Thermodynamics-I

SOLUTIONS

EXERCISE - O

1. **Ans. (B)**

Closed system $\Rightarrow$ exchange of energy is allowed but exchange of matter is not allowed.

2. **Ans. (C)**

Closed container not insulated $\Rightarrow$ can exchange energy but not matter.

3. **Ans. (C)**

system & surrounding are always separated by a real or imaginary boundary (in the case of universe).

4. **Ans. (B)**

$\frac{x}{y}$ is intensive variable (ratio of extensive variable becomes intensive).

5. **Ans. (D)**

Internal energy and enthalpy are state functions

6. **Ans. (A)**

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

$= -3 \times (6 - 4)$

$= -6$ litre-atm

$= -6 \times 101.3 = -607.8$ J

7. **Ans. (A)**

W.D = Area under the PV curve = Area of rectangle

$w_{A-B} = -3P_0(4V_0 - V_0) = -9P_0V_0$

$w_{C-D} = -P_0(V_0 - 4V_0) = +3P_0V_0$

w_{A-D} & $w_{B-C} = 0$ (V = constant)

Net W.D $= -9P_0V_0+3P_0V_0 = -6P_0V_0$

8. **Ans. (C)**

Work done = are enclosed by ellipse

$= \pi (a \times b)$

$a = \frac{V_2 - V_1}{2}$; $b = \frac{P_2 - P_1}{2}$

$= \frac{\pi}{4}(P_2 - P_1)(V_2 - V_1)$

9. **Ans. (B)**

Internal energy is state function it is not path dependent $\Delta U = U_f - U_i$

System return to initial state $U_f = U_i$

$\Delta U = 0$

10. **Ans. (A)**

$\Delta U = q + w$

$w = -P_{ext}dV \Rightarrow dV = 0$

$w = 0$

$\Delta U = q$

$\Delta U = 200$ J

11. **Ans. (A)**

In vacuum $P_{ext} = 0$

$w = -P_{ext}\,\Delta V$

$w = 0$

12. **Ans. (C)**

$U = \frac{nfRT}{2}$

$U \propto f$

13. **Ans. (D)**

Isothermal $\Rightarrow \Delta U = 0$

14. **Ans. (D)**

First law (1 cal = 4.2 J)

$\Delta U = q + w$

$\Delta U = 100 \times 4.2 - (300)$

$\Delta U = 420 - 300$

$\Delta U = 120$ J

15. **Ans. (A)**

Work done by system = –8 J

Heat = + 40 J

$\Delta U = q + w$

$40 - 8 = \Delta U$

$\Delta U = 32$ J

16. **Ans. (C)**

$\Delta U = q + w$

$300 = 400 + 0.5 \times \Delta V \times 100$

$\Delta V = 2$ L

17. **Ans. (A)**

q = +500KJ (WD. By system)

Area under P.V curve = $-(2\times2+\frac{1}{2}\times2\times2)10^5$ (1 bar = 10^5pascal)

$\Delta U = q + w$

$\Delta U = 500 - 600 = -100$KJ

18. **Ans. (A)**

For monoatomic gas $C_p = \frac{5}{2}R$; $C_v = \frac{3}{2}R$

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

19. Ans. (B)

Enthalpy of system (H) = U + PV

It is the sum of internal energy and PV.

20. Ans. (A)

Molar heat capacity at constant volume = C_V

Molar heat capacity at constant volume = $\frac{R}{\gamma-1}$

1 mole $\rightarrow \frac{R}{\gamma-1}$

M g $\rightarrow \frac{R}{\gamma-1}$

Specific heat capacity at constant volume 1 gm $\rightarrow \frac{R}{M(\gamma-1)}$

21. Ans. (C)

For diatomic gas

n = 1 $C_V = \frac{5R}{2}$, $C_P = \frac{7R}{2}$

AB $\Rightarrow$ Constant volume

T_A = 300K, T_B = 600K

$q_B = \Delta U = nC_V\Delta T$

$q_V = 1\times\frac{5R}{2}(600-300)$

$q_V = 750R$

CA $\Rightarrow$ Constant pressure

$q_P = \Delta H = nC_P\Delta T$

$q_P = 1\times\frac{7R}{2}(300-400)$

$q_V = -350R$

22. Ans. (B)

At constant pressure

$\Delta H = nC_p\Delta T$

$\Delta U = nC_v\Delta T$

Required function = $\frac{-\Delta w}{\Delta H} = 1-\frac{\Delta U}{\Delta H} = 1-\frac{C_V}{C_P} = 1-\frac{1}{\gamma}$

23. Ans. (B)

Maximum work a gas does if it is allowed to expand iso-thermally

$w_{max} = -P_{ext}\Delta V$, $w_{max} \propto P_{ext}$

24. Ans. (A)

TV^2 = constant

$T_1V_1^2 = T_2V_2^2$

$400 \times 4^2 = T_2 \times 8^2$

$T_2 = \frac{400\times16}{64}$ = 100 K

$\Delta H = nC_p\Delta T$

$= 2 \times \frac{5}{2}R \times (-300) = -1500R$

25. Ans. (B)

$\Delta H = \Delta U + (-3)RT$

$\Delta H - \Delta U = -3\ RT$

26. Ans. (A)

Formula based from reversible isothermal process of work done $\int dw = -\int_{V_1}^{V_2} PdV$

27. Ans. (D)

Isochoric heating

$\Rightarrow$ V = constant $\Rightarrow \Delta V = 0$

Heating $\Rightarrow$ T $\uparrow$ $\Rightarrow \Delta T > 0$

$\Rightarrow \Delta U > 0$

$w = -P_{ext}dv = 0$ ($\Delta V = 0$)

First law of thermodynamics

$\Delta U = q + w$ ($w = 0$)

$\Delta U = q$

$\Delta U > 0$

$q > 0$

28. Ans. (C)

For isothermal process PV = constant

$\Rightarrow \left(\frac{dP}{dV}\right) = -\left(\frac{P}{V}\right)$ = slope of isothermal curve

For adiabatic process, PV^{γ} = constant

$\Rightarrow \left(\frac{dP}{dV}\right) = -\left(\frac{\gamma P}{V}\right)$ = slope of adiabatic curve

Clearly, $\left(\frac{dP}{dV}\right)_{adiabatic} = \gamma \left(\frac{dP}{dV}\right)_{isothermal}$

