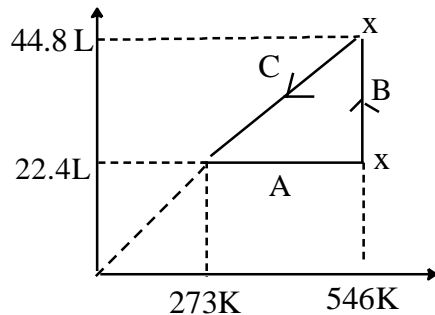
$$T = \frac{5P_0}{R} V - \frac{2P_0}{RV_0} V^2$$

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

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

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

18.



$$P_1 = 1 \times \frac{0.082 \times 273}{22.4} = 1 \text{ atm}$$

$$P_2 = 1 \times \frac{0.0082 \times 546}{22.4} = 2 \text{ atm}$$

$$P_3 = 1 \times \frac{0.082 \times 546}{44.8} = 1 \text{ atm}$$

A is isochoric

$$W = 0$$

$$q = \Delta E = 1 \times \frac{3}{2} \times 8.314 \times (546 - 273) = 3404.583 \text{ J}$$

$$\Delta H = 1 \times \frac{5}{2} \times 8.314 \times (546 - 273)$$

B is isothermal

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

$$W = -q = -1 \times R \times 546 \text{ K} \left( \frac{44.8}{22.4} \right) = -R \ln 2 \times 546$$

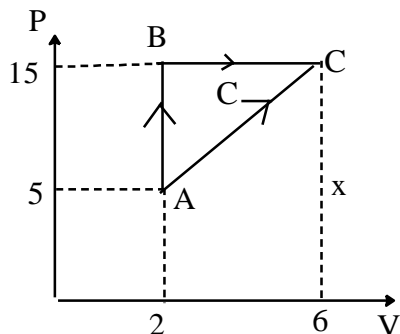
C is isobaric

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

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

$$Q = \Delta H = 1 \times \frac{5}{2} \times R \times 273 \quad W = R \times 273$$

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



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

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

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

$$W = -40\text{J}$$

$$\therefore \Delta E = q + W$$

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

$$\Rightarrow E_C = 160 + 10 = 170\text{J}$$

(c)  $w_{AB} = 0$

$$q = \Delta E$$

$$\Rightarrow q = 10\text{J}$$

20.  $\Delta H = \Delta E + \Delta nRT$

$$= -14.2 \text{ kcal/mol} + \frac{1 \times 2 \times 298}{1000}$$

$$= (-14.2 + 0.6) \text{ kcal}$$

$$= -13.6 \text{ kcal}$$

21.  $q = nc\Delta T$

$$= \frac{213.5}{18} \times 18 \times 75$$

$$= 16.012 \text{ kcal}$$

$$22. \quad V_1 = 3 \text{ dm}^3 \longrightarrow 5.0 \text{ dm}^3$$

$$P_{\text{net}} = 3 \text{ atm}$$

$$\Rightarrow \omega = -3 \times 2 \text{ atm} \approx -6 \times 100 \text{ J}$$

$$q = \omega \because q = mc\Delta T (\because C \text{ in } \text{g}^{-1})$$

$$\Rightarrow 6 \times 100 = 180 \times 4.18 (\Delta T)$$

$$0.8 \sim \Delta T$$

$$\Rightarrow T - 290 = 0.8$$

$$\Rightarrow T = 290.8 \text{ K}$$

23. P is constant

$$(a) \quad \text{So, } Q = \Delta H = 22.2 \text{ kJ}$$

$$(b) \quad \Delta H_V = \frac{22.2}{10/18} = 39.96 \text{ kJ / mole}$$

$$(c) \quad W = -(n_g)RT$$

$$= -\frac{10}{18} \times 8.314 \times 373$$

$$= -1722.85 \text{ J}$$

$$= -1.72 \text{ kJ}$$

$$(d) \quad \Delta E = Q + W$$

$$= 22.2 - 1.72$$

$$= 20.48 \text{ kJ}$$

$$24. \quad 0.4 = 1 - \frac{T_C}{T_H}$$

$$0.55 = 1 - \frac{T_C - 60}{T_H}$$

$$0.55 = 1 - \frac{T_C}{T_H} + \frac{60}{T_H}$$

$$0.15 = \frac{60}{T_H}$$

$$T_H = \frac{60}{0.15} = 400$$

$$T_C = 240$$

$$25. \quad \Delta S = \frac{\Delta H}{T} \Rightarrow 29.4 = \frac{4.60 \times 10^3}{T}$$

$$\Rightarrow T \approx 156.5 \text{ K}$$

$$26. \quad \sum \frac{dq_{\text{rev}}}{T} = \sum ds$$

Since S is a state function cycle integral will be Zero.

