

HINTS & SOLUTIONS

EXERCISE - 1

Single Choice

- Entropy is extensive property & others are intensive properties.
- The compressor has to run for longer time releasing more heat to the surroundings.
- In a reversible process, the driving and the opposite forces are nearly equal, hence the system and the surroundings always remain in equilibrium with each other.

- A → B, volume is not changing (Isochoric)
B → C Isobaric
C → A Temperature is constant (Isothermal)

- (D) $w = -P_{\text{ext}} \Delta V = -\Delta n_g RT$ and Δn_g is -ve for I and II also $\Delta V = -ve$ for IV

$$9 \quad H = W = i^2 R t = \frac{V^2 t}{R} = \frac{120 \times 120 \times (10 \times 60)}{6}$$

$$= 14.4 \times 10^5 \text{ joule}$$

- Case (i) $\Delta V = 0, W = 0$
Case (ii) $P = \text{constant}, W = -P(2V_1 - V_1) = -PV_1$

$$14. \quad W = -2.303 nRT \log \frac{V_2}{V_1}$$

$$= -2.303 \times 1 \times 8.314 \times 10^7 \times 298 \log \frac{20}{10}$$

$$= -298 \times 10^7 \times 8.314 \times 2.303 \log 2.$$

- At constant volume $\Delta H = \Delta U + V\Delta P$
 $\Rightarrow -560 = \Delta U + 10 \times (-30) \times 0.1 \Rightarrow \Delta U = -530 \text{ kJ}$

- Let final common temperature is T_f
Heat gained by Zinc piece = Heat lost by water
 $0.4(T_f - 20) \times 65.38 = 4.2(100 - T_f) \times 180 \Rightarrow T_f = 97.3^\circ \text{C}$

- We know that $\Delta E = Q + W = 600 + (-300) = 300 \text{ J}$
 $W = -300$, because the work done by the system.

- Bomb calorimeter is commonly used to find the heat of combustion of organic substances which consists of a sealed combustion chamber, called a bomb. If a process is run in a sealed container then no expansion or compression is allowed, so $w = 0$ and $\Delta U = q$.

$$\Delta U < 0, w = 0$$

- For isochoric process $\Delta V = 0$ so $q_v = \Delta E$ i.e. heat given to a system under constant volume is used up in increasing ΔE .

- When a real gas is forced through a porous plug into a region of low pressure, it is found that due to expansion, the gas on the side of low pressure gets cooled.

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is known as Joule-Thomson effect.

$$24. \quad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \Rightarrow 300 \times V^{1/3} = T_2 (8V)^{1/3} \Rightarrow T_2 = 150 \text{ K}$$

$$W = nC_v(T_2 - T_1) = 1 \times 3R(150 - 300) = 3 \times 2(-150) = -900 \text{ cal}$$

- $\Delta H =$ heat given. So, process is isobaric.
 $w = -P_{\text{ext}}(\Delta V) = -1 \times 2 \text{ litre.atm} = -202.6 \text{ J}$
Hence, $q = 202.6 \text{ J} = \Delta H$. and $\Delta E = q + w = 0$.

- State 1 \longrightarrow State 2
(1 L, 10 atm, 300 K) (4L, 5 atm, 600 K)

$$\text{Heat given, } q = 50 \times (600 - 300) = 15000 \text{ J}$$

$$W = -P_{\text{ext}}(V_2 - V_1) = -1(4 - 1) = -3 \text{ L atm} = -300 \text{ J}$$

$$\Delta E = q + W = 15000 - 300 = 14700 \text{ J}$$

$$\Delta H = \Delta E + P_2 V_2 - P_1 V_1 = 14700 \text{ J} + (20 - 10) \times 100 \text{ J} = 15.7 \text{ KJ}$$

- In isothermal reversible process ideal gas has constant temperature and so $\Delta E = 0$ and $\Delta H = \Delta E = 0$.

- Mixing of non-reacting gases increases randomness and so increase entropy.

- NaNO_3 is a solid, which is converted to liquid ions.

- Reaction is endothermic and no. of moles increases on decomposition.

$$37. \quad \Delta S_{\text{gas}} = nC_{v,m} \ln \frac{T_2}{T_1} = 2 \times \left(\frac{5}{2} - 1 \right) R \ln 2 = 3R \ln 2$$

$$38. \quad \Delta S = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = C_{v,m} \ln 2 + R \ln \left(\frac{1}{2} \right)$$

$$= (C_{v,m} - R) \ln 2$$

$$41. \quad \Delta S_{\text{gas}} = nC_{v,m} \ln \frac{T_2}{T_1} = 2 \times \frac{3}{2} R \ln \frac{573}{473} = 3R \ln \left(\frac{573}{473} \right)$$

$$42. \Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

For adiabatic process ($Q = 0$)

$$\Delta E = W \Rightarrow nC_v \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1} \therefore \Delta S = 0.$$

$$44. \Delta S_{\text{system}} = nR \ln \frac{V_2}{V_1} = 2 \times R \times \ln 2 = 11.52 \text{ J/K}$$

$$\Delta S_{\text{surrounding}} = -\frac{3.41 \times 1000}{310} = -11 \text{ J/K}$$

$$\Delta S_{\text{total}} = +11.52 - 11 = +0.52 \text{ J/K}$$

$$46. \text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{g}) \Delta H_{\text{vap}} = \Delta S_{\text{vap}} T_{\text{B.P.}} = x_1 T_1$$

$$\Delta H_f(\text{H}_2\text{O}, \text{g}) = \Delta H_f(\text{H}_2\text{O}, \text{l}) + \Delta H_{\text{vap}} = x_2 + x_1 T_1$$

$$\Delta H_{\text{reaction}} = 2\Delta H_f(\text{CO}_2, \text{g}) + 3\Delta H_f(\text{H}_2\text{O}, \text{g}) - \Delta H_f(\text{C}_2\text{H}_6, \text{g})$$

$$= 2x_3 + 3(x_2 + x_1 T_1) - x_4 = 2x_3 + 3x_2 + 3x_1 T_1 - x_4.$$

$$47. \Delta S_{(\text{system})} = \frac{1 \times -401.7}{368} = -1.09 \text{ JK}^{-1}$$

The ice-water both absorbs the 401.7 J mol^{-1} at temperature 273 K

$$\therefore \Delta S_{\text{surrounding}} = \frac{1 \times 401.7}{273} = 1.47 \text{ JK}^{-1} \text{ and } \Delta S_{(\text{universe})}$$

$$= -1.09 + 1.47 = 0.38 \text{ JK}^{-1}$$

48. Equilibrium at standard state means equilibrium constant is 1.

$$51. \Delta G = (\Delta H) - T(\Delta S)$$

$\downarrow \quad \quad \downarrow$
 $-ve \quad -ve$

since both are $-ve$, the reaction would have a $-ve \Delta G$

$$\text{below a temperature of } \frac{33000}{58} \text{ K } (= 569\text{K})$$

52. It is because of the fact that for spontaneity, the value of $\Delta G = (\Delta H - T\Delta S)$ should be < 0 . If ΔS is $-ve$, the value of $T\Delta S$ shall have to be less than ΔH or the value of ΔS has

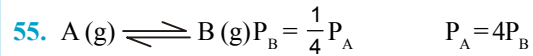
$$\text{to be less than } \frac{\Delta H}{T} \text{ i.e., } \frac{x}{298}.$$

54. ΔG for $3\text{Fe}(\text{s}) + 2\text{O}_2(\text{g}) \longrightarrow \text{Fe}_3\text{O}_4(\text{s})$ can be obtained by taking

$$[(2) + 4 \times (1)] \times \frac{1}{3}$$

$$\text{Hence, we get } \Delta G_f = [-19 + 4 \times (-177)] \times \frac{1}{3} = -242.3 \text{ kcal}$$

for 1 mole Fe_3O_4



$$K_p = \frac{P_B}{P_A} = \frac{P_A/4}{P_A} = \frac{1}{4}$$

At equilibrium, $\Delta G = 0$.

$$\Delta G^\circ = -RT \ln K_p = -RT \ln \frac{1}{4} = RT \ln 4$$

58. Work is not a state function because it depends upon the path followed.

61. In isothermal process, $\Delta T = 0$
 In isobaric process, $\Delta P = 0$
 In adiabatic process, $q = 0$.
 In isochoric process $\Delta V = 0$

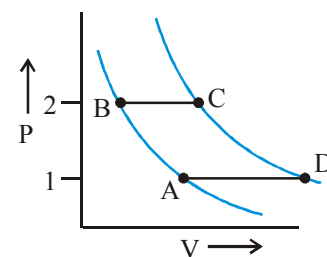
62 For IV volume is constant (isochoric)
 For I pressure is constant (isobaric)

63. Process direction in V - P diagram is clockwise so, process direction in P - V diagram is anti-clockwise.
 Net work done on the system = Area of the ellipse

$$= \pi \times \frac{(P_2 - P_1)}{2} \times \frac{(V_2 - V_1)}{2}$$

64. At A and D the temperatures of the gas will be equal, so $\Delta E = 0, \Delta H = 0$
 Now $w = w_{AB} + w_{BC} + w_{CD} = -P_0 V_0 - 2P_0 V_0 \ln 2 + P_0 V_0$
 $= -2P_0 V_0 \ln 2$

66. W_{net} = area enclosed



$$V = \frac{nRT}{P}$$

$$V_A = \frac{2R \times 300}{1} = \frac{600R}{1}$$

$$V_B = \frac{2R \times 300}{2} = \frac{300R}{1}; V_C = \frac{2R \times 400}{2} = \frac{400R}{1}$$

$$V_D = \frac{800R}{1}$$

$$W_{AB} = -nRT_A \ln \frac{V_B}{V_A} = -2R(300) \ln \frac{1}{2} = 600 R \ln 2$$

$$W_{BC} = -2(400-300)R = -200 R$$

$$W_{CD} = -2R(400) \ln \frac{V_D}{V_C} = -800 R \ln 2$$

$$W_{AD} = -1(600R - 800R) = 200 R$$

$$W_{\text{Total}} = W_{AB} + W_{BC} + W_{CD} + W_{AD} = -200 R \ln 2 - 100 R \ln 4$$

67. I – Work done by the system in case of infinite stage expansion is more than single stage expansion.
 III – Single stage process is a irreversible process.
 IV – We have 5 points on PV diagram.