29. Ans. (D)

For reversible adiabatic process,

$w = -P_{ext}\left[\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right]$

$P_2 = P_{ext} = 2$ atm

$P_1 = 1$ atm

$T_1 = 300$ K

$w = -(2\text{ atm})\left[\frac{2(R).T_2}{2\text{atm}} - \frac{2R(350)}{1\text{ atm}}\right]$ and $w = 2C_v(T_2 - 350) = 2 \times \frac{5}{2} R\,(T_2 - 350)$

$5R(T_2 - 350) = (750\ R - 2\ RT_2)$

$5T_2 - 1750 = 1400 - 2T_2$

$7T_2 = 3150$; $T_2 = 450$ K

$w = 2 \times C_v(450 - 350)$

$= 2 \times \frac{5}{2} R \times (100) = 500\ R$

30. Ans. (B)

Polytropic Process is given by :

$PV^n = C$

work-done for a polytropic process :

$$w = \frac{P_2V_2 - P_1V_1}{1-n} = \frac{mR(T_2 - T_1)}{1-n} \text{ (m = no. of mole)}$$

$C_p - C_v = R$ and $\frac{C_p}{C_v} = \gamma \quad \therefore C_v = \frac{R}{\gamma - 1}$

$\Delta U = mc_v(T_2 - T_1)$

$$\Delta U = m\frac{R}{\gamma - 1}(T_2 - T_1) = w\frac{(1-n)}{(\gamma - 1)}$$

$$q = \Delta U + w = w\left[1 + \frac{(1-n)}{(\gamma - 1)}\right] = w\frac{(\gamma - n)}{(\gamma - 1)}$$

$$q = \left(\frac{\gamma - n}{\gamma - 1}\right) \times w$$

31. Ans. (C)

$T_A = 600K, V_A = 1L$

$P_A \times V_A = 1 \times RT_A$

$P_A = 600R$

$T_B = 300K$

$V_B = 4L$

$P_BV_B = 1 \times R \times 300$

$$P_B = \frac{300}{4}R = 75R$$

$P_AV_A^x = P_BV_B^x$

$(600R)(1)^x = (75R)(4)^x$

$600R \times 1 = 75R \times (4)^x$

$4^x = 8$

$2^{2x} = 2^3$

$2x = 3$

$$\boxed{x = \frac{3}{2}}$$

32. Ans. (A)

$$-w = \int PdV = \int 10.\frac{dV}{V} = 10 \ln \frac{V_2}{V_1} = 10 \times \ln 10 \text{ atm L} = 23 \text{ atm L} = 2332.2 \text{ J}$$

$(q = \Delta U - w)$

$q = 420 + 2332.2 = 2752.2$ J

33. (A,B,C)

Isolated system boundary must be rigid, adiabatic (insulated) & impermeable.

34. Ans. (B,C,D)

Temperature, Molar heat exchanged at constant volume, Molar heat exchanged at constant pressure intensive as well as state functions.

35. Ans. (A, C)

Density, Boiling point independent on the quantity of matter.

36. **Ans. (A,C,D)**

B $\Rightarrow$ Heat = path function

A,C,D $\Rightarrow$ state function

37. **Ans. (A,B)**

Intensive $\Rightarrow$ Molar conductivity & E.M.F of a cell

extensive $\Rightarrow$ Resistance & heat capacity

38. **Ans. (C,D)**

$B \longrightarrow C$ $\quad V\downarrow \Rightarrow T\downarrow$ $\quad (P = \text{constant } V \propto T)$

Exothermic process

$A \longrightarrow B$ $\quad P\downarrow \Rightarrow T\downarrow$ $\quad (V = \text{constant } P \propto T)$

Exothermic process

$C \longrightarrow A \quad \rightarrow$ For cyclic process $\Delta V = 0$

$P\uparrow V\uparrow T\uparrow\uparrow$

$\Delta U = q + w$

$\Delta U = +ve$

$\Delta U = q - P_{ext}(\Delta V)$

$\underset{+ve}{\Delta U} + \underset{+ve}{P_{ext}(\Delta V)} = q,\ q = +ve$ endothermic

39. **Ans. (A,B,C)**

Both P & V are increasing so temperature will also increase. Interforce $\Delta U > 0$

As volume is increasing

So, $w < 0$

$\Delta U = q + w$

$q = \Delta U - w$

$\boxed{\Delta U > 0}$ $\quad \boxed{w < 0}$

$\boxed{q > 0}$

40. **Ans. (A,B,C)**

diatomic gas

DOF $\Rightarrow f = 5$

$C_V = \frac{fR}{2}$, $C_P = C_V + R$

$C_V = \frac{5R}{2}$, $C_P = \frac{7R}{2}$

$\gamma = \frac{C_P}{C_V} = \frac{7}{5} = 1.4$

41. **Ans. (A,C,D)**

Constant volume ($\Delta H = 0$)

$w = -Pdv = 0$

$\Delta U = nC_V\Delta T = \frac{nR}{\gamma - 1}\Delta T$

$\Delta U = nC_V\Delta T = \frac{10 \times R}{(1.2-1)} \times 20$

$\Delta U = nC_V\Delta T = 1000\ R$

$\Delta H = \gamma\Delta U = 1200\ R$

EXERCISE - S

1. Ans. (4)

Intensive properties : Temperature , Molar volume , Molar heat capacity, viscosity defined for 1 mole so they are intensive.

2. Ans. (3.29)

Mol. wt. of benzene, $C_6H_6 = (6 \times 12) + (6 \times 1) = 78$ g mol^{-1}

(i) 78 g benzene require heat for vaporisation = 30.8 kJ

50 g benzene require heat for vaporisation

$= \frac{30.8}{78} \times 50 = 19.74$ kJ

(ii) 100 watt heater gives energy = 100 J s^{-1} [$\because$ 1 W = 1 js^{-1}]

$\therefore$ Time required to get 19.74 kJ energy

$= \frac{19.74\,\text{kJ}}{100\,\text{Js}^{-1}} \times 1000$

$= 197.4$ s $= 197.4$ s $\times \frac{1\text{ min}}{60\,\text{s}}$

= 3.29 minutes

3. Ans. (– 810.4)

Since the gas is allowed to expand against the external pressure, the work done is negative and is irreversible.