$$27. \quad 28.8 = \frac{30.5 \times 10^3}{T}$$

$$\Rightarrow T = 1059\text{K}$$

$$28. \quad dS = \int \frac{dQ}{T}$$

$$dS = \int \frac{C_p dT}{T}$$

$$= \int \frac{25.5}{T} dT + \int 13.6 \times 10^{-3} dT - \int 42.5 \times 10^{-7} T dT$$

$$= 25.5 [\ln T]_{300}^{600} + 13.6 \times 10^{-3} (600 - 300)$$

$$- 42.5 \times 10^{-7} \times \left[ \frac{T^2}{2} \right]_{300}^{600}$$

$$= 25.5 \ln 2 + 13.6 \times 10^{-3} \times 300 - \frac{42.5 \times 10^{-7}}{2} \times (600^2 - 360^2)$$

$$= 17.67 + 4.08 - \frac{42.5}{2} \times 10^{-7} \times 6^2 - 3^2 \times 10^4$$

$$= 17.67 + 4.08 - 573 - 75 \times 10^{-3}$$

$$= 21.177 \text{JK}^{-1} \text{mol}^{-1}$$

$$29. \quad \Delta S = 2 \times 239.7 - (152.3 + 223)$$

$$= 479.4 - 375.3$$

$$= 104.1 \text{J} / \text{mol}^{-1} \text{K}$$

$$\Delta G = 29300 - 298 \times 104.1$$

$$= -1721.8$$

$$30. \quad \Delta G = \Delta H - T\Delta S$$

$$= -2808 \times 10^3 - 310 \times 182.4$$

$$= -2864.5 \text{kJ}$$

$$31. \quad \text{Na(s)} + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{NaCl(s)}$$

$$\Delta S = 72 - \left[ 51 + \frac{223}{2} \right] = -90.5 \text{JK}^{-1} \text{mol}^{-1}$$

$$\frac{1}{2} \text{N}_2 - 2\text{H}_2 + \frac{1}{2} \text{Cl}_2 \longrightarrow \text{NH}_4\text{Cl(s)}$$

$$\Delta S = 95 - \left[ \frac{1}{2} \times 192 + 2 \times 131 + \frac{1}{2} \times 223 \right]$$

$$= 95 - (96 + 262 + 111.5)$$

$$= 95 - 419.5$$

$$= -374.5 \text{JK}^{-1} \text{mol}^{-1}$$

Graphite  $\rightarrow$  Diamond

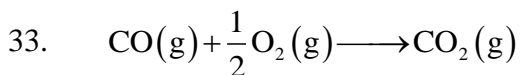
$$\Rightarrow \Delta S = -[5.19 - 2.43] = -3.26 \text{JK}^{-1} \text{mol}^{-1}$$

$$32. \quad \Delta H = -106.7 - (-139.3) = 32.6 \text{ kJ / mol}$$

$$\Delta G = 32.6 \times 10^3 - 298 \times 94.98$$

$$= 32600 - 28304$$

$$= +ve$$



$$\Delta H^\circ = -393.5 - [-110.5 + 0]$$

$$\Delta H^\circ = -283 \text{ kJ / mol}$$

$$\Delta S^\circ = 213.7 - \left[ 197.6 + \frac{205}{2} \right]$$

$$\Delta S^\circ = -86.4 \text{ JK}^{-1} \text{ mol}$$

$$\Delta G^\circ = -283000 - 298 \times (-86.4)$$

$$\Delta G^\circ = -257.25 \text{ kJ}$$

$$34. \quad \Delta H = \Delta E + (-1) \times 8.314 \times 298$$

$$\Delta H = -10.46 - \frac{2477.5}{1000}$$

$$= -12.9375$$

$$\Delta G = -12.94 \times 10^3 - 298 \times (-43.93)$$

$$= 151 \text{ J}$$

$$= +0.151 \text{ kJ mol}^{-1}$$

Not feasible.