69. latent heat of vaporisation of water = 2.25×10^6 J/kg
 $\Delta H = 2.25 \times 10^6$ J/kg.
 work done = $-P_{\text{ext}}(V_2 - V_1)$
 $\Delta H = 2.25 \times 10^6$ J/kg
 $\Delta H = \Delta U + P\Delta V$

(a) Now, volume of water $V = \left(\frac{m}{d}\right) = \frac{1}{1000} \text{ M}^3 = 1 \text{ L}$

(b) volume of steam = $\frac{1000}{0.6} = 1666.67 \text{ L}$

$$2.25 \times 10^6 = \Delta U + 1[1666.67 - 1]101.325$$

$$\Delta U = 22.5 \times 10^5 - 1.68 \times 10^5 = 20.8 \times 10^5 = 2.08 \times 10^6 \text{ J}$$

70. Volume = $5 \times 10 \times 3 = 150 \text{ m}^3 = 150 \times 10^3 \text{ L}$;
 $T = 27^\circ\text{C} = 300 \text{ K}$; $P = 1 \text{ atm}$
 $PV = nRT \Rightarrow 1 \times 150 \times 10^3 = n \times 0.082 \times 300$
 $\Rightarrow n = 6097.6$
 Total energy released per second = $150 \times 50 = 7500 \text{ J/sec}$.
 Amount of energy released by persons = energy gained by air $\Rightarrow [7500] t_{\text{sec}} = n C [dT]$
 $\Rightarrow 7500 t_{\text{sec}} = 6097.6 \times \frac{7}{2} \times 8.312 \times 15$
 $\Rightarrow t_{\text{sec}} = 354.87 \text{ sec} = \frac{354.87}{60} = 5.91 \text{ minutes}$.

EXERCISE - 2

Part # 1 : Multiple Choice

6. $\Delta H = (n_1 C_{p,m_1} + n_2 C_{p,m_2}) \Delta T = \left(0.5 \times \frac{7}{2} R + 0.5 \times 4R\right) (-100)$
 $= -375 R$ and $\Delta U = \left(0.5 \times \frac{5}{2} R + 0.5 \times 3R\right) (-100) = -275 R$.

13. $\Delta S = nC_v \ln \left(\frac{T_f}{T_i}\right) + nR \ln \left(\frac{V_f}{V_i}\right) = 5 \ln \frac{373}{298} + 2 \ln 10$

$$\Delta H = nC_p \Delta T = n(C_v + R) \Delta T = 1 \times 7 \times 75 = 525 \text{ cal}$$

14. Boiling of a liquid at normal boiling point is a equilibrium process and on decreasing the pressure equilibrium will go forward and ΔG will be negative and vice versa.

16. Avg. $C_{v,m} = \frac{n_1 C_{v,m_1} + n_2 C_{v,m_2}}{n_1 + n_2} = \frac{1 \times 3R + 2 \times \frac{3}{2} R}{3} = 2R$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \Rightarrow 320 \times \frac{3}{12}^{-1} = T_2 \times (4)^{3/2-1} \Rightarrow T_2 = 160 \text{ K}$$

$$\Delta U = (n_1 + n_2) C_{v,\text{avg}} \Delta T = 3 \times 2R \times (160 - 320) = -960 R$$

17. $dE = dW + dQ$; $-dW = dQ - dE \therefore \frac{dQ}{dW} = \frac{dQ}{dQ - dE}$

$$= \frac{c_p}{(c_p - c_v)} = \frac{7R}{2R} \left(c_p = \frac{7R}{2}\right)$$

19. (A) $w = -nR \Delta T = -2 \times 8.314 \times 100 = -1662.8 \text{ J}$

$$\Delta U = n \int_{300}^{400} C_{v,m} dT = 2 \times \int_{300}^{400} (20 + 10^{-2} T) dT$$

$$= 2 \left[20 \times 100 + \frac{10^{-2}}{2} (400^2 - 300^2) \right] = 4700 \text{ J}$$

$$4700 = q - 1662.8$$

$$\therefore q = 6362.8 \text{ J}$$

22. $T \propto \frac{1}{\sqrt{V}}$; $TV^{1/2} = \text{constant}$

For adiabatic process, $TV^{\gamma-1} = \text{constant}$

$$\therefore \gamma - 1 = \frac{1}{2}, \gamma = \frac{3}{2}$$

24. Molar mass = 102 gram/mole
 $P = 650 \text{ torr}$; $T = 77 + 273 = 350 \text{ K}$

$$Q = i \times t = 0.25 \times 600 = 150$$

$$E = Q \times V = 150 \times 12 = 1800 \text{ J}$$

This heat is supplied to the system at constant pressure that's why this is used for change in enthalpy

\therefore For vaporisation of 1.8 gram, amount of heat required $q = 1800 \text{ J}$

\therefore For vaporisation of 102 gram, amount of heat required $q = \frac{1800}{1.8} \times 102 \text{ J}$

$$= 102 \times 10^3 \text{ J} = 102 \text{ KJ/mole}$$

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

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

For determination of ΔU per mol ($\Delta n_g = 1$)

$$102 \text{ (KJ/mol)} = \Delta U + (1 \times 8.3 \times 350) \times 10^{-3}$$

$$\Rightarrow \Delta U = 102 - 2.9 = 99.1 \text{ KJ/mole}$$

25. Given energy = 1560 kJ

$$\text{Utilised energy} = \frac{1560 \times 50}{100} = 780 \text{ kJ}$$

44 kJ Utilised energy for evaporation of $\text{H}_2\text{O} = 18 \text{ gram}$

\therefore 780 kJ Utilised energy for evaporation of

$$\text{H}_2\text{O} = \frac{18}{44} \times 780 = 319 \text{ gm}$$

27. This is adiabatic irreversible process so, for this process

$PV^\gamma = \text{Constant}$, is not applicable

$$W = -P_{\text{ext}}(V_2 - V_1)$$

But for adiabatic process

$$W = dU = \left(\frac{P_2 V_2 - P_1 V_1}{\gamma - 1} \right)$$

$$PV = nRT$$

$$\Rightarrow 10 \times 10 = n \times 0.082 \times 273 \Rightarrow n = 4.47 \text{ moles}$$

$$-P_{\text{ext}}(V_2 - V_1) = \left(\frac{P_2 V_2 - P_1 V_1}{\gamma - 1} \right)$$

$$\Rightarrow -1 \times (V_2 - 10) = \frac{1 \times V_2 - 10 \times 10}{1.67 - 1}$$

$$\Rightarrow (10 - V_2) = \frac{V_2 - 100}{0.67} \Rightarrow 6.7 - 0.67 V_2 = V_2 - 100$$

$$\Rightarrow 106.7 = 1.67 V_2 \Rightarrow V_2 = 64$$

$$\therefore nR[T_2 - T_1] = P_2 V_2 - P_1 V_1$$

$$\Rightarrow 4.47 \times 0.082 [T_2 - 273] = 64 - 100 = -36$$

$$\Rightarrow (T_2 - 273) = -98.2 \Rightarrow T_2 = 174.8 \text{ K}$$

28. $q = 0, \Delta U = W$

$$nC_v(T_2 - T_1) = -P_{\text{ext}}(V_2 - V_1)$$

$$n \frac{3}{2} R(T_2 - 300) = -2 \left(\frac{nRT_2}{2} - \frac{nR \times 300}{1} \right)$$

$$\Rightarrow \frac{3}{2} (T_2 - 300) = (600 - T_2) \Rightarrow T_2 = 420 \text{ K}$$

$$W = nC_v(T_2 - T_1) = 2 \times \frac{3}{2} \times 2 (420 - 300) = 720 \text{ cal.}$$

$$32. 0.40 = aT_1^3 + bT_1 \Rightarrow 0.40 = a \times (1000) + b \times 10$$

$$\Rightarrow 0.4 = 1000a + 10b \quad \dots(1)$$

$$0.92 = aT_2^3 + bT_2 \Rightarrow 0.92 = a \times 8000 + 20b$$

$$\dots(2)$$

from Eqs. (1) and (2)

$$a = 2 \times 10^{-5}, b = 0.038$$

$$S_m = \int \frac{aT^3 + bT}{T} \cdot dT = \frac{a[T_2^3 - T_1^3]}{3} + b[T_2 - T_1]$$

$$= 0.427 \text{ J/K-mol}$$

35. As dew formation is spontaneous process, therefore, entropy or randomness of the universe will increase. As randomness of the system has decreased but randomness of the surrounding will increase larger so that change is positive.

$$36. \text{(D) No. of moles of sucrose} = \frac{34.2}{342} = 0.1$$

$-(\Delta G)_{T,P}$ = useful work done by the system

$$-\Delta G = -\Delta H + T \cdot \Delta S = + (6000 \times 0.1) + \frac{180 \times 0.1 \times 300}{1000}$$

$$= 605.4 \text{ kJ.}$$

$$37. \text{(A) } \Delta G_{200}^\circ = \Delta H_{200}^\circ - T \Delta S_{200}^\circ$$

$$\Delta H_{200}^\circ = 20 - 4 = 16 \text{ kJ/mol}$$

$$\Delta H_{T_2}^\circ = \Delta H_{T_1}^\circ + \Delta C_p [T_2 - T_1]$$

$$\Delta H_{400}^\circ = \Delta H_{200}^\circ + \frac{20 \times 200}{1000} \text{ kJ/mol} = 16 + 4$$

$$= 20 \text{ kJ/mol.}$$

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

$$\Delta H = \sum \Delta H_P - \sum \Delta H_R$$

$$\Delta H = -110.5 + 266.3 = 155.8 \text{ KJ}$$

$$\Delta S = \sum S_P - \sum S_R$$

$$\Delta S = 197.6 + 27.28 - (57.5 + 5.74) = 161.64 \text{ J/mole K}$$

For reaction to be spontaneous, $\Delta G < 0$

$$\Delta H - T\Delta S < 0 \Rightarrow T > \frac{\Delta H}{\Delta S} = \frac{155800}{161.64} = 964 \text{ K}$$

Part # II : Assertion & Reason

1. Work done against vacuum is zero. It is free expansion.

EXERCISE - 3

Part # I : Matrix Match Type

- (A) Reversible isothermal expansion of ideal gas
 $W = -2.303 nRT \log \frac{V_2}{V_1}$ and $\Delta E = \Delta H = 0$ (as $\Delta T = 0$)

(B) Reversible adiabatic compression of an ideal gas
 $PV^\gamma = \text{constant}$ and $W = \frac{nR(T_2 - T_1)}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$

(C) Irreversible adiabatic expansion of an ideal gas
 $W = \frac{nR(T_2 - T_1)}{\gamma - 1}$

(D) Irreversible isothermal compression of an ideal gas
 $\Delta H = 0$ (as $\Delta T = 0$)
- (A) A process carried out infinitesimally slowly is called reversible process

(B) A process in which no heat enters or leaves the system is called adiabatic process

(C) A process carried out at constant temperature is called isothermal process

(D) A process in equilibrium has $\Delta G = 0$

(E) $A(s) \longrightarrow A(g)$
 process of conversion of solid to gas is called sublimation

(F) In a cyclic process, state function have no change in their value. So, $\Delta E = 0, \Delta H = 0$.
- (A) $\Delta G_{\text{sys}} = 0 \Rightarrow$ equilibrium and free energy is zero. So, no useful work.