$\therefore$ $w_{irr} = -P_{ext}(V_2 - V_1) = -1 \times (10 - 2) = -8$ atm L

$\therefore$ 1 atm L = 101.3 J

$= -8 \times 101.3$

$= -810.4$ J

4. Ans. (290.8)

g. mol. wt. of $H_2O = (2 \times 1) + 16 = 18$ g

C = 4.184 J g$^-$ K$^-$

= 4.184 × 18 J mol$^-$ K$^-$

n = 10 mol; ΔT = ?

Since work has been done against external pressure, it is negative as well as irreversible.

So: $w = -P_{ext} \times \Delta V = -3$ atm $\times (5 - 3)$ dm^3 or l = – 6 atm L (1 atm L = 101.3 J)

$w = -607.8$ J

Since work is used to heat 10 mol of water

$w = n \times C \times \Delta T$

$\therefore$ $\Delta T = \frac{607.8\text{J}}{10 \times 4.184 \times 18} = 0.8$ K

$\therefore$ Final temperature = 290 K + 0.8 K = 290.8 K

5. Ans. (–4.00)

No. of moles, n = 1

P_{ext} = 1 atm

$\Delta V = V_2 - V_1$ = 5 litre – 1 litre = 4 litre

$W_{gas} = -P_{ext.} \cdot \Delta V$ = –1 atm × 4 litre = –4 litre atm

W_{gas} = –4 litre atm

6. Ans. (8250.00)

As ideal gas

$\Delta U = nC_v \Delta T$

$= 1 \times \frac{5R}{2} \times (800 - 500)$

$= \frac{5}{2} \times \frac{25}{3} \times 300$

= 6250 J

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

$= -2 \cdot (20 - 10)$ bar-L

= –20 × 100 joule

By 1st law $\Delta U = q + W$

6250 = q + (–2000)

q = 8250 Joule

7. Ans. (303.9)

P_1 = 3 atm, V_1 = 1.5 L, T = 273 K

P_2 = 1 atm, V_2 = ?;

At constant temperature, T

$P_1V_1 = P_2V_2$; 3 × 1.5 = 1 × V_2; V_2 = 4.5 L

External pressure being different from that of H_2 pressure, w is irreversible and negative.

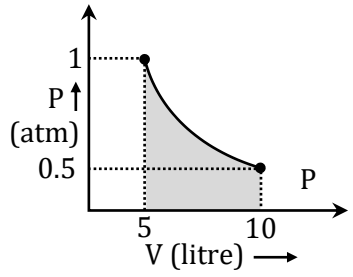
So, $w = -P_{ext} (V_2 - V_1) = -1 (4.5 - 1.5)$

$= -3$ atm L $\quad \therefore$ 1 atm L = 101.3 J

$= -3 \times 101.3$

= –303.9 J

8. Ans. (3.50)



$P_1V_1 = 1 \times 5$

$P_2V_2 = 0.5 \times 10$

As $P_1V_1 = P_2V_2 \Rightarrow$ Isothermal

$$W = - \; P_1V_1\ell n\left(\frac{P_1}{P_2}\right)$$

$$= - \; 1\times5\times\ell n\left(\frac{1}{0.5}\right)$$

$$= - \; 5 \times \ell n2$$

$$= - \; 3.5$$

Shaded area = $|-3.5|$

$= 3.5$

9. Ans. (–900.00)

As external pressure is constant $\Rightarrow$ Irreversible process

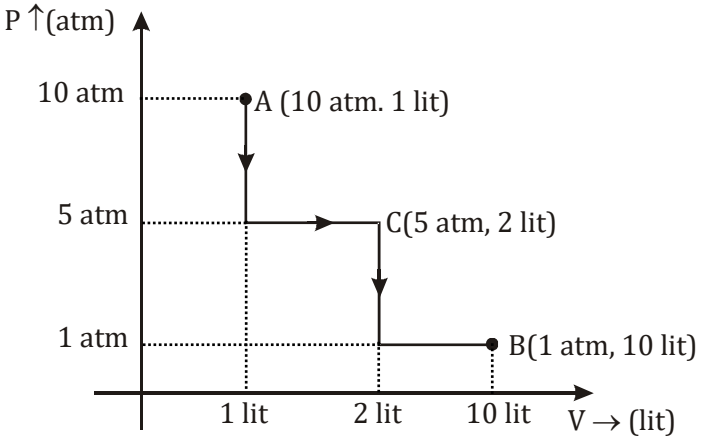
$\omega = - P_{ext}.(V_2 - V_1)$

$= - 10^5 \cdot (10^{-2} - 10^{-3})$

$= - 10^5 \cdot 10^{-2} \cdot (1 - 0.1)$

$= - 900$ Joule

10. Ans. (13.00)



Ideal gas isothermal

So $\Delta U_{A\,to\,B} = 0$

Or $\boxed{q_{AtoB} = -w_{AtoB}}$

Isothermal expansion, 1st against 5 atm then against 1 atm

Due to Isothermal expansion, T is constant means

$P_AV_A = P_C \cdot V_C$

$10 \times 1 = 5 \times V_C \Rightarrow \boxed{V_C = 2\,lit}$

Total area under P.V. curve

$A = 5 \times (2 - 1) + 1 \times (10 - 2)$

$= 13$ lit atm

So work done by gas $w_{A\,to\,B} = - A = - 13$ lit atm (expansion)

Now $\boxed{q_{AtoB} = -w_{AtoB} = +13\,lit\,atm}$

11. Ans. (9.00)

No. of moles of gas $\Rightarrow$ n = 1

W_{AB} = – area under P – V

$= -\frac{1}{2}(7.5-3)\text{lit.}\times(2\times8)\text{atm}$

W_{AB} = –22.5 atm lit.

$\Delta U_{AB} = n\,C_{Vm}\Delta T = \frac{n.R}{Y-1}(T_2-T_1) = \frac{1}{Y-1}\,(nRT_2 - nRT_1)$

$= \frac{P_2V_2-P_1V_1}{Y-1}$

$= \frac{2\text{atm}\times7.5\text{lit}-8\text{atm}\times3\text{lit}}{\frac{5}{3}-1}$

$= -\frac{27}{2}\text{lit atm}$

$\therefore$ ΔU_{AB} = –13.5 lit. atm

So $\Delta U_{AB} = q_{AB} + W_{AB}$

$\Rightarrow$ $q_{AB} = \Delta U_{AB} - W_{AB}$

= – 13.5 lit. atm – (–22.5 lit. atm)

q_{AB} = 9 atm lit.