$$(I) \quad \Delta H = -94.05 - [-57.8 - 26.42] = -9.83 \text{ kcal}$$

$$(II) \quad \Delta G = 0 + (-94.24) - [-54.64 - 32.79]$$

$$= -6.81 \text{ kcal / mol}$$

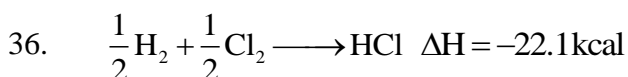
$$(III) \quad -6.81 \times 10^3 = -9.83 \times 10^3 - 298 \times \Delta S$$

$$\Rightarrow \Delta S = -10.13 \text{ cal}$$

$$(IV) \quad \Delta H = \Delta E (\because \Delta n = 0)$$

$$\Delta E = -9.83 \text{ kcal / mol}$$

$$(V) \quad \Delta S = 31.2 + 81.1 - [x + 47.3] = -10.13 = +45.13 \text{ cal mol}^{-1} \text{ K}^{-1}$$



$$\frac{\Delta H_{350} - \Delta H_{300}}{350 - 300} = 1 \times 6.8 - \left[ \frac{6.82}{2} + \frac{7.7}{2} \right]$$

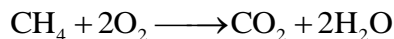
$$\frac{\Delta H_{350} - 22.1 \text{ kcal}}{50} = \frac{6.8 - 7.26}{1000} = -\frac{0.46}{1000}$$

$$\Delta H_{350} + 22.1 \text{ kcal} = -\frac{23}{1000}$$

$$\Rightarrow \Delta H_{350} = -22.123 \text{ kcal}$$

37.  $1 \text{ m}^3 = 1000 \ell$

$$\Rightarrow 1000 \ell = \frac{1000}{22.7} \text{ mole}$$

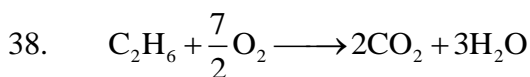


$$\Delta H = -2 \times 241.6 - 398.8 - (-76.2)$$

$$= -805.8 \text{ kJ/mol}$$

$$\therefore \text{Heat evolved} = \frac{1000}{22.7} \times 805.8 \text{ kJ/mol}$$

$$= 35.498 \text{ MJ}$$



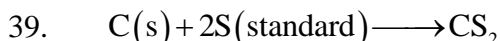
$$\Delta H = -\frac{3120}{2}$$

$$\Rightarrow -\frac{3120}{2} = [2 \times -395 + 3 \times -286] - \Delta H_f^\circ(\text{C}_2\text{H}_6)$$