(B) $\Delta S_{\text{universe}} > 0 \Rightarrow$ Spontaneous process and able to do useful work.

(C) $\Delta S_{\text{universe}} < 0 \Rightarrow$ Nonspontaneous process and unable to do useful work.

(D) $\Delta G_{\text{sys}} > 0 \Rightarrow$ Nonspontaneous process and unable to do useful work.
- (A) For reversible process $\Delta S_{\text{universe}} = 0$ and for adiabatic process $\Delta S_{\text{system}} = 0$

(B) For reversible process $\Delta S_{\text{universe}} = 0$, and in vaporisation entropy of system increases

(C) Number of gaseous moles decreases. So, entropy of system decreases and N_2 is more stable. So, process is spontaneous. For spontaneous process $\Delta S_{\text{universe}} > 0$

(D) Number of gaseous moles increases. So, entropy of system increases.

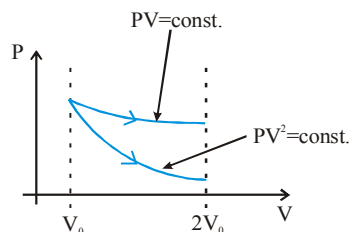
Part # II : Comprehension

Comprehension # 1 :

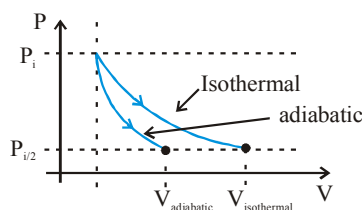
- $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O \quad \Delta H = -57.8 \text{ kcal/mole}$
 $c_v(N_2) = c_p(N_2) - R = 6.3 \text{ cal/}^\circ\text{C mole}$
 $c_v(H_2O) = 9.3 \text{ cal/}^\circ\text{C mole}$
 Assuming that both H_2 & O_2 are consumed.
 For 100 moles of air taken 40 moles of H_2O is formed.
 80 moles of N_2 left.
 $\therefore 40 \times 57.8 \times 10^3 = 80 \times 6.3 \times (T_2 - T_1) + 40 \times 9.3 \times (T_2 - T_1)$
 $T_2 = 2937 \text{ K.}$
- For rigid and adiabatic container $W = 0, Q = 0 \Rightarrow \Delta U = Q - W = 0$
 $E_2 - E_1 = 0$ So $E_2 = E_1$.

Comprehension # 2 :

- Work done in isothermal process will be more than $PV^2 = \text{const}$, process whatever be the value of K_1 and K_2 as is shown in the diagram.



- Clearly $(V_f)_{\text{isothermal}} > (V_f)_{\text{adiabatic}}$



- $P^\circ, V^\circ \xrightarrow[\text{isothermal}]{\text{irreversible}} 2V^\circ, \frac{P^\circ}{2}$
 $\begin{matrix} \text{reversible} \\ \text{adiabatic} \end{matrix} \nearrow P_1, V^\circ$
 $\begin{matrix} \text{reversible} \\ PV^2 = K \end{matrix} \searrow P_2, V^\circ$

For reversible adiabatic,

$$\frac{P^\circ}{2} (2V^\circ)^\gamma = P_1 V_0^\gamma \Rightarrow P_1 = P^\circ 2^{\gamma-1}$$

For reversible $PV^2 = K$

$$\frac{P^\circ}{2} (2V^\circ)^2 = P_2 V_0^2 \Rightarrow P_2 = 2P^\circ$$

So, $P_2 > P_1$
 Since final volume is same
 $P \propto T$
 So, $T_2 > T_1$

Comprehension # 3 :

- Since $\Delta E = q + w = 80 - 30 = 50$
So for ADB
 $\Delta E = q + w$; $50 = q - 10$; $q = 60$ J
- In ADB process, DB process is isochoric so $w_{DB} = 0$
So, $\Delta E_{AD} = q_{AD} + w_{AD}$
 $-40 = q_{AD} + (-10)$; $q_{AD} = -30$ J
Now, $q_{AB} = q_{AD} + q_{DB}$; $60 = -30 + q_{DB}$
 $q_{DB} = 90$ J

Comprehension # 4 :

- Reaction to be spontaneous
 $\Delta G < 0 \Rightarrow \Delta H - T\Delta S < 0$
 $\Rightarrow \Delta T > \frac{\Delta H}{\Delta S} \Rightarrow T > \frac{100 \times 10^3}{.05 \times 10^3} \Rightarrow T > 2000$ K.
- Use $\Delta G = \Delta H - T\Delta S$
 $\Delta G = -15 - \frac{300 \times (-7.2)}{1000} = -12.84$ Kcal mol⁻¹

Comprehension # 5 :

- $\Delta S = 2.303 \times 1 \times C_p \log \left(\frac{600}{300} \right) = 23.03$
 $\Rightarrow C_p = \frac{10}{\log 2}$
 $C_v = C_p - R = \frac{10}{\log 2} - 8.3$
- For reaction to be spontaneous,
 $\Delta G < 0 \Rightarrow \Delta H - T\Delta S < 0$
 $\Rightarrow T < \frac{\Delta H}{\Delta S} \Rightarrow T < 428.6$ K.

Comprehension # 6 :

- $\Delta H = \Delta H_{CH_3OH} - \Delta H_{CO} - \Delta H_{H_2} = 201 + 114 - 2 \times 0 = -87$
- $\Delta S_{320} = \Delta S_{300} + \Delta C_p \ln \frac{T_2}{T_1} = -16 + (-43) \ln \frac{320}{300} = -18.58$
 $\Delta C_p = 44 - 29.4 - 2 \times 28.8 = -43$.
- $\Delta_r G_{320}^\circ = \Delta_r H_{320}^\circ - T \cdot \Delta_r S_{320}^\circ$
 $= -87.86 - \frac{320 \times (-18.58)}{1000} = -81.91$ kJ/mol.

Comprehension # 7 :

- $U = \alpha \sqrt{V}$ Here U = Kinetic energy of ideal gas
 $U = nC_v T$
 $\Rightarrow nC_v T = \alpha \sqrt{V}$... (i)
 $T = \frac{PV}{nR}$... (ii)
sub. (2) in (1)
 $\left(\frac{C_v}{R} \right) \cdot PV = \alpha \sqrt{V}$
 $\Rightarrow P = \left(\frac{\alpha \cdot R}{C_v} \right) \frac{1}{\sqrt{V}}$
 $w = -\int P dV = - \left(\frac{\alpha R}{C_v} \right) \int \frac{dV}{\sqrt{V}}$
 $= -(\alpha) (\gamma - 1) \cdot \frac{1}{(1/2)} (\sqrt{V}) \Big|_{V_1}^{V_2}$
 $w = -2(\alpha) (\gamma - 1) (\sqrt{V_2} - \sqrt{V_1})$
work done by the gas = -w = 2(α)
 $(\gamma - 1) (\sqrt{V_2} - \sqrt{V_1})$
- For diatomic gas with no vibrational degree of freedom
 $C_v = \frac{3}{2} R + 2 \times \frac{1}{2} R$
 $C_v = 5/2 R$
 $\Delta U = \alpha (\sqrt{V_2} - \sqrt{V_1}) = 100$ J
 $w = 2(\alpha) (\gamma - 1) (\sqrt{V_2} - \sqrt{V_1}) = (2) (\gamma - 1) \times 100$
 $\therefore \gamma = \frac{C_p}{C_v} = \frac{7}{5}$
 $(\gamma - 1) = \left(\frac{7}{5} - 1 \right) = \left(\frac{2}{5} \right)$
 $w = (2) \left(\frac{2}{5} \right) (100) J = 80$ J
- $\Delta U = q + w \Rightarrow 100 J = q - 80 J$
 $q = 180$ J

EXERCISE - 4

Subjective Type

- 1.(i) $\text{H}_2\text{O}(\text{g}) \longrightarrow \text{H}_2\text{O}(\ell)$
 $V_{(\text{g})} > V_{(\ell)}$
 $W = -P_{\text{ext}}(V_{(\ell)} - V_{(\text{g})})$
 $W = +ve$
- (ii) $\text{H}_2\text{O}(\text{s}) \longrightarrow \text{H}_2\text{O}(\text{g})$
 $V_{(\text{g})} > V_{(\text{s})}$
 $W = -ve$
- (iii) $\text{H}_2\text{O}(\ell) \longrightarrow \text{H}_2\text{O}(\text{s})$
 $V_{(\text{s})} > V_{(\ell)}$
 $W = -P_{\text{ext}}(V_{(\text{s})} - V_{(\ell)})$
 $= -ve$
- (iv) $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$
 $W = -P_{\text{ext}}(V_2 - V_1)$
 $= -P_{\text{ext}}(n_2RT - n_1RT)$
 $= -\Delta n_g RT$
 $W = +ve$
- (v) $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 $W = -P_{\text{ext}} \Delta V$
 $\Delta V > 0$
 $= -ve$
2. $\Delta E = -65 \text{ J}$ $w = 20 \text{ J}$
 $\Delta q = \Delta V - w$ $-65 = \Delta V - 20$
 $\Delta V = -45 \text{ J}$
3. $\Delta H_{\text{glucose}} = -2808 \text{ kJ mol}$
- (a) Energy need to climb 3m = $Mgh = 62.5 \times 10 \times 3$
 $\Delta q = 1875 \text{ Joule}$
- Now useful energy from 1 mole of glucose = $2808 \times \frac{1}{4}$
 $= 702 \text{ kJ}$
- \Rightarrow No. of mole of glucose required = $\frac{1875}{702 \times 10^3}$
 $= 2.67 \times 10^{-3} \text{ mole}$
grams of glucose = $180 \times 2.67 \times 10^{-3} = 0.4807 \text{ gm}$
- (b) Energy need to climb 3000 m will be 10^3 time.
 \Rightarrow wt. should be 10^3 time = 0.4807 kg
4. $q_p = q_v + \Delta n_g RT$
 $40.66 \times 2 = q_v + 2 \times 8.314 \times 373$
 $\Rightarrow q_v = (81.32 - 6.202) \text{ kJ}$
 $q_v = 75.118 \text{ kJ}$