12. Ans. (–3.00)

As adiabatic $\Rightarrow$ q = 0

$\Delta U = w = -P_{ext}.(V_2 - V_1)$

$= -1.(5-2)$

$= -3$ bar L

13. Ans. (–562.50, –1.20)

As irreversible adiabatic process:

$nC_V(T_2 - T_1) = -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$

$n\times3R.(T_2-400) = -1\left(\frac{nRT_2}{1} - \frac{nR.400}{16}\right)$

$3(T_2-400) = -T_2 + \frac{400}{16}$

$4T_2 = 1200 + 25$

$\Rightarrow T_2 = \frac{1225}{4}\text{K}$

$w = nC_V(T_2-T_1) = 1\times3R\times\left(\frac{1225}{4}-400\right)$

= – 562.5 cal.

For reversible adiabatic : $P_1^{1-Y}T_1^Y = P_2^{1-Y}T_2^Y$

$$\Rightarrow \quad \left(\frac{16}{1}\right)^{1-4/3} = \left(\frac{T_2}{400}\right)^{4/3}$$

$(2^4)^{-1/4} \Rightarrow T_2/400 \Rightarrow T_2 = 200$ K

$w = nC_V(T_2 - T_1)$

$= 1 \times 3R \,.\, (200 - 400)$

$= -1200$ cal $= -1.2$ Kcal

14. Ans. (500.00)

A monoatomic ideal gas $\left(Y = \frac{5}{3}\right)$ compressed, adiabatically irreversibly from 4 lit to 1 lit against 1 bar

$\Rightarrow \quad w_{irr} = -P_{ext}(V_2 - V_1)$

$= -1$ bar $(1$ lit $- 4$ lit$)$

$= +3$ bar lit

$= 300$ J $\quad (1$ bar lit $= 100$ J$)$

Adiabatic process $q = 0$

$\Delta U = w \quad \Rightarrow \quad \Delta U = 300$ J

for ideal gas $\frac{\Delta H}{\Delta U} = \frac{C_P}{C_V} = Y$

$$\Delta H = \frac{5}{3} \times 300 = 500$$

$$\boxed{\Delta H = 500 J}$$

15. Ans. (3.50)

As V-T graph is passing through origin $\Rightarrow$ Isobaric process

$q = nC_p \Delta T$

Work done by the gas $= nR\Delta T$

$$\frac{q}{W} = \frac{C_p}{R} = \frac{7\frac{R}{2}}{R} = 3.5$$

16. Ans. 1440.00 , (1440.03 to 1440.04)

$H_2O(s) \quad \rightleftharpoons \quad H_2O(l)$ At constant pressure 1 atm, $q = 1440$ cal

1 mole

$V_{H_2O(s)} = 0.0196$ lit. $\quad V_{H_2O(\ell)} = 0.018$ lit

For solid and liquid reactions, we assume almost negligible volume and pressure change occurs so

$\Delta H = \Delta U = 1440$ cal

17. Ans. (–3.90 to –4.00)

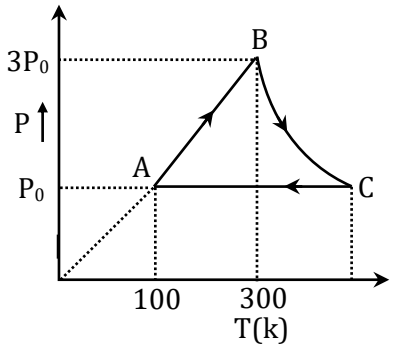
$$W = -nRT \ \ell n\left(\frac{P_1}{P_2}\right)$$

$$= -1 \times R \times 300 \times \ell n \frac{5}{1}$$

$$\simeq -4 \text{ kJ}$$

18. Ans. (–800.00)

Number of moles of gas n = 1 (ideal gas)



Path AB

It $P_A = P_0$

$P_B = 3P_0$ $(P \propto T)$

$W_{AB} = 0$ (isochoric)

Path BC

$P_BT_B = P_CT_C$

$\Rightarrow$ $3P_0 \times 300 = P_0 \times T_C \Rightarrow T_C = 900\ K$

$PT = \text{constant} \Rightarrow P.\left(\frac{PV}{nR}\right) = \text{constant} \Rightarrow \boxed{P.V^{1/2} = k}$

$PV^x = k'$

$x = \frac{1}{2}$

$w_{BC} = \frac{nR\Delta T}{x-1}$

$= \frac{1\times 2cal\times(T_C - T_B)}{x-1} = \frac{1\times 2cal\times(900-300)}{-\frac{1}{2}}$

$w_{BC} = -2400$ cal

Path CA Isobaric path

$w_{CA} = -nR\Delta T_{CA} = -1 \times 2cal \times (100 - 900) = +1600$ cal

$w_{net} = w_{AB} + w_{BC} + w_{CA}$

$= 0 - 2400 + 1600$

$\boxed{w_{net} = -800\ cal}$

19. Ans. (–0.25)

$PV^2 = C$

$\left(\frac{nRT}{V}\right)V^2 = k$

$TV = k$

$\Rightarrow \quad T_1V_1 = T_2V_2$

$273 \times 1 = T_2 \times 2$

$T_2 = \frac{273}{2}K$

$C_m = C_V + \frac{R}{1-x}$

$= \frac{3R}{2} + \frac{R}{1-2}$

$= \frac{R}{2}$

$q = nC_M\Delta T$

$= \frac{1}{22.4} \times \frac{R}{2} \times \left(\frac{273}{2} - 273\right)$

$= \frac{1}{22.4} \times \left(\frac{22.4}{2 \times 273}\right) \times \left(\frac{-273}{2}\right) = -0.25$ atm-L

20. Ans. ((a) 3.67 ; (b) 2566.67 ; (c) –466.67 ; (d) 2100.00)

Process following path $\frac{P}{V^2}$ = constant

$\boxed{PV^{-2} = constant}$

For polytropic process: PV^x = constant

$\boxed{x = -2}$

(a) Molar heat capacity : $C_m = C_{Vm} + \frac{R}{1-x}$

$= \frac{3}{2}R + \frac{R}{1-(-2)}$

$= \frac{3}{2}R + \frac{R}{3} = \frac{11}{6}R = \frac{11}{3}$ cal/K.mole

$\boxed{C_m = \frac{11}{3}\frac{Cal}{K.mole}}$

(b) Heat absorbed (q)