$$\Delta H_f^\circ(\text{C}_2\text{H}_6) = -(790 + 858) + \frac{3120}{2}$$

$$= -1648 + 1560$$

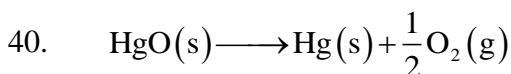
$$= -88 \text{ kJ/mol}$$



$$\Rightarrow \Delta H_f = +108.76 + [-393.3 + 2 \times -293.72]$$

$$= +108.76 - [393.3 + 2 \times 293.72]$$

$$= +128.02 \text{ kJ}$$



$$\Delta H_R = 0 - (-90.8 \text{ kJ mol}^{-1})$$

$$= +90.8 \text{ kJ/mol}$$

$$1 \text{ mole HgO} \longrightarrow 90.8 \text{ kJ}$$

$$n_{\text{Hg}} = \frac{41.84}{90.8} = 0.461$$

$$m_{\text{Hg}} = 0.465 \times 200.6 = 92.44$$

$$\therefore \Delta H = \Delta E + \Delta nRT$$

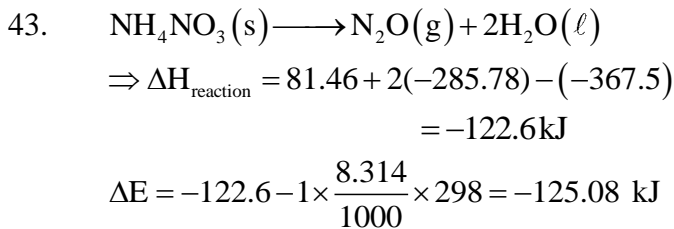
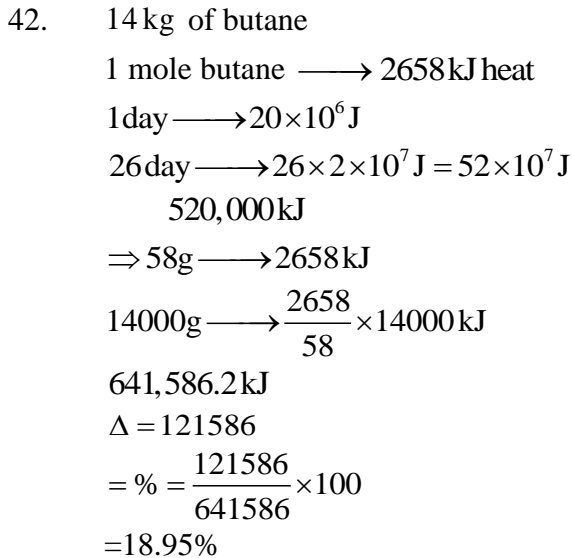
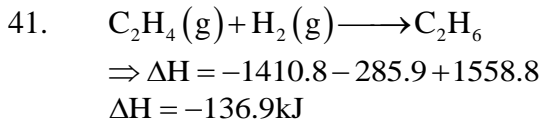
$$90.8 = \Delta E + \frac{1}{2} \times \frac{8.314 \times 298}{1000}$$

$$90.8 \text{ kJ} = \Delta E + 1.24 \text{ kJ}$$

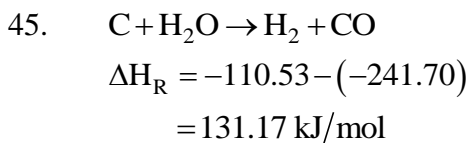
$$89.56 \text{ kJ} = \Delta E \quad \Rightarrow 89.56 \text{ kJ} \longrightarrow 1 \text{ mole Hg}$$

$$n_{\text{Hg}} = \frac{41.84}{89.56} = 0.4672$$

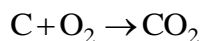
$$m_{\text{Hg}} = 0.4672 \times 200.6 = 93.72$$



44.  $\Delta H = -337 - 68.4 - (-373)$   
 $= -32.4 \text{ kcal}$



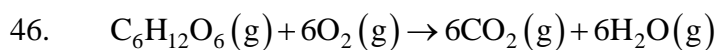
So, total heat required  $= 131.17 \times \frac{100}{12}$



$\Delta H_{\text{R}} = -393.51 \text{ kJ/mole}$

$131.17 \times \frac{100}{12} = 393.51 \times \frac{x}{12}$

$\Rightarrow x = \frac{100}{3} = 33.33 \text{ g}$

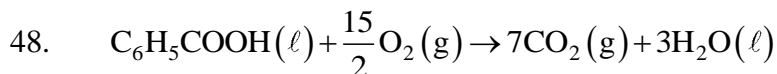


$$\Delta n_g = 6$$

$$\Delta U = -651000 - 6 \times 2 \times 290 \\ = 654,480$$

$$47. \quad n_{\text{CH}_4} = \frac{89.03}{890.3} = \frac{1}{10} \Rightarrow W_{\text{CH}_4} = 1.6 \text{ g}$$

$$n_{\text{CO}_2} = \frac{89.03}{890.3} = \frac{1}{10} \Rightarrow W_{\text{CO}_2} = 4.4 \text{ g}$$



$$\Delta U_R = -\frac{23.85 \times 0.55}{\frac{0.5}{122}} = -3200.67$$

$$\Delta H_R = -3200.67 + \left( -\frac{1}{2} \times \frac{8.314}{1000} \times 288 \right) = -3201.87$$