5. $\Delta H = 1 \text{ kcal}$
 $\Delta H = \Delta E + P\Delta V$
 $1 \times 10^3 \times 4.18 = \Delta E + 1.013 \times 10^5 \times 3 \times 10^{-3}$
 $\Delta E = (4180 - 30.39) \text{ Joule} = \left(\frac{4149.61}{4.18}\right) \text{ cal}$
 $\Delta E = 0.993 \text{ kcal}$
6. $\text{NH}_4\text{CN}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \longrightarrow \text{N}_2(\text{g}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell)$
- $\Delta H_{298} = \Delta E + \Delta n_g RT = -742.7 + \frac{1}{2} \times 8.314 \times 298$
 $= -742.7 + 1.239$
 $\Delta H_{298} = -741.46$
7. $\Delta H = 1440 \text{ cal}$
 $\Delta H = \Delta E + P(V_2 - V_1)$
 $1440 = \Delta E + 1.013 \times 10^5 (0.0180 - 0.0196) \times 10^{-3}$
 $\Delta E = 1440 - 1.013 \times 0.0016 \times 10^{-3}$
 $\Delta E = 1440.168$
8. $W = \int P_{\text{ext}} dV$
 $= -\int P(V_2 - V_1) = -1.01 \times 10^5 (0.1) \times 10^{-3}$
 $W = -10.1 \text{ J}$
9. $\text{Zn}(\text{s}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
 $\Delta H = -36.5 \text{ kJ}$
 $\Delta Q = \Delta E - W - 36.5 \text{ kJ}$
 $= \Delta E + 1.01 \times 10^5 (500 \times 50 \times 10^{-6})$
 $\Delta E = -39.03 \text{ kJ}$
 $W = -P_{\text{ext}}(V_2 - V_1) = -1.013 \times 10^5 \times 500 \times 50 \times 10^{-6}$
 $W = -2.53$
10. $W_{\text{irr}} = -nRT \left(1 - \frac{P_2}{P_1}\right) = -5 \times 8.314 \times 300 \left(1 - \frac{1}{4}\right)$
 $W_{\text{irr}} = -9.353 \text{ kJ}$
 $W_{\text{rev}} = -2.303 nRT \log\left(\frac{V_2}{V_1}\right)$
 $W_{\text{rev}} = -2.303 \times 5 \times 8.314 \times 300 \log 4$
 $W_{\text{rev}} = -17.29 \text{ kJ}$
and $\Delta q = \Delta E - W$
at $\Delta T \rightarrow 0$ $\Delta E \rightarrow 0$ $\Delta H \rightarrow 0$
 $W_{\text{rev}} = -q = 17.29 \text{ kJ}$

11. $n_1 = 1$

$$T_1 V_1^{27} = T_2 V_2^{27} \quad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\left(\frac{T_1}{T_2}\right) = \left(\frac{V_2}{V_1}\right)^{\gamma-1} \quad T_2 = 300 \left(\frac{1}{27}\right)^{\frac{1}{3}}$$

$$T_2 = 100 \text{ K}$$

$$\text{Adiabatic condition } \Delta Q = 0 \Rightarrow \Delta E = W = nC_v(T_2 - T_1)$$

$$W = 1 \times 25 \times -200 \quad W = -5.000 \text{ kJ/mole}$$

12. Process reversibly adiabatic

$$T_1 = 298.15 \text{ K} \quad V_2 = 2V_1$$

$$T_2 = 248.44 \text{ K} \quad PV^\gamma = K \quad PV = nRT$$

$$\frac{T}{V} \cdot V^\gamma = K \quad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\left(\frac{T_1}{T_2}\right) = \left(\frac{V_2}{V_1}\right)^{\gamma-1} \quad \left(\frac{298.15}{248.44}\right) = 2^{\gamma-1}$$

$$1.2 = 2^{\gamma-1} \quad \log 1.2 = \log 2 \cdot (\gamma-1)$$

$$\gamma - 1 = \frac{\log 1.2}{\log 2} \quad \gamma - 1 = 0.263$$

$$\text{Now } nC_v(T_2 - T_1) = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

$$C_{v,m} = \left(\frac{R}{\gamma - 1}\right) = \frac{nR(T_2 - T_1)}{(\gamma - 1)}$$

$$C_{v,m} = \frac{8.314}{0.263} \quad C_{v,m} = 31.61$$

13. $W = -2.303 nRT \log\left(\frac{P_1}{P_2}\right)$

$$= -2.303 \times 1 \times 8.314 \times 298 \log\left(\frac{1}{5}\right)$$

$$W = -3.988 \text{ kJ}$$

14.

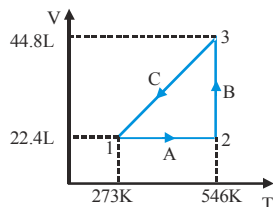


Table-1			
State	P	V	T
1	1	22.4L	273
2	2atm	22.4	546K
3	1atm	44.8	546K

State - 1

$$PV = nRT \Rightarrow P = 1 \text{ atm}$$

State - 2

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow P_2 = 2 \text{ atm}$$

$$P_2 = \frac{546}{273} \times 1 \text{ atm}$$

State - 3

$$P_1 V_1 = P_2 V_2$$

$$2 \times 22.4 = 44.8 \times P_2$$

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

Step	Name of process	q	w	ΔE	ΔH
A	Isochoric	$\frac{3}{2}R(273)$	0	$\frac{3}{2}R(273)$	$\frac{5}{2}R(273)$
B	Isotherm	$546R \ln 2$	$-546R \ln 2$	0	0
C	Isotherm	$\frac{5}{2}R(273)$	$R(273)$	$\frac{3}{2}R(273)$	$\frac{5}{2}R(273)$
overall					

State - A \rightarrow (Isochoric)

$$W = 0 \quad \Delta q = \Delta E$$

$$\Rightarrow 1 \times \frac{3}{2} R(273)$$

$$\Delta H = nC_p dT \quad \Delta H = 1 \times \frac{5}{2} R(273)$$

State - B \rightarrow (Isothermal)

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

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

$$\text{is } Q = -w = +2.303 \times 1 \times 8.314 \log(2) \times 546$$

$$Q = 546 R \ln 2 \quad W = -546 R \ln 2$$

$$\Delta E = nC_v \Delta T \quad W = nR(T_2 - T_1)$$

State - C \rightarrow (Isobaric)

$$\Delta q = \Delta E - w = \Delta E + P(V_2 - V_1)$$

$$\text{or } \Delta H = \Delta E + P\Delta V = \frac{5}{2} R(-273)$$

15. $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$

$$\Delta C_{p, \text{reaction}} = C_{p, H_2O(l)} - C_{p, H_2(g)} - \frac{1}{2} C_{p, O_2(g)}$$

$$= 75.312 - 38.83 - \frac{1}{2} \times 29.16$$

$$\Delta C_{p, \text{reaction}} = 21.90 \text{ kJ}$$

$$\Delta H_{373}^{\text{reaction}} = \Delta H_{298} + nC_p \Delta T$$

$$= (-285.76 + 1 \times 21.9 \times 75 \times 10^{-3}) \text{ kJ}$$

$$\Delta H_{373} = -284.12 \text{ kJ}$$

16. $C_p = 22.34 + 48.1 \times 10^{-3} \text{ TJK}^{-1} \text{ mol}^{-1}$

$$\Delta H = \int_{T_1}^{T_2} nC_p dT = \int_{T_1}^{T_2} (22.34 + 48.1 \times 10^{-3} T) dT$$

$$= 22.34 \times 298 + \frac{48.1 \times 10^{-3} \times 298 \times 3}{2} \times 298$$

$\Delta H = 13.064 \text{ kJ/mole}$

$W = -P(V_2 - V_1) = -nR(T_2 - T_1)$

$W = -20477$

$\Delta E = 13.064 - 2.477$

$\Delta E = 10.587 \text{ kJ}$

17. $\Delta S = 28.8 \text{ J/K}$ $\Delta H = 30.5 \text{ kJ}$

$$\Delta H = T\Delta S \quad \frac{30.5 \times 10^3}{28.8} = T = 1059 \text{ K}$$

18. $\Delta S = \frac{nC_p dT}{T}$

$$= 1 \times \int \left(\frac{25.5}{T} + 13.6 \times 10^{-3} - 42.5 \times 10^{-7} T \right) dT$$

$$= 2303 \times 25.5 \log 2 + 13.6 \times 10^{-3} \times 300 - 42.5 \times 10^{-7} \frac{(600^2 - 300^2)}{2}$$

$\Delta S = 20.618 \text{ kJ}$



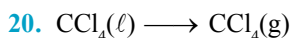
$\Delta S_{\text{Br}} = 152.3$ $\Delta S_{\text{Cl}_2(\text{g})} = 223.0$

$\Delta S_{\text{BrCl}(\text{g})} = 239.7 \text{ J mol}^{-1} \text{ K}^{-1}$

$\Delta S_R = 2 \times 239.7 - 223 - 152.3 = 104.4$

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

$= 29300 - 298 \times 104.4 = -1721.8 \text{ J}$



$P = 1 \text{ atm}$

$T = 298 \text{ K}$ $\Delta S = 94.98 \text{ JK}^{-1}$

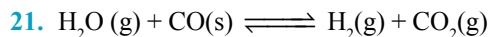
$\Delta_r H = \Delta H_p - \Delta H_r = (-106.7 + 139.3) \text{ kJ}$