$q = nC_m\Delta T$

$q = 1 \times \frac{11}{3}\frac{Cal}{k.mol}(800 - 100)$

For T_2

$\frac{P}{V^2} = k \Rightarrow \frac{nRT/V}{V^2} = K$

$\frac{T}{V^3} = k^1$

$= \frac{11}{3}\times(800-100)$

$= 2566.67$ cal

$\boxed{q = 2566.67 \text{ Cal}}$

$\frac{T_1}{V_1^3} = \frac{T_2}{V_2^3}$

$\Rightarrow \quad T_2 = T_1\left(\frac{V_2}{V_1}\right)^3$

$= 100\left(\frac{2}{1}\right)^3$

$\boxed{T_2} = 800K$

(C) Work $w = \frac{nR\Delta T}{x-1}$ (for polytropic)

$= \frac{1\times 2cal\times(800-100)}{-2-1}$

$\boxed{w = -466.67 \text{ cal}}$

(D) $\Delta U = q + w$

$= 2566.67 - 466.67 = 2100$ cal

$\Rightarrow \boxed{\Delta U = 2100 \text{ cal}}$

21. Ans. (6)

NH_3 is a non–liner molecule

Translational DOF = 3

Rotational DOF = 3

Vibrational DOF (at room temp.) = 0

So total DOF = 6

22. Ans. (i) 9, 3, 2, 4 (ii) 9, 3, 3, 3 (iii) 3, 3, 0, 0 (iv) 12, 3, 3, 6

(i) CO_2 : Total degrees of freedom = 3 × atomicity = 3 × 3 = 9

Translational degrees of freedom = 3

Rotational degrees of freedom = 2 [CO_2 is linear]

Vibrational degrees of freedom = 9 – (3 + 2) = 4

(ii) SO_2 : Total degrees of freedom = 3 × 3 = 9

Translational degrees of freedom = 3

Rotational degrees of freedom = 3 [SO_2 is bent]

Vibrational degrees of freedom = 9 – 3 – 3 = 3

(iii) He : Total degrees of freedom = 3 × 1 = 3

Translational degrees of freedom = 3

Rotational and vibrational degrees of freedom = 0

(iv) NH_3 : Total degrees of freedom = 3 × 4 = 12

Translational degrees of freedom = 3

Rotational degrees of freedom = 3 [NH_3 non linear]

Vibrational degrees of freedom = 12 – 3 – 3 = 6

23. Ans. (a) 170.00 (b) 10.00

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

$U_A = +10$ J

$\Delta V_{AC} = U_C - U_A = U_C - 10$ J (And $\Delta U_{AC} = w_{AC} + q_{AC}$)

$\Rightarrow \quad \Delta U_{AC} = -\frac{1}{2} \times (6-2) \times (5+15) \frac{N}{m^2}.m^3 + 200J$

$\Rightarrow \quad U_C - 10J = -\frac{1}{2} \times 4 \times 20\ J + 200\ J$

$\Rightarrow \quad U_C - 10J = -40J + 200\ J$

$U_C = 170$ J

(b) $W_{AB} = 0$ (Isochoric)

$\Delta U_{AB} = 10$ J

So, $\Delta U_{AB} = 9_{AB} + W_{AB}$

$10\ J = q_{AB} + 0$

$\Rightarrow \quad q_{AB} = +10$ J

24. Ans. (9900)

Molar volume of liquid at 1 bar pressure = 100 mL = V_1

molar volume of liquid at 100 bar pressure = 100 – 1 = 99 mL = V_2

Since the change in pressure is very large, it is irreversible process.

$W = -P(V_2 - V_1)$

$= -100$ bar $(99 - 100)$ mL

$= +100$ bar mL

The container being isolated,

$q = 0$

But, $\Delta U = q + w$

So, $\Delta U = 0 + 100$ bar mL $= 100$ bar mL

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

$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$

$\Delta H = 100 + (100 \times 99 - 1 \times 100)$

$= 100 + 9800$

$= 9900$ bar ml

25. Ans. (420.00)

For ideal gas

$\Delta H = nC_p \Delta T$

$= 1 \times \frac{7R}{2} \times (360 - 300)$

$= \frac{7}{2} \times 2 \times 60$

$= 420$ calorie

EXERCISE - JEE (Main) PYQ

1. **Ans. (2)**

$\Delta U_{AB} = q_{AB} + w_{AB} = 2 + (-5) = -3$ kJ/mol

$\Delta U_{BC} = -5$ kJ/mol

For cyclic process, $\Delta U = 0$

$\Delta U_{AB} + \Delta U_{BC} + \Delta U_{CA} = 0$

$\Delta U_{CA} = -\Delta U_{AB} - \Delta U_{BC}$

$\Delta U_{CA} = -(-3) - (-5) = 8$ kJ/mol

$\Delta U_{CA} = q_{CA} + w_{CA}$

$8 = q_{CA} + 3$

$q_{CA} = +5$ kJ/mol

Heat absorbed has positive sign.

2. **Ans. (2)**

For reversible isothermal expansion,

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

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

$|w| = nRT(\ln V_2 - \ln V_1)$

$|w| = nRT \ln V_2 - nRT\, V_1$

$y = mx + c$

So, slope of curve 2 is more than curve 1 and intercept of curve 2 is more negative than curve 1.

3. **Ans. (2)**

We know that,

$w = -P_{ext}(V_f - V_i)$

$w = -4\ Nm^{-2}(1 - 5)m^3$

$w = 16\ Nm \Rightarrow 16\ J$

For isothermal compression,

$\Delta U = q + w$

$\Rightarrow$ $q = -w = -16$ J ($\because$ $\Delta U = 0$ for isothermal process)

From calorimetry,

Heat given = $n\ C\ \Delta T$

$$\text{So, } 16 = \frac{1\times 24\text{J}\times\Delta T}{\text{mol K}}$$

$\therefore$ Change in temperature, $\Delta T = \frac{2}{3}$ K

4. **Ans. (3)**

$w = -P\Delta V$

$= -(1\text{ bar}) \times (9\text{ L})$

$= -(10^5\text{ Pa}) \times (9 \times 10^{-3})\ m^3$

$= -9 \times 10^2$ N.m [$\because$ 1 Pa = 1 N/m^2]

$= -900\text{ J} = -0.9\text{ kJ}$

5. **Ans. (3)**

$w = 10$ kJ

$q = -2$ kJ

$\Delta U = q + w = -2 + 10 = 8$ kJ

6. **Ans. (2)**

From first law of thermodynamics, $\Delta U = q + w$

For adiabatic process, $q = 0$

$\therefore \quad \Delta U = w$

For isothermal process, $\Delta U = 0 \Rightarrow q = -w$

For cyclic process, $\Delta U = 0 \Rightarrow q = -w$

For isochoric process, $w = 0 \Rightarrow \Delta U = q$

7. **Ans. (3)**

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

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

8. **Ans. (1)**

For ideal gas, C_p and C_v are dependent on temperature only.