$$49. \quad \frac{120}{180} \times 2880 \times \frac{1}{4} = 100 \times x \\ x = 4.8$$

$$50. \quad \Delta_R C_P = 2 \times 4R - \frac{7}{2}R - 3 \times \frac{7}{2}R = -6R$$

$$\Delta H_{323\text{K}} = \Delta H_{300\text{K}} + \int_{300}^{323} -6R dT \\ = -91.94 - \frac{6 \times 8.31 \times 23}{1000} = -93.09$$

$$51. \quad \Delta_R C_P = \left( \frac{8}{5}\alpha + 4\beta T \right) - 3 \times (\alpha + \beta T) = -\frac{7}{5}\alpha + \beta T$$

$$\Delta H_{600\text{K}} = \Delta H_{300\text{K}} + \frac{1}{1000} \int_{300}^{600} \left( -\frac{7}{5}\alpha + \beta T \right) dT \\ = -100 - \frac{7}{5}\alpha \times \frac{300}{1000} + \frac{\beta}{2000} (600^2 - 300^2) \\ = -100 - 0.42\alpha + 135\beta$$

$$52. \quad \Delta H_{\text{C, Propene}} = 3 \times (-393.5 - 285.8) - 20.42 = -2058.32$$

$$\Delta H_{\text{C, Cyclopropene}} = -2058.32 - 33 = -2091.32$$

$$53. \quad (1) + (2) - (3)$$

$$\Delta H_f = -48 - 68.4 + 14 = -102.4$$



$$54. \quad \Delta_R C_P = \left(7.3 + \frac{3}{100} T\right) - \left(7.3 + \frac{2}{100} T\right) = \frac{T}{100}$$

$$\begin{aligned} \Delta H_{1000K} &= \Delta H_{300K} + \frac{1}{1000} \int_{300}^{1000} \frac{T}{100} \times dT \\ &= -41.8 + \frac{1}{1000} \times \frac{1000^2 - 300^2}{200} = -37.25 \text{ kJ} \end{aligned}$$

$$55. \quad -105 = 20.5 + 96 + 28.75 + x - 159.5$$

$$x = -90.75 \text{ kcal/mole}$$

56. Delong and petit law

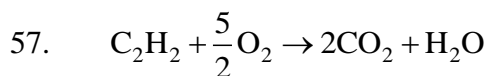
$$0.0276 \times \text{At.wt} \approx 6.4$$

$$\Rightarrow \text{At.wt} \approx 232$$

$$\frac{79.34}{\frac{232}{x}} = \frac{114.79 - 79.34}{35.5} \Rightarrow x = 2.92$$

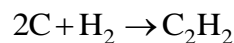
So, exact value of  $x$  is 3.

$$\frac{79.34}{\frac{\text{AW}}{3}} = \frac{114.79 - 79.34}{35.5} \Rightarrow \text{AW} = 238.36$$



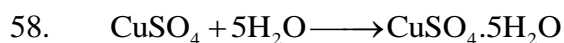
$$\Delta H = -312 = 2 \times (-94.38) + (-68.38) - \Delta H_{f, \text{C}_2\text{H}_2}$$

$$\Delta H_{f, \text{C}_2\text{H}_2} = 54.86$$



$$\Delta H = 54.86 = 2 \times 150 + 2 \times 51.5 - 2 \times 93.6 - \text{BE}_{\text{C}\equiv\text{C}}$$

$$\text{BE}_{\text{C}\equiv\text{C}} = 160.94$$



$$\Delta H = -15.9 - 2.8 = -18.7$$

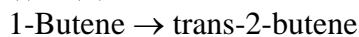


$$\Delta H_R = 36.8 - 28 = 8.8 \text{ kcal/mole}$$

$$n_{\text{HAuBr}_4} = \frac{0.44}{8.8} = \frac{1}{20}$$

$$\% \text{ conversion} = \frac{1}{20} \times 100 = 5\%$$

60. (i) – (ii)



$$\Delta H = \Delta H_1 - \Delta H_2 = -649.8 + 647 = -2.8$$

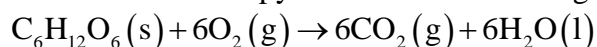
$$\text{So, } \Delta H_1 = -1, \Delta H_2 = 1.8$$