$= 32.6 \text{ kJ/mol}$

$\Delta_r G = \Delta H_R - T\Delta S$

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

$\Delta_r G = 4.296 \text{ kJ/mol}$



(i) $\Delta_r H_{298}^\circ$
 $= \Delta_r H_{\text{H}_2(\text{g})} + \Delta_r H_{\text{CO}_2(\text{g})} - \Delta_r H_{\text{CO}(\text{s})} - \Delta_r H_{\text{H}_2\text{O}(\text{g})}$
 $= -94.05 + 26.42 + 57.8 = -9.83 \text{ k cal/mol}$

(ii) $\Delta_r G = -94.24 + 0 + 32.79 + 54.64$

$\Delta_r G = -6.81$

(iii) $\Delta_r G = \Delta_r H - T\Delta_r S - 6.81 = -9.83 - 298 \Delta_r S$

$$\frac{9.83 - 6.81}{298} = -\Delta_r S$$

$\Delta_r S = -10.13 \text{ cal/mole}$

(iv) but at constant P

$\Delta H = \Delta E + \Delta PV \quad \because \Delta n_g = 0$

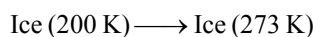
$\Delta_r H = \Delta_r E_{298} = -9.83 \text{ k cal/mol}$

(v) $S_{298}^\circ [\text{H}_2\text{O}(\text{g})]$

$\Delta_r S = \Delta_r S_{\text{H}_2\text{O}(\text{g})} + \Delta_r S_{\text{CO}} - \Delta_r S_{\text{H}_2} - \Delta_r S_{\text{CO}}$
 $-10.13 = -\Delta_r S_{\text{H}_2\text{O}(\text{g})} + 47.3 + 31.2 + 51.1$

$\Delta_r S_{\text{H}_2\text{O}(\text{g})} = 45.13 \text{ cal/K mole}$

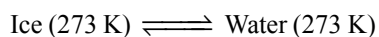
22. Step-1



$$\Delta S_1 = m C_p \ln \frac{T_2}{T_1} = 1 \times 2.09 \times 10^3 \ln \frac{273}{200}$$

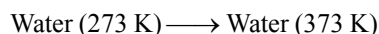
$\Delta S_1 = 650.312 \text{ J/}^\circ\text{C}$

Step-2



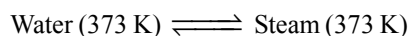
$$\Delta S_2 = \frac{\Delta H_f}{273} = \frac{3.34 \times 10^5}{273} = 1223.44 \text{ J/}^\circ\text{C}$$

Step-3



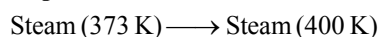
$$\Delta S_3 = 1 \times 4.18 \times 10^3 \ln \frac{373}{273} = 1304.6 \text{ J/}^\circ\text{C}$$

Step-4



$$\Delta S_4 = \frac{\Delta H_v}{373} = \frac{22.6 \times 10^5}{373} = 6058.98 \text{ J/}^\circ\text{C}$$

Step-5



$$\Delta S_5 = 1 \times 2.09 \times 10^3 \ln \frac{400}{373} = 146.06 \text{ J/}^\circ\text{C}$$

$\Delta S_T = 9383.4 \text{ J/}^\circ\text{C}$

23. $\gamma = \frac{5}{3}$, $P_1 = 1 \text{ atm}$, $T_1 = 300 \text{ K}$, $P_2 = 2 \text{ atm}$

(a) $PV^\gamma = \text{constant}$

$$P^{1-\gamma} T^\gamma = \text{constant}$$

$$TP^{(1-\gamma)/\gamma} = \text{constant}$$

$$T_1 P_1^{(1-\gamma)/\gamma} = T_2 P_2^{(1-\gamma)/\gamma}$$

$$T_2 = 300 \left(\frac{1}{2} \right)^{-2/5} = 395.85$$

$$w = \Delta U = n C_v dT = 1 \times \frac{3}{2} \times 8.314 \times 95.85$$

$$w = 1195.37 \text{ J}$$

$$V_2 = \frac{nRT_2}{P_2} = 16.25 \text{ L}$$

(b) $\Delta U = w$

$$1 \times 1.5 \times 8.314 (T_2 - 300)$$

$$= -2 \times 101.3 \left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1} \right)$$

$$(T_2 - 300) = 1.333 \left(300 - \frac{T_2}{2} \right)$$

$$T_2 = 420 \text{ K} \quad V_2 = \frac{nRT_2}{P_2} = 17.24 \text{ L}$$

$$w = \Delta U = 1.5 \times 8.314 (420 - 300)$$

$$w = 1496.52 \text{ J}$$

24. $V_1 = 20 \text{ L}$, $\gamma = 7/5$, $T_1 = 673 \text{ K}$,

$$P_1 = 0.2 \text{ MPa} = 2 \text{ atm}, P_2 = 0.7 \text{ MPa} = 7 \text{ atm}$$

$$n = \frac{P_1 V_1}{RT_1} = 2.5$$

(i) $\Delta U = \Delta H = 0$

$$q = -w = nRT \ln \frac{P_1}{P_2} = 2.5 \times 8.314 \times 673 \ln \frac{7}{2}$$

$$q = 17.52 \text{ kJ} \quad w = -17.52 \text{ kJ}$$

(ii) $P_1 V_1^\gamma = P_2 V_2^\gamma$

$$7(20)^\gamma = 2(V_2)^\gamma \Rightarrow V_2 = (3.5)^{5/7} = 48.92 \text{ L}$$

$$T_2 = \frac{P_2 V_2}{nR} = 470.46 \text{ K}$$

$$q = 0, w = \Delta U = 2.5 \times 2.5 \times 8.314 (470.46 - 673)$$

$$w = \Delta U = -10.524 \text{ kJ}$$

$$\Delta H = 2.5 \times 3.5 \times 8.314 (470.46 - 673) = -14.73 \text{ kJ}$$

(iii) $q = w = \Delta U = \Delta H = 0$

(iv) $q = 0, \Delta U = w$

$$2.5 \times 2.5 \times 8.314 (T_2 - 673)$$

$$= -101.3 \times 2 \times 2.5 \times 0.0821 \left(\frac{T_2}{2} - \frac{T_1}{7} \right)$$

$$T_2 - 673 = -0.79 \left(\frac{T_2}{2} - 96.142 \right)$$

$$T_2 = 536.91 \text{ K}$$

$$w = \Delta U = 2.5 \times 2.5 \times 8.314 (-136) = -7.1 \text{ kJ}$$

$$\Delta H = 2.5 \times 3.5 \times 8.314 (-136) = -9.9 \text{ kJ}$$

(v) $\Delta U = \Delta H = 0$

$$V_2 = \frac{nRT}{P_2} = \frac{2.5 \times 0.821 \times 673}{2} = 69 \text{ L}$$

$$w = -P_2 (V_2 - V_1) = -2 \times 49 = -98.13 \text{ L-atm}$$

$$w = -98.13 \times 101.3 = -9940.9 \text{ J}$$

$$w = -9.94 \text{ kJ} \quad q = -w = 9.94 \text{ kJ}$$

25.(i) The entropy change of the system ΔS_{sys} will be same in all the three process as it is state function.

$$\Delta S_{\text{sys}} = nR \ln \frac{V_2}{V_1} = 1 \times 8.314 \ln 3 = 9.134 \text{ J/K}$$

For reversible process

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

$$\Delta S_{\text{surr}} = -\Delta S_{\text{sys}} = -9.134 \text{ J/K}$$

(ii) $\Delta S_{\text{sys}} = 9.134 \text{ J/K}$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irrev.}}}{T} = - \left[\frac{q_{\text{rev.}} - 836.6}{298} \right]$$

$$= -\Delta S_{\text{sys}} + 2.807$$

$$\Delta S_{\text{T}} = \Delta S_{\text{sys}} + (-\Delta S_{\text{sys}} + 2.807) = 2.807 \text{ J/K}$$

(iii) For free expansion system doesn't absorb any heat so

$$q = 0$$

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

$$\Delta S_{\text{T}} = \Delta S_{\text{sys}} = 2.807 \text{ J/K}$$

26. (i) $\Delta S_{\text{sys}} = 0, \Delta S_{\text{surr}} = 0, \Delta S_{\text{T}} = 0$

(ii) $\Delta U = w, \Rightarrow n C_v (T_2 - T_1) = -P_2 (V_2 - V_1)$

$$0.5 \times 1.5 \times 8.314 (T_2 - 473)$$

$$= -101.3 \times 2 \times 0.5 \times 0.0821 \left(\frac{T_2}{2} - \frac{473}{5} \right)$$

$$T_2 - 473 = -1.333 \left(\frac{T_2}{2} - 94.6 \right)$$

$$T_2 = 359.49 \text{ K}$$

$$\Delta S_{\text{sys.}} = n \left[C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \right]$$

$$= 0.5 \left[2.5 \times 8.314 \ln \frac{359.49}{473} + 8.314 \ln \frac{5}{2} \right]$$

$$\Delta S_{\text{sys.}} = 0.957 \text{ J/K}$$

since no heat is transferred $q = 0$

$$\Delta S_{\text{surr.}} = 0$$

$$\Delta S_{\text{T}} = \Delta S_{\text{sys.}} = 0.957 \text{ J/K}$$

(iii) In free expansion $q = w = \Delta U = 0$

T is constant.

$$\Delta S_{\text{sys.}} = nR \ln \frac{P_1}{P_2} = 0.5 \times 8.314 \times \ln \frac{5}{2} = 3.81 \text{ JK}$$

$$\Delta S_{\text{surr.}} = 0$$

$$\Delta S_{\text{T}} = \Delta S_{\text{sys.}} = 3.81 \text{ J/K}$$

27. $P_1 = 1 \text{ atm}$, $V_1 = 1 \text{ L}$

$P_2 = 1001 \text{ atm}$, $V_2 = 0.99 \text{ L}$ Let $P = a + bV$

On finding $a = 100001$, $b = -10^5$ so

$$P = (100001 - 10^5 V)$$

$$w = -\int P dV = \int_{V_1}^{V_2} (100001 - 10^5 V) dV$$

$$w = -100001 (V_2 - V_1) + \frac{10^5}{2} (V_2^2 - V_1^2)$$

$$w = -100001 (-0.01) + \frac{10^5}{2} (-0.0199) = 5.01 \text{ L-atm}$$

$$w = 501 \text{ J} \quad \Delta U = w = 501 \text{ J}$$

$$\Delta H = \Delta U + (P_2 V_2 - P_1 V_1)$$

$$= 501 + (1001 \times 0.99 - 1 \times 1) \times 100 = 99500 \text{ J}$$

$$\Delta H = 99.5 \text{ kJ}$$

28.(i) $\Delta S_{\text{sys.}} = n C_v \ln \frac{T_2}{T_1} = 1 \times \frac{3}{2} R \ln \frac{1000}{100} = \frac{3}{2} R \ln 10$

$$\Delta S_{\text{T}} = 0 \text{ (Reversible process)}$$

$$\Delta S_{\text{surr.}} = -\Delta S_{\text{sys.}} = -\frac{3}{2} R \ln 10$$

(ii) $\Delta S_{\text{sys.}} = \frac{3}{2} R \ln 10$

$$w = 0$$

$$q = \Delta U = -\frac{3}{2} R (900)$$

$$\Delta S_{\text{surr.}} = -\frac{q}{T} = \frac{3R(900)}{2 \times 1000} = \frac{3}{2} R (0.9)$$

$$\Delta S_{\text{T}} = \frac{3}{2} R \ln 10 - \frac{3}{2} R (0.9) = \frac{3}{2} R (1.402)$$