$C_p = \frac{7}{2} R$ (Independent of P)

$C_v = \frac{5}{2} R$ (Independent of V)

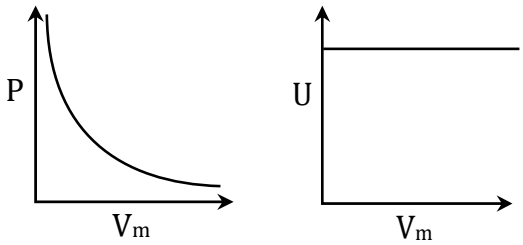
Thus, C_p will not change with pressure.

9. **Ans. (3)**

Isothermal expansion

$PV_m = K$ (graph - C)

$P = \frac{K}{V_m}$ (graph - A)



Therefore (B) and (D) are not correct representation.

10. **Ans. (0)**

In expansion against vacuum

$P_{ext} = 0$

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

$w = 0$

11. **Ans. (48)**

Work done is given by the area under the trapezium.

$\therefore \quad 6 \times 6 + \frac{1}{2} \times 4 \times 6 = 48$ J

12. **Ans. (6.25)**

$\Delta U = nC_v\Delta T$

$5000 = 4 \times C_v(500 - 300)$

$C_v = 6.25\ JK^{-1}\ mol^{-1}$

13. **Ans. (82)**

HCl	+	NaOH	→	NaCl	+	H_2O
0.04		0.03		–		–
		–		0.03		0.03

Heat released (q) = $0.03 \times 57.1 \times 1000 = 1713$ J

$q = mc\Delta T$

$1713\ J = 500\ g \times 4.18 \times \Delta T$

v = 500 mL

$$\Delta T = \frac{1713}{500 \times 4.18}$$

$= 0.8196 \approx 82 \times 10^{-2}$ K

14. **Ans. (741)**

$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(l)$$

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

$$\Delta n_g = 2 - \frac{3}{2} = 0.5$$

$$\Delta H_{298} = -742.24 + \frac{0.5 \times 8.314 \times 298}{1000}$$

$= -742.24 + 1.24 = -741$ kJ.

15. **Ans. (57)**

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

$\Delta H = -59.6 + 1 \times 8.314 \times 300 \times 10^{-3} = -57.10$

16. **Ans. (2)**

$C_{p,m} = C_{v,m} + R$

$\Rightarrow C_{v,m} = 20.785 - 8.314 = 12.471\ J\ k^{-1}\ ml^{-1}$

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

$$\Rightarrow n = \frac{5000}{12.471 \times 200} = \frac{25}{12.471} \approx 2$$

17. **Ans. (1)**

Adiabatic boundary does not allow heat exchange thus heat generated in container can't escape out thereby increasing the temperature.

In case of Diathermic container, heat flow can occur to maintain the constant temperature.

18. **Ans. (4)**

Extensive $\Rightarrow$ Mole, Volume, Gibbs free energy.

Intensive $\Rightarrow$ Molar mass, Molar heat capacity, Molarity, E^{θ} cell.

19. Ans. (1200)

Power of heater = 60 W

= 60 J/sec

Total energy emitted

= 60 × 100 = 6000 J

Heat capacity × temp difference = 6000

Heat capacity $= \frac{6000}{5} = 1200 JK^{-1}$

20. Ans. (620)

$1 \to 2 \Rightarrow$ Isobaric process

$2 \to 3 \Rightarrow$ Isochoric process

$3 \to 1 \Rightarrow$ Isothermal process

$W = W_{1\to2} + W_{2\to3} + W_{3\to1}$

$= \left(-P(V_2 - V_1) + 0\left[-P_1V_1 \ln\left(\frac{V_2}{V_1}\right)\right]\right)$

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

$= -20 + 20\ln 2$

$= -20 + 20\times 2.3\times 0.3$

$= -6.2 \text{ bar L}$

$|W| = 6.2 \text{ bar l} = 620 \text{ J}$

EXERCISE - JEE (Advanced) PYQ

1. Ans. (A,C,D)

Since temperature is constant in any isothermal process $T_1 = T_2$

Form ideal gas equation $T_2 = \frac{P_2V_2}{nR}$ and $T_3 = \frac{P_3V_2}{nR}$

from the graph $P_2 > P_3$ so $T_2 > T_3$

So relation between temperature $T_1 = T_2 > T_3$

The work done is the area under P–V curve. Since the isothermal curve is above the adiabatic curve at all times, the area under the isothermal curve is greater,

$W_{isothermal} > W_{adiabatic}$

$\Delta V = nC_v\Delta t$

$\Delta U_{isothermal} = nC_v(T_1 - T_2) = 0$ (Since $P_1 = T_2$)

and for adiabatic process we have

$\Delta U_{adiabatic} = nC_v(T_2 - T_1) < 0$; (Since $T_1 > T_3$)

Thus $\Delta U_{isothermal} > \Delta U_{adiabatic}$

Final Answer

$T_1 = T_2 > T_3$

$W_{isothermal} > W_{adiabatic}$

$\Delta U_{isothermal} > \Delta U_{adiabatic}$

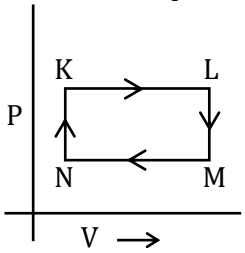
correct Answer $\to$ (A,C,D)

2. **Ans. (B)**

The isobaric process is carried out at constant pressure whereas isochoric is carried out at constant volume.