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



$$\Delta H_{\text{C}} = 6 \times \Delta H_{\text{f}}(\text{CO}_2) + 6 \times \Delta H_{\text{f}}(\text{H}_2\text{O}) - \Delta H_{\text{f}}(\text{C}_6\text{H}_{12}\text{O}_6)$$

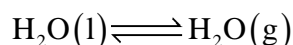
$$\Delta H^{\circ} = 6(-400) + 6(-300) - (-1300) = -2900 \text{ kJ/mol}$$

For one gram of glucose, enthalpy of combustion

$$\Delta H^{\circ} = -\frac{2900}{180} = -16.11 \text{ kJ/g}$$

13. (b)

Given conditions are boiling conditions for water due to which system is in equilibrium .



$$\Delta S_{\text{total}} = 0$$

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

$$\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$$

For process ,  $\Delta S_{\text{system}} > 0$

$$\Delta S_{\text{surroundings}} < 0$$

14. (c)

From 1<sup>st</sup> law of thermodynamics

$$q_{\text{sys}} = \Delta U - w = 0 - [-P_{\text{ext}} \Delta V]$$

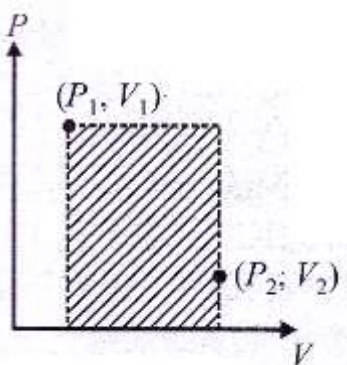
$$= 3.0 \text{at} \times (2.0\text{L} - 1.0\text{L}) = 3.0\text{L} - \text{atm}$$

$$\begin{aligned} \therefore \Delta S_{\text{surr}} &= \frac{(q_{\text{rev}})_{\text{surr}}}{T} = -\frac{q_{\text{sys}}}{T} \\ &= -\frac{3.0 \times 101.3 \text{ J}}{300 \text{ K}} = -1.013 \text{ J/K} \end{aligned}$$

15. (a)  
 $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{diamond})$  (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,  $P_{\text{ext}} = 0$ , so  $w = 0$ , hence  $\Delta U = 0$   
 Therefore,  $\Delta T = 0$ ,  $T_2 = T_1$  and  $P_2 V_2 = P_1 V_1$   
 However, the process is adiabatic irreversible, so we can't apply  $P_2 V_2^\gamma = P_1 V_1^\gamma$ .  
 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,  $T_2 < T_1$   
 $\therefore \Delta T = -\text{ve}$  and also  $\Delta U = -\text{ve}$   
 (B) In free expansion,  $P_{\text{ext}} = 0, \therefore W = 0$   
 From 1<sup>st</sup> law of thermodynamics,  
 $\Delta U = q + W$   
 $\therefore \Delta U = q$

If expansion is carried out isothermally,  $\Delta U = 0$

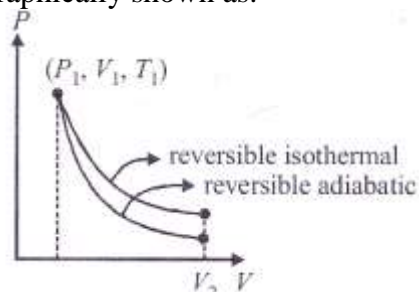
Hence  $q = 0$

$\therefore$  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

$$(a) \quad q_{AC} = \Delta U_{AC} = nC_{v,m} (T_2 - T_1) = \Delta U_{BC}$$

$$W_{AB} = -nRT \ln \left( \frac{V_2}{V_1} \right) \text{ (pressure is not constant)}$$

$$(b) \quad W_{BC} = -P_2 (V_1 - V_2) = P_2 (V_2 - V_1)$$

$$q_{BC} = \Delta H_{BC} = nC_{p,m} (T_2 - T_1) = \Delta H_{AC}$$

$$(c) \quad \Delta H_{CA} = nC_{p,m} (T_1 - T_2)$$

$$(d) \quad \Delta U_{CA} = nC_{v,m} (T_1 - T_2)$$

$$\Delta H_{CA} < \Delta U_{CA} \text{ since both are negative } (T_1 < T_2) \text{ and } C_{p,m} > C_{v,m}$$

6. (a, c)

Enthalpy of formation is the enthalpy change for formation of 1 mole of substance from its elements present in the most stable natural form.