29. $G = H - TS = U + PV - TS$

$$dG = dU + PdV + VdP - TdS - SdT$$

$$w = 0, dV = 0, dU = dq = T dS \text{ so}$$

$$dG = TdS + VdP - TdS - SdT$$

$$dG = VdP - SdT \Rightarrow \Delta G = V\Delta P - \int SdT$$

$$VdP = V(P_2 - P_1)$$

$$\frac{P_2}{T_2} = \frac{P_1}{T_1} \Rightarrow \frac{P_2}{400} = \frac{1}{300} \Rightarrow P_2 = \frac{4}{3}$$

$$VdP = 24.6 (4/3 - 1) = 8.2 \text{ L-atm} = 820 \text{ J}$$

$$\int SdT = \int_{T_1}^{T_2} (10 + 0.01T) dT = 10(T_2 - T_1) + 0.005(T_2^2 - T_1^2)$$

$$SdT = 10(100) + 0.005(400^2 - 300^2) = 1350$$

$$\Delta G = 820 - 1350 = -530 \text{ J}$$

30. $n = 2$

$$V_1 = \frac{2 \times 0.0821 \times 300}{1} = 49.26 \text{ L}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow \frac{49.26}{300} = \frac{V_2}{550} \Rightarrow V_2 = 90.31 \text{ L}$$

(i) $w = -P\Delta V = 1(90.31 - 49.26) = -41.05 \text{ L-atm}$

$$w = -41.05 \times 101.3 = -4158.36 \text{ J} = -4.15 \text{ k}$$

$$q = \Delta H = \int n C_p dT$$

$$= 2 \left[12.552(T_2 - T_1) + \frac{8.368 \times 10^{-3}}{2} (T_2^2 - T_1^2) \right]$$

$$q = \Delta H = 2 \left[12.552(250) + \frac{8.368 \times 10^{-2}}{2} (212500) \right]$$

$$q = \Delta H = 24.04 \text{ kJ}$$

$$C_v = C_p - R = 4.238 + 8.368 \times 10^{-2} \text{ T}$$

$$\Delta U = \int n C_v dT = 19.9 \text{ kJ}$$

(iii) $w = 0$

$$q = \Delta U = 19.9 \text{ kJ}$$

$$\Delta H = \int n C_p dT = 24.04 \text{ kJ}$$

31. At 298 K,

$$\Delta G^\circ = -6333 \text{ kJ/mole}$$

$$\Delta H^\circ = -5737 \text{ kJ/mole}$$

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

$$\text{so } \Delta S^\circ = 2 \text{ kJ/mole}$$

At 310 K

$$\Delta G = -5737 - 2 \times 310 = -6357 \text{ kJ/mole}$$

$$\text{Additional non-PV work} = |\Delta G - \Delta G^\circ| = 24 \text{ kJ/mole}$$

32. $\Delta_r C_p = 33.305 - 75.312 = -42.007 \text{ J/K mole}$

$$\Delta_r S_{323} = \frac{\Delta H}{T} = \frac{40639}{323} = 108.95 \text{ J/K mole}$$

$$d(\Delta_r S) = \frac{\Delta_r C_p dT}{T}$$

$$\Delta_r S_{373} - \Delta_r S_{323} = \Delta_r C_p \ln \frac{T_2}{T_1}$$

$$\Delta_r S_{373} = 108.95 - \left(-42.007 \ln \frac{373}{323} \right) = 115 \text{ J/K mole}$$

$$d(\Delta_r H) = \Delta_r C_p dT$$

$$\Delta_r H_{373} - \Delta_r H_{323} = -42.007 (50)$$

$$\Delta_r H_{373} = 42739.35 \text{ J/mole}$$

$$\Delta_r G_{323} = 42739.35 - 323 (115)$$

$$= 5594.35 \text{ J} = 5.59 \text{ kJ/mole}$$

EXERCISE - 5

Part # I : AIEEE/JEE-MAIN

1. $W = -P\Delta V$
 $= -1 \times 10^5 (1 \times 10^{-2} - 1 \times 10^{-3})$
 $= -1 \times 10^5 \times 9 \times 10^{-3} = -900 \text{ J.}$
3. For spontaneous process, $\Delta G = -ve$, $K > 1$ and $E_{\text{cell}}^{\circ} = +ve$.
4. In isolated system, the expansion of gas is carried out adiabatically. Since heat exchange between system and surrounding is not possible i.e. $q = 0$ and secondary w_{rev} is always greater than w_{irr} therefore for reversible process there must be comparatively higher decreases in internal energy i.e. ΔU for reversible process will be more negative. Hence, final temperature in reversible process will be smaller than irreversible process.
 $\therefore (T_{\text{P}})_{\text{irrev}} > (T_{\text{P}})_{\text{rev}}$
6. In an isolated system, there is no exchange of energy or matter between the system and surrounding. For a spontaneous process in an isolated system, the change in entropy is positive, i.e. $\Delta S > 0$.
 Most of the spontaneous chemical reactions are exothermic. A number of endothermic reaction are spontaneous e.g melting of ice (an endothermic process) is a spontaneous reaction.
 The two factors which are responsible for the spontaneity of process are
 (i) tendency to acquire minimum energy
 (ii) tendency to acquire maximum randomness.
7. $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$
 for a spontaneous process $\Delta G^{\circ} < 0$
 $\Rightarrow \Delta H^{\circ} - T\Delta S^{\circ} < 0 \Rightarrow T\Delta S^{\circ} > \Delta H^{\circ} \Rightarrow T > \frac{\Delta H^{\circ}}{\Delta S^{\circ}}$

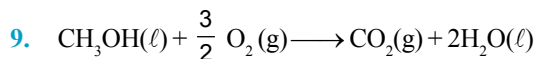
$$\Rightarrow T > \frac{179.1 \times 1000}{160.2} \Rightarrow T > 1117.9 \text{ K} \approx 1118 \text{ K.}$$

8. $\Delta S^{\circ} \text{ reaction} = 50 - \frac{1}{2} (60) - \frac{3}{2} (40) = -40 \text{ JK}^{-1}$

For reaction to be at equilibrium

$$\Delta G = 0$$

$$\Delta H - T\Delta S = 0 \Rightarrow T = \frac{\Delta H}{\Delta S} = \frac{30000}{40} = 750 \text{ K}$$



$$\Delta G_r = \Delta G_f(\text{CO}_2, \text{g}) + 2\Delta G_f(\text{H}_2\text{O}, \ell) - \Delta G_f(\text{CH}_3\text{OH}, \ell) - \frac{3}{2} \Delta G_f(\text{O}_2, \text{g})$$

$$= -394.4 + 2(-237.2) - (-166.2) - 0 = -394.4 - 474.4 + 166.2 = -868.8 \times 166.2$$

$$\Delta G_r = -702.6 \text{ kJ}$$

$$\% \text{ efficiency} = \frac{702.6}{726} \times 100 = 97\%.$$

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

For spontaneous reaction ΔG must be negative

At equilibrium temperature $\Delta G = 0$

to maintain the negative value of ΔG

T should be greater than T_c .

11. $\Delta S = nR \ln \frac{V_2}{V_1} = 2.303 nR \log \frac{V_2}{V_1}$

$$= 2.303 \times 2 \times 8.314 \times \log \frac{100}{10} = 38.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

12. Negative $\Delta_r G^{\circ}$ value indicates that +2 oxidation state is more stable for Pb^{2+} . Also it is supported by inert pair effect that +2 oxidation state is more stable for Pb and +4 oxidation state is more stable for Sn.

13. $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$
 $-RT \ln K = \Delta H^{\circ} - T\Delta S^{\circ}$

$$\ln K = - \frac{\Delta H^{\circ} - T\Delta S^{\circ}}{RT}$$

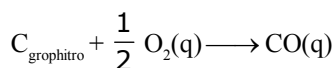
14. The process is isothermal expansion Hence,

$$q = -w \quad \Delta u = 0$$

$$q = +208 \text{ J}$$

$$w = -208 \text{ J (expansion work)}$$

15. $\Delta H_c^{\circ}(\text{c}) = -393.5 \quad \Delta H_c^{\circ}(\text{w,g}) = -283.5$



$$\Delta H_f^{\circ}(\text{w,g}) = \Delta H_c^{\circ}(\text{c}) - \Delta H_c^{\circ}(\text{co, g})$$

$$= -393.5 + 283.5 = -110.0 \text{ KJ.}$$

17. From 1st law : $\Delta U = q + w$
 For adiabatic process : $q = 0$
 $\therefore \Delta U = w$
 \therefore Work involve in adiabatic process is at the expense of change in internal energy of the system.