From PV = nRT for isochoric process

$P \alpha T$ and for isobaric process $V \alpha T$



$K \rightarrow L \Rightarrow$ Isobaric process

$L \rightarrow M \Rightarrow$ Isochoric process

$M \rightarrow N \Rightarrow$ Isobaric process

$N \rightarrow K \Rightarrow$ Isochoric process

3. **Ans. (C)**

$K \rightarrow L$

Volume increases at constant pressure, hence the gas will be heated

$L \rightarrow M$

Pressure decrease at constant volume, it will take place by cooling

$M \rightarrow N$

Volume decreases at constant pressure, it will take place by cooling the gas

$N \rightarrow K$

Pressure increases at constant volume, it will take place by heating

4. **Ans. (A, B, C)**

(A) $q = 0$

(B) $T_2 = T_1$

(C) $P_2V_2 = P_1V_1$

This is free expansion & it is irreversible power

Here W, q, ΔE are zero ΔT is also zero

q is zero (insulated vessel)

$T_2 = T_1$

($w = -P_{ext} \Delta V$ = zero as $P_{ext} = 0$)

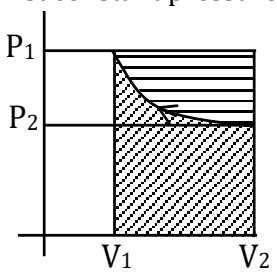
$\Delta E = nC_v\Delta T \Rightarrow$ zero

correct Answer (A), (B), (C)

PV^{γ} = constant applicable for irreversible power

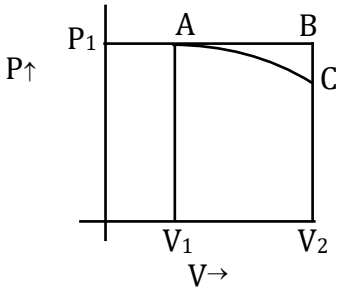
5. **Ans. (ABD)**

(A) The work done on the gas is maximum when it is compressed reversibly from (P_2V_2) to (P_1V_1) against constant pressure



$W_{irr} > w_{rev}$

(B) The work done on the gas is les when it' expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to when expanded reversibly from V_1 to V_2 under thermal conditions



AB : Reversible isothermal

AC : Reversible adiabatic

$|W_{AB}|>|W_{AC}|$

(C) The change in internal energy of the gas (i) zero if it's expanded reversibly with $T_1 = T_2$ and (ii) negatives if it's expanded reversibly under adiabatic conditions with $T_1 \neq T_2$

$\Delta U = nC_v\Delta T = 0$ (isothermal)

$\Delta U = q + w = -ve$ $(q = 0\ w < 0)$

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

(D) If the expansion is carried out freely it is simultaneously both isothermal as well as adiabatic

$q = 0$ (adiabatic) $w = 0$ (free expansion)

$\Delta V = 0 \Rightarrow \Delta T = 0$ (isothermal)

correct option (A), (B) and (D)

6. Ans. (B,C)

(A) $q_{AC} = \Delta U_{AC} = nC_v(T_2 - T_1) = \Delta U_{BC}\ nC_v(T_2 - T_1)$

$W_{AB} = -nRT\ell n\ \frac{V_2}{V_1}$ (Reversible process)

(B) $q_{BC} = -P_2(V_1-V_2) = P_2(V_2-V_1) = nC_p\ (T_2 - T_1)$

(C) $\Delta H_{AC} = nCp(T_1 - T_2) = nCp(T_2 - T_1)$

$\Delta V_{CA} = nCv(T_1 - T_2) = -nCv(T_2 - T_1)$

$Cp>Cv$

$\Delta H_{AC} < \Delta V_{CA}$

(D) $q_{BC} = \Delta H_{BC} = nC_p\ (T_2 - T_1)$ Heat at constant pressure

$= \Delta H_{AC} - nC_p(T_2 - T_1)$

$\Delta H_{CA} = nC_p\ (T_1 - T_2) = -$ ve $(T_2 > T_1)$

$\Delta U_{CA} = nCv\ (T_1 - T_2) = -ve$

$\Delta H_{CA} < \Delta U_{CA}$

7. Ans. (A,B,C)

$w = -\int P_{ext.} dV$

for Vander-Waal gas $\left(P + \frac{a}{v^2}\right)(v - b) = RT$

$$P = \frac{RT}{(v-b)} - \frac{a}{V^2}$$

$$w = -\int\left(\frac{RT}{v-b} - \frac{a}{v^2}\right).dV$$

Above expression is applicable for reversible process of a Vander Waal gas.

8. Ans. (7)

For $A \rightarrow B$ $\qquad 600V_1^{\gamma-1} = 60V_2^{\gamma-1}$ $\quad (\gamma = 5/3)$

(Reversible adiabatic)

$\Rightarrow$ $600\ (V_1)^{2/3} = 60\ (V_2)^{2/3}$

$$\Rightarrow\ 10 = \left(\frac{V_2}{V_1}\right)^{2/3}$$

$$\Rightarrow\ 10 = \left(\frac{V_2}{10}\right)^{2/3}$$

$\Rightarrow$ $V_2 = 10(10)^{3/2} = 10^{5/2}$

Now, $q_{net} = RT_2\ ln\ 10 = 60\ R\ ln\ 10 = q_{AB} + q_{BC}$

$\because$ $q_{AB} = 0$

$$\Rightarrow\ q_{BC} = 60\ R\ ln\ 10 = 60\ R\ ln\ \frac{V_3}{V_2} \qquad [\because\ B \rightarrow C \text{ is reversible isothermal}]$$

$$\Rightarrow\ 60\ R\ ln\ 10 = 60\ R\ ln\left(\frac{V_3}{10^{5/2}}\right)$$

$$\Rightarrow\ \log 10 = \log V_3 - \frac{5}{2}$$

$$\Rightarrow\ \log V_3 = \frac{7}{2} \Rightarrow 2\log V_3 = 7$$

JEE (Main) Practice Paper

SECTION-A

1. Ans. (1)

Heat gain by zinc = Heat loosed by water

$M_{Zn}S_{Zn}(T_f - T_i) = m_{H_2O}S_{H_2O}(100 - T_f)$

$(65.38\text{ gm})\left(\frac{0.4J}{g}°C\right)(T_f - 20°C) = (180\text{ gm})(4.20J/g°C)(T_f - 100°C)$

$T_f = \frac{(65.38)(0.4)(20)+(180)(4.20)(100)}{(65.38)(0.4)+(180)(4.20)}$

$T_f = 97.3°C$

2. Ans. (3)

First Law of thermodynamics

$\Delta U = Q - w$ Q = 45J (heat absorbed)

$\Delta U = 45 - 70$ Q = 70J (work done by the system)