7. (a, b, c)

P-V work done is applicable for reversible isobaric as well as isothermal and adiabatic process.

$$w = -\int P_{\text{ext}} \cdot dV$$

For van der Waals equation

$$P_{\text{ext}} = P = \left( \frac{RT}{v-b} - \frac{a}{v^2} \right)$$

$$w = -\int dv \left( \frac{RT}{v-b} - \frac{a}{v^2} \right) \quad \dots\dots(i)$$

Equation (i) is not applicable to irreversible process. Therefore work done is calculated assuming pressure is constant throughout the process.

8. (a, b, d)  
 From state I to II (Reversible isothermal expansion):  
 $T \rightarrow \text{constant}$ ,  $\Delta V \rightarrow +\text{ve}$ ,  $\Delta S \rightarrow +\text{ve}$ ,  $\Delta H \rightarrow 0$   
 $\Delta P \rightarrow -\text{ve}$   
 From state II to III (Reversible adiabatic expansion):  
 $q \rightarrow 0$ ,  $\Delta V \rightarrow +\text{ve}$ ,  $\Delta S \rightarrow \text{constant}$   
 $\Delta H \rightarrow -\text{ve}$ ,  $\Delta P \rightarrow -\text{ve}$ ,  $\Delta T \rightarrow -\text{ve}$   
 $\therefore$  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)  
 $K \rightarrow L \Rightarrow V$  increasing at constant P  
 Hence, T increases (Heating)  
 $L \rightarrow M \Rightarrow P$  decreasing at constant V  
 Hence, T decreases (Cooling),  
 $M \rightarrow N \Rightarrow V$  decreasing at constant P  
 Hence, T decreases (Cooling),  
 $N \rightarrow K \Rightarrow P$  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)  
 $\text{SnO}_2(\text{s}) + \text{C}(\text{s}) \longrightarrow \text{Sn}(\text{s}) + \text{CO}_2(\text{g})$   
 $\Delta_f H^\circ = [-394] - [-581] = 187 \text{ kJ / mole} = 187 \times 10^3 \text{ J / mol}$   
 $\Delta_f S^\circ = [52 + 210] - [56 + 6] = 200 \text{ JK}^{-1} \text{ mol}^{-1}$   
 $T = \frac{\Delta_f H^\circ}{\Delta_f S^\circ} = \frac{187 \times 10^3}{200} = 935 \text{ K}$
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)  
 $T_1 = 900\text{K}$   
 Calculation of  $T_2$  after reversible adiabatic process  
 $\Delta U = nC_v dT$   
 $\Rightarrow -1800R = 1 \frac{5}{2} R (T_2 - 900)$   
 $T_2 = 180\text{K}$

$$W_{II} = -nRT_2 \ln \frac{V_3}{V_2} = W_I$$

$$\Rightarrow -1 \times R \times 180 \ln \frac{V_3}{V_2} = -1800R$$

$$\Rightarrow \ln \frac{V_3}{V_2} = 10$$

3. (166.28)

$$\text{Slope} = \frac{dy}{dx} = \frac{d(\ln K)}{d(10^4/T)}$$

$$\Rightarrow \frac{-\Delta H^\phi}{10^4 R} = \frac{-7 - (-3)}{12 - 10}$$

$$\Rightarrow \Delta H^\phi = 2 \times 10^4 \times 2 = 2 \times 10^4 \times 8.314 \text{ J/mol}$$

$$= 166.28 \text{ kJ/mol}$$

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:

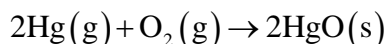
$$\ln \left( \frac{p_z}{1} \right) = -\frac{\Delta H^\phi}{RT} + \frac{\Delta S^\phi}{R}$$

$$\text{We get, } -3 = -\frac{2 \times 10^4 \times R}{R \times 1000} + \frac{\Delta S^\phi}{R}$$

$$\Rightarrow S^\phi = 17R \Rightarrow \Delta S^\phi = 17 \times 8.314 \text{ J/K-mol}$$

$$\Rightarrow \Delta S^\phi = 141.34 \text{ J/K-mol}$$

5. (90.39)



$$\Delta_r H^\circ = 2\Delta_f H^\circ(\text{HgO}, s) - 2\Delta_f H^\circ(\text{Hg}, g) - \Delta_f H^\circ(\text{O}_2, g)$$

$$= 2\Delta_f H^\circ(\text{HgO}, s) - 2\Delta_f H^\circ(\text{Hg}, g) \quad \dots\dots\dots(i)$$

$$[\because \Delta_f H^\circ(\text{O}_2, g) = 0]$$

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 = 20kJ / K at 298K]

$$= -[20(312.8 - 298)] - 3RT$$

$$= -296 - 3 \times 8.3 \times 10^{-3} \times 298 \text{ kJ} = -303.42 \text{ kJ}$$

Hence, from equation (i)

$$-303.42 = 2\Delta_f H^\circ (\text{HgO}, s) - 2 \times 61.32$$

$$\text{Or, } 2\Delta_f H^\circ (\text{HgO}, s) = -180.78 \text{ kJ}$$

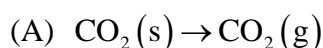
$\therefore$  Standard Molar Enthalpy of formation of HgO

$$= \frac{-180.78}{2} = -90.39 \text{ kJ}$$

$$\Rightarrow |X| = 90.39$$

### Matrix-Match

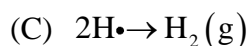
1. (A) – P, R, S ; (B) – R, S ; (C) – T ; (D) – P, Q, T



It is phase transition. The process is endothermic (sublimation). Gas is produced, so entropy increases.

(B) On heating  $\text{CaCO}_3$  decomposes. So, process is endothermic.

The energy increases as gaseous product is formed.



Entropy decrease as number of gaseous particles decreases.

(D) The transition between different allotropes is considered as phase transition.

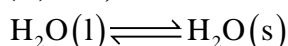
White and red P are allotropes.

Due to polymeric nature of red P, its entropy is less than that of white P.

Red P is more stable than white.

So,  $\Delta H$  is –ve

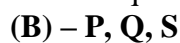
2. (A) – R, T ; (B) – P, Q, S ; (C) – P, Q, S ; (D) – P, Q, S, T



It is at equilibrium at 273 K and 1 atm

So,  $\Delta S_{\text{sys}}$  is negative.

As it is equilibrium process, so  $\Delta G = 0$



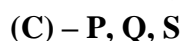
Expansion of 1 mole of an ideal gas in vacuum under isolated condition

Hence,  $w = 0$

$$\text{And } q_p = C_p dT (\because dT = 0)$$

$$\Rightarrow q = 0$$

$$\Delta U = C_v dT (\because dT = 0) \Delta U = 0$$



Mixing of two ideal gases at constant temperature

Hence,  $\Delta T = 0$

$$\therefore q = 0; \Delta U = 0$$

$$\text{Also } w = 0 (\Delta U = q + w)$$



Reversible heating and cooling of gas follows same path; also initial and final position is same.

$$\text{Hence, } \left. \begin{array}{l} q = 0 \\ w = 0 \end{array} \right\} \text{ Path same}$$



$$\left. \begin{array}{l} \Delta U = 0 \\ \Delta G = 0 \end{array} \right\} \text{State function}$$

Subjective

1.  $\Delta H = -114.52 \text{ J}$
2.  $\Delta H^\circ = -285.4 \text{ kJ/mol}$ ,  $\Delta G^\circ = -257.2 \text{ kJ/mol}$
3. (ii)  $-W = q = 620.77 \text{ J}$ , (iii)  $\Delta H = 0$ ,  $\Delta U = 0$ ,  $\Delta S = 0$
4.  $\Delta U = 0.1 \text{ litre atm}$ ,  $\Delta H = 9.9 \text{ litre atm}$
5.  $-557 \text{ kJ/mol}$