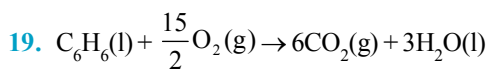
18. From thermodynamics

$$\ln k = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

for exothermic reaction, $\Delta H = -ve$

$$\text{slope} = \frac{-\Delta H^0}{R} = +ve$$

So from graph, line should be a & b.



$$\Delta n_g = 6 - 7.5 = -1.5 \text{ (change in gaseous mole)}$$

$$\Delta U \text{ or } \Delta E = -3263.9 \text{ kJ} \Rightarrow \Delta H = \Delta U + \Delta n_g RT$$

$$\Delta n_g = -1.5 \Rightarrow R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$T = 298 \text{ K}$$

$$\text{So } \Delta H = -3263.9 + (-1.5)8.314 \times 10^{-3} \times 298 = -3267.6 \text{ kJ}$$

$\Delta H =$ Heat at constant pressure

$\Delta U / \Delta E =$ Heat at constant volume

$R =$ gas constant

Part # II : IIT-JEE ADVANCED

1. $\therefore H = E + PV$ and $\Delta H = \Delta E + P\Delta V$
 $P\Delta V = nRT$
 $\therefore \Delta H = \Delta E + nRT$
 For isothermal and reversible process
 $\Delta T = 0$
 $\therefore \Delta H = \Delta E + 0$
 $\therefore \Delta E = 0$
 $\therefore \Delta H$ is also equal to zero.
3. Given that, $\Delta H_{\text{vaps}} = 30 \text{ kJ/mol} = 30 \times 10^3 \text{ J/mol}$
 $\Delta S_{\text{vaps}} = 75 \text{ J/mol}$
 We know that, $\Delta S = \frac{\Delta H_{\text{vap}}}{T_{B,P}}$
 $\therefore \Delta H = T\Delta S \Rightarrow 30 \times 10^3 = T \times 75$. **$T = 400 \text{ K}$** .
4. In adsorption there in bond formation between the gases and solid surface which decrease the entropy.
5. (a) (i) ΔG^0 for the reaction
 $\Delta G^0_{\text{reac.}} = 2\Delta G^0_f(\text{NO}_2) - \Delta G^0_f(\text{N}_2\text{O}_4)$
 $100 - 100 = 0$
 Now, $\Delta G = 2.303 RT \log Q_p + \Delta G^0$
 Here $Q_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{100}{10} = 10 \text{ atm}$

So, $\Delta G = 2.303 RT \log Q_p + 0 = 2.303 RT \log Q_p = 2.303 RT \log_{10} 10 = 2.303 RT = 5.7 \text{ kJ/mole}$

(ii) Since Q_p is more than K_p
 (calculate K_p by putting the value of ΔG^0 in the equation $\Delta G^0 = 2.303 RT \log K_p$, as $\Delta G^0 = 0$ that's why K_p comes as 1.)
 Hence, the reaction will proceed in backward direction.

6. $\Delta U = W$
 $nC_v(T_2 - T) = -P \times (V_2 - V_1)$
 $\frac{3}{2} R(T_2 - T) = -1 \Rightarrow \therefore T_2 = T - \frac{2}{3 \times 0.0821}$
7. From first law of Thermodynamics, $\Delta E = q + w$
 $\Rightarrow nC_v dT = nCdT - PdV$ (1)
 Now according to process, $P = V$ and according to ideal gas equation, $PV = nRT$
 We have, $V^2 = nRT$
 On differentiating, $2VdV = nRdT$ and
 $PdV = VdV = \frac{nRdT}{2}$
 So, from first equation we have,
 $nC_v dT = nCdT - \frac{nRdT}{2}$
 So, $C_v = C - \frac{R}{2}$ Hence, $C = \frac{4R}{2}$
9. $A \longrightarrow C; \Delta S = 50; C \longrightarrow D; \Delta S = 30;$
 $D \longrightarrow B; \Delta S = -20$
 For $A \longrightarrow B; \Delta S = 50 + 30 - 20 = 60$
10. $\Delta G^0 = \Delta H^0 - T\Delta S^0 = -54.07 \times 1000 - 298 \times 10 = -54070 - 2980 = -57050$
 $\Delta G^0 = -2.303 RT \log_{10} K$
 $-57050 = -2.303 \times 298 \times 8.314 \log_{10} K = -5705 \log_{10} K$
 $\log_{10} K = 10$
11. $H_2O(l, 1 \text{ bar}, 373 \text{ K}) \longrightarrow H_2O(g, 1 \text{ bar}, 373 \text{ K})$
 $\Delta S > 0; \Delta H > 0; \Delta G = 0$
12. At equilibrium ΔG (Gibbs energy) = 0 but ΔG^0 (standard Gibbs energy) $\neq 0$
 As ΔG (Gibbs energy) is more negative reaction will be more spontaneous.
13. Statement 2 is IInd law of thermodynamics which concludes that total heat can never be converted into equivalent amount of work.
16. Process shown by solid line is reversible isothermal
 So, work $W_s = -4 \times 0.5 \ln(5.5/0.5) = -2 \ln 11 \text{ L atm}$
 For dotted process (three step irreversible) work done will be
 $W_d = -\{4 \times 1.5 + 1 \times 1 + \frac{2}{3} \times 2.5\} \text{ L atm}$

$$= - \left\{ 6 + 1 + \frac{5}{3} \right\} \text{ L atm.} = - \frac{26}{3} \text{ L atm.}$$

$$\text{so, } \frac{W_d}{W_s} = \frac{26}{3 \times 2 \ln 11} \approx 2.$$

17 (A) $\text{CO}_2(\text{s}) \longrightarrow \text{CO}_2(\text{g})$

It is phase transition. The process is endothermic (sublimation).

Gas is produced, so entropy increases.

(B) On heating CaCO_3 decomposes. So, process is endothermic.

The entropy increases as gaseous product is formed.

(C) $2\text{H}\bullet \longrightarrow \text{H}_2(\text{g})$

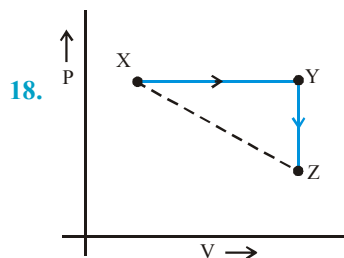
Entropy decreases as number of gaseous particles decreases.

(D) It is phase transition.

White and red P are allotopes.

Red P is more stable than white.

So ΔH is - ve.

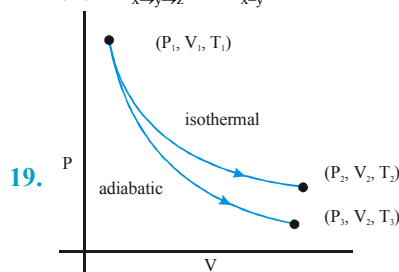


(A) $\Delta S_{x \rightarrow z} = \Delta S_{x \rightarrow y} + \Delta S_{y \rightarrow z}$ (Correct)

(B) $W_{x \rightarrow y} = W_{x \rightarrow z} + W_{y \rightarrow z}$ (Incorrect)

(C) $W_{x \rightarrow y \rightarrow z} = W_{x \rightarrow z}$ (Correct)

(D) $\Delta S_{x \rightarrow y \rightarrow z} = \Delta S_{x \rightarrow z}$ (Incorrect)



(A) $T_1 = T_2$ (due to isothermal)

(B) $T_3 > T_1$ (incorrect) cooling will take place in adiabatic expansion)

(C) $W_{\text{isothermal}} > W_{\text{adiabatic}}$ { with sign, this is incorrect }

(D) $\Delta U_{\text{isothermal}} = 0 > \Delta U_{\text{adiabatic}} = -ve$

So, answer is (A) and (D)

20. For $\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O}(\text{g})$ at $T = 100^\circ\text{C}$, 1 atm equilibrium exists. $\therefore \Delta G = 0, \Delta H - T\Delta S = 0$

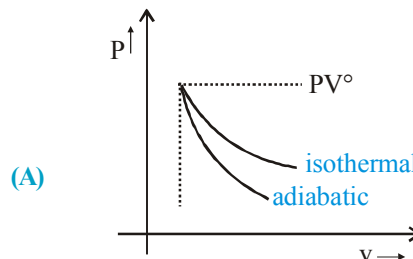
$\Delta H = T\Delta S > 0$ for system, since evaporation is endothermic

$$\therefore (\Delta S)_{\text{system}} > 0, \text{ also } (\Delta S)_{\text{surrounding}} = \frac{q_{\text{surr}}}{T_{\text{surr}}}$$

Heat gained by system = heat lost by surroundings.

$$\therefore q_{\text{surr.}} < 0 \therefore (\Delta S)_{\text{surr.}} < 0$$

22. $P_1 V_1 T_1$



$$|W_{\text{isothermal}}| > |W_{\text{adiabatic}}|$$

(B) (i) zero $T_1 = T_2 = T = \text{constant } \Delta E = nC_v \Delta T = 0$

(ii) positive $T_1 \neq T_2$ (During adiabatic expansion internal energy decrease)

(C) $P_{\text{ext}} = 0$ isothermal $\rightarrow \Delta E = 0 \therefore q = 0$

(D) $W = 0$ adiabatic $\rightarrow q = 0 \therefore \Delta E = 0$

23. At equilibrium

$$G_{\text{graphite}} = G_{\text{Diamond}}$$

$$G_{\text{graphite}}^\circ + V_{\text{graphite}} \cdot dp = G_{\text{Diamond}}^\circ + V_{\text{Diamond}} \cdot dp$$

$$(G_{\text{Diamond}}^\circ - G_{\text{graphite}}^\circ) = (V_{\text{graphite}} - V_{\text{Diamond}}) dp$$

$$2900\text{J} = 2 \times 10^{-6}\text{m}^3 \times (P_f - P_i)$$

$$P_f - P_i = \frac{29}{2} \times 10^8 \text{ Pa} \Rightarrow P_f - P_i = \frac{29}{2} \times 10^8 \times 10^{-5}$$

$$= \frac{29000}{2} \text{ bar} \Rightarrow P_f = 1 + \frac{29000}{2} = 14501 \text{ bar}$$

25. AC \Rightarrow isochoric process

AB \Rightarrow isothermal process

BC \Rightarrow isobaric process

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

$$\Rightarrow W_{AB} = -nRT, \ln\left(\frac{V_2}{V_1}\right)$$

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

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

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

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

$$\Delta H_{CA} < U_{CA} \text{ since both are negative } (T_1 < T_2)$$

26. As temperature increases concentration of product decreases
so reaction is exothermic $\Rightarrow \Delta H^\circ < 0$

$$\frac{\ln K_{T_1}}{\ln K_{T_2}} > 1 \Rightarrow \ln K_{T_1} > \ln K_{T_2}$$

so, $K_{T_1} > K_{T_2}$ Also, $\frac{\ln K_{T_1}}{\ln K_{T_2}} > \frac{T_2}{T_1}$

or

$$T_1 \ln K_{T_1} > T_2 \ln K_{T_2} \Rightarrow -RT_1 \ln K_{T_1} < -RT_2 \ln K_{T_2}$$

or $\Delta G_{T_1}^\circ < \Delta G_{T_2}^\circ$

or $\Delta H^\circ - T_1 \Delta S^\circ < \Delta H^\circ - T_2 \Delta S^\circ$

As $\Delta G_{T_1}^\circ < \Delta G_{T_2}^\circ$, since as temperature increases ΔG increases this is possible only when $\Delta S^\circ < 0$

MOCK TEST

3. $H = W = i^2 R t = \frac{V^2 t}{R} = \frac{120 \times 120 \times (10 \times 60)}{6} = 14.4 \times 10^5 \text{ joule}$

4. (D) $w = -P_{\text{ext}} \Delta V = -\Delta n_g RT$ and Δn_g is -ve for I and II also $\Delta V = -ve$ for IV
6. For isochoric process $\Delta V = 0$ so $q_v = \Delta E$ i.e. heat given to a system under constant volume is used up in increasing ΔE .
8. Reaction is endothermic and no. of moles increases on decomposition.

9. $\Delta S_{\text{gas}} = nC_{v,m} \ln \frac{T_2}{T_1} = 2 \times \left(\frac{5}{2} - 1\right) R \ln 2 = 3 R \ln 2$

10. $\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = C_{v,m} \ln 2 + R \ln \left(\frac{1}{2}\right)$
 $= (C_{v,m} - R) \ln 2$

11. It is because of the fact that for spontaneity, the value of $\Delta G = (\Delta H - T\Delta S)$ should be < 0 . If ΔS is -ve, the value of $T\Delta S$ shall have to be less than ΔH or the value of ΔS has

to be less than $\frac{\Delta H}{T}$ i.e., $\frac{x}{298}$.

12. $\Delta G = (\Delta H) - T(\Delta S)$

$\downarrow \quad \quad \downarrow$
 -ve -ve

since both are -ve, the reaction would have a -ve ΔG

below a temperature of $\frac{33000}{58} \text{ K} (= 569\text{K})$

18. $\Delta S = nC_v \ln \left(\frac{T_f}{T_i}\right) + nR \ln \left(\frac{V_f}{V_i}\right) = 5 \ln \frac{373}{298} + 2 \ln 10$

$$\Delta H = nC_p \Delta T = n(C_v + R) \Delta T = 1 \times 7 \times 75 = 525 \text{ cal}$$

19. Work done against vacuum is zero. It is free expansion.

21. Rearranging the relationship $\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_m}$

We have $T = \frac{\Delta H_{\text{fus}}}{\Delta S_{\text{fus}}}$
 $= \frac{12.36 \times 10^3 \text{ J mol}^{-1}}{9.250 \text{ JK}^{-1} \text{ mol}^{-1}} = 1336 \text{ K}$

This $1336 - 273$, or 1063°C

22. (i) $q = -w = nRT \ln \frac{V_2}{V_1} = 2722.26 \text{ J}$

$$\Delta S_{\text{gas}} = nR \ln \frac{V_2}{V_1} = 8.314 \times 2.303 \times \log 3 = 9.135 \text{ JK}^{-1}$$

$$= -\Delta S_{\text{surr}}$$

$$\Delta S_{\text{total}} = 0 \text{ (reversible)}$$

(ii) $q = 2722.26 - 836.8 = 1885.46 \text{ J}$

As entropy is a state function and ΔS of system will be same as above one.

$$\Delta S_{\text{gas}} = 9.135 \text{ JK}^{-1}$$

$$\Delta S_{\text{surr}} = -\frac{1885.46}{298} = -6.327 \text{ JK}^{-1}$$

$$\Delta S_{\text{total}} = 2.808 \text{ JK}^{-1}$$

(iii) $\Delta S_{\text{gas}} = 9.135 \text{ JK}^{-1}$

$$q = 0 \Rightarrow \Delta S_{\text{surr}} = 0 \text{ and } \Delta S_{\text{total}} = 9.135 \text{ JK}^{-1}$$

23. (a) In case of adiabatic reversible expansion,

$$dq_{\text{rev}} = 0 \Rightarrow \Delta S = 0.$$

- (b) In case of irreversible adiabatic expansion :

$$W = -P_{\text{ext}}(V_2 - V_1) = -3(16 - 8) = -3 \times 8 = -24 \text{ L. atm}$$

$$\Delta U = q + w \text{ here } q = 0 \Rightarrow \Delta U = W$$

$$\Rightarrow nC_v(T_2 - T_1) = -24$$

$$\Rightarrow 1 \times 1.5 R(T_2 - T_1) = -24$$

$$\Rightarrow T_2 - T_1 = \frac{-24}{1.5 \times 0.082} \Rightarrow T_2 = 805 \text{ K}$$

$$\Delta S = nC_v \ln \left(\frac{T_2}{T_1}\right) + R \ln \left(\frac{V_2}{V_1}\right) = 1.5 \times 8.314 \ln \left(\frac{805}{1000}\right)$$

$$+ 8.314 \ln 2 \Rightarrow \Delta S = 3.06 \text{ JK}^{-1}$$

- (c) In case of free expansion (Adiabatically)

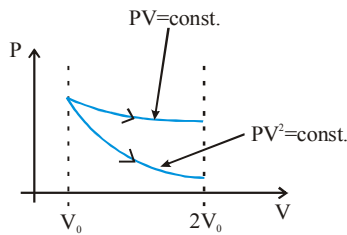
$$W = 0, \quad q = 0, \quad \Delta U = 0$$

$$\Rightarrow nC_v(T_2 - T_1) = 0 \Rightarrow T_2 = T_1$$

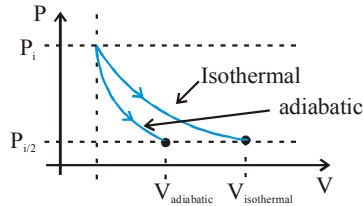
$$\Delta S = nR \ln \left(\frac{V_2}{V_1}\right) = R \ln (2) = 5.76 \text{ J/K.}$$

24. Work done in isothermal process will be more than $PV^2 = \text{const}$, process whatever be the value of K_1 and K_2

as is shown in the diagram.



25. Clearly $(V_f)_{\text{isothermal}} > (V_f)_{\text{adiabatic}}$



28. $P^\circ, V^\circ \xrightarrow[\text{isothermal}]{\text{irreversible}} 2V^\circ, \frac{P^\circ}{2} \xrightarrow[\text{reversible}]{\text{adiabatic}} P_1, V_1$
 $\xrightarrow[\text{reversible}]{PV^2=K} P_2, V_2$

For reversible adiabatic,

$$\frac{P^\circ}{2} (2V^\circ)^\gamma = P_1 V_1^\gamma \Rightarrow P_1 = P^\circ 2^{\gamma-1}$$

For reversible $PV^2 = K$

$$\frac{P^\circ}{2} (2V^\circ)^2 = P_2 V_2^2 \Rightarrow P_2 = 2P^\circ$$

So, $P_2 > P_1$

Since final volume is same

$P \propto T$

So, $T_2 > T_1$

29. (A) Reversible isothermal expansion of ideal gas

$$W = -2.303 nRT \log \frac{V_2}{V_1} \text{ and } \Delta E = \Delta H = 0 \text{ (as } \Delta T = 0)$$

(B) Reversible adiabatic compression of an ideal gas

$$PV^\gamma = \text{constant and } W = \frac{nR(T_2 - T_1)}{\gamma - 1}$$

$$= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

(C) Irreversible adiabatic expansion of an ideal gas

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

(D) Irreversible isothermal compression of an ideal gas

$$\Delta H = 0 \text{ (as } \Delta T = 0)$$

30. (A) A process carried out infinitesimally slowly is called reversible process

(B) A process in which no heat enters or leaves the system is called adiabatic process

(C) A process carried out at constant temperature is called isothermal process

(D) A process in equilibrium has $\Delta G = 0$

(E) $A(s) \longrightarrow A(g)$

process of conversion of solid to gas is called sublimation

(F) In a cyclic process, state function have no change in their value. So, $\Delta E = 0, \Delta H = 0$.

31. $\Delta H = 30.84 \text{ kJ/mole}$

$$PV = nRT \Rightarrow 1 \times V_2 = 1 \times 0.082 \times 353$$

$$\Rightarrow V_2 = (0.082 \times 353) \text{ Lit.}$$

as initial volume is negligible so, $\Delta H = \Delta E + P_2 V_2$

$$\Delta H = \Delta E + \Delta n_g RT \Rightarrow 30.84 = \Delta E + 1 \times 8.3 \times 353 \times 10^{-3}$$

$$\Delta E = 27.91$$

$$Q = i \times t = (0.5 \times t)$$

$$\text{Energy} = Q \times V = 0.5 \times t \times V = 0.5 \times 12 \times t = 6t$$

$$6t = 30.84 \times 1000 \times 0.1$$

$$t = 514 \text{ sec.}$$

$$33. \int dw = \int -P.dV = - \int 20. \frac{dV}{V} = -20 \ln \frac{V_2}{V_1} = -46.06$$

$$\text{L-atm} = -4665.8 \text{ J}$$

$$\Delta U = q + w \Rightarrow 400 = q - 4665.8 \Rightarrow q = 5065.8 \text{ J}$$

34. n (no. of moles of O_2) = 4

$$V_1 = 20 \text{ Lit.} \quad V_2 = 60 \text{ Lit.}$$

$$T_1 = 270 \text{ K}$$

$$W = -P_{\text{ext}} dV$$

$$W = -\frac{600}{760} \times (60 - 20) = -\frac{600 \times 40}{760} = -31.58 \text{ L-atm}$$

$$= -31.58 \times 101.35 \text{ J} = -3.2 \text{ kJ}$$

In case of adiabatic process,

$$dE = dq + dw \text{ \& } dE = dw \text{ (} \because dq = 0)$$

$$\Delta E = W = -3.2 \text{ kJ}$$

$$W = \frac{nR}{\gamma - 1} (T_2 - T_1) = -3200 \Rightarrow \Delta T = \frac{-3200(1.4 - 1)}{4 \times 8.312}$$

$$\Delta T = -38 \text{ K}$$

$$\Delta H = nC_p \Delta T = 4 \times \frac{7}{2} R (-38) = -4.42 \text{ kJ.}$$