$\Delta U = -25$ J ΔU = change in internal Energy

3. Ans. (2)

First Law of thermodynamics

$\Delta U = Q + w$

$w = -P\Delta V$, $\Delta V = 0$, $w = 0$

$\Delta U = q = 500$ J

$w = 0$

Heat supplied to the system = +ve

[$\Delta U = 500$] [$Q = 500$]

4. Ans. (2)

$q = nC_p\Delta T$

$q = 0{\cdot}25 \times \frac{5}{2}R \times \Delta T$; Ar is monoatomic gas

$q = 0{\cdot}25 \times \frac{5}{2} \times 8.314 \times (36 - 20)$; $C_p = \frac{5}{2}R$

$q = 0{\cdot}25 \times \frac{5}{2} \times 8.314 \times 16$; $T_2 = 36°C$

q = 83.2 joule. ; $T_1 = 20°C$

5. Ans. (2)

$C_v = 12.5$ Joule/k mol

$\gamma = \frac{C_p}{C_v}$

$\gamma = \frac{C_v + R}{C_v}$ $\boxed{\therefore C_p - C_v = R}$

$\gamma = \frac{8.314 + 12.5}{12.5}$

$\gamma = 1.665$

An adiabatic reversible process of ideal gas equation we have

$PV^{\gamma} = K$

$$\gamma = \frac{C_p}{C_v}$$

Adiabatic process, pressure and volume of a sample of gas changes from (P_1V_1) to (P_2V_2) then
We have

$P_1 (V_1)^{\gamma} = P_2 (V_2)^{\gamma}$

Thus

$$P = \frac{K}{V^{\gamma}}$$

Work done by gas in this process is

$$w = -\int p.dV$$

Where limit integration goes from V_1 to V_2

Putting $P = \frac{K}{V^{\gamma}}$

$$w = \frac{-\left(P_1V_1 - P_2V_2\right)}{\gamma - 1}$$

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

$$= \frac{-2 \times 8.314 \times \left(300 - 200\right)}{1.665 - 1}$$

= –2500 J

= –2.5 kJ

6. Ans. (1)

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

ΔH = Heat given at constant pressure

ΔU = Heat given at constant volume

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

Δn_g = the difference between the number of gaseous moles of products and number of gaseous mol/ es in the reactant

$2C_6H_6 (l) + 15O_2C_g \longrightarrow 12CO_2 (g) + 6H_2O(l)$

$\Delta n_g = -3$

$\Delta H - \Delta U = -3 \times 8.314 \times 298$ J

= –7.432 KJ

7. Ans. (2)

Heat capacity is the amount of Heat added to a substance to raise it's temperature by one kelvin.

Hence at constant pressure, the molar Heat capacity is given by the ratio $\frac{dH}{dT}$

At constant pressure, water is in equilibrium with ice.

When Heat dH is supplied to the system.

The temperature change dT is zero as the heat supplied is utilized for the phase transition.

Hence, the molar Heat capacity of water in equilibrium with ice at constant pressure is infinite.

8. **Ans. (3)**

$T = \text{const} \Rightarrow \Delta U = 0 \qquad \Delta U = q + w \Rightarrow q = -w$

$$(8\text{ bar } 4\text{L}) \xrightarrow[w_1]{P_{ext} = 2\text{ bar}} (2\text{bar}, 16\text{L}) \xrightarrow[w_2]{P_{ext} = 1\text{bar}} (1\text{bar}, 32\text{L})$$

$w = w_1 + w_2 = -P_{ext}(V_2 - V_1) - P_{ext}(V_3 - V_2)$

$= -2(16 - 4) - 1(32 - 16)$

$= -24 - 16 = -40$ bar L $= -4000$ J.

$\therefore \quad q = -w = \boxed{4000\text{ J}}$

9. **Ans. (2)**

$$T \propto \frac{1}{\sqrt{V}}$$

$TV^{1/2} = \text{constant}$

For adiabatic process, $TV^{1/2} = TV^{\gamma - 1} = \text{constant}$

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

10. **Ans. (3)**

From the question, $\Delta U = w$ ...(i)

But from the 1st law of thermodynamics

$\Delta U = q + w$ ...(ii)

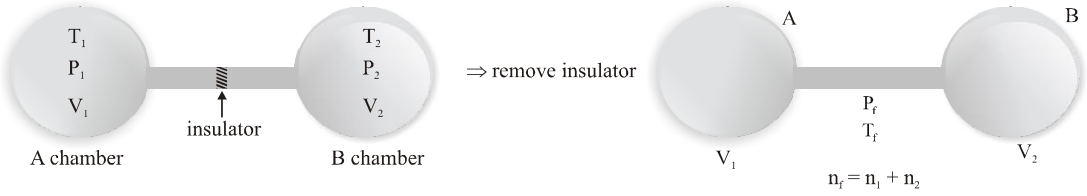
From equation (i) and (ii)

$q = 0$

Therefore, the process is adiabatic.

11. **Ans. (1)**

Two insulated chambers of gas



insulated chamber so $q_{net} = 0$

$W_{net} = 0$ (No work done due to intermixing of gases)

So according First law of thermodynamics:

$$\Delta U_{net} = q_{net} + w_{net}$$

$\Rightarrow \Delta U_{net} = 0 \qquad \Rightarrow \Delta U_A + \Delta U_B = 0$

$\Rightarrow n_1 C_{Vm} \Delta T_A + n_2 C_{Vm} \Delta T_B = 0$

$$\Rightarrow n_1(T_f - T_1) + n_2(T_f - T_2) = 0 \Rightarrow T_f = \frac{n_1 T_1 + n_2 T_2}{n_1 + n_2}$$

$$\Rightarrow T_f = \frac{\left(\frac{P_1 V_1}{R}\right) + \left(\frac{P_2 V_2}{R}\right)}{\left(\frac{P_1 V_1}{RT_1} + \frac{P_2 V_2}{RT_2}\right)} = \boxed{\frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_2 + P_2 V_2 T_1} = T_f}$$

12. **Ans. (2)**

$PV^3 = \text{constant}$

$PV \propto T$

$V \propto \frac{T}{P}$

$p\left(\frac{T}{P}\right)^3 = \text{constant}$

$T^3 \propto P^2$

$\frac{T_1^3}{P_1^2} = \frac{T_2^3}{P_2^2}$

$\left(\frac{T_1}{T_2}\right)^3 = \left(\frac{P_1}{P_2}\right)^2$

$\left(\frac{300}{T_2}\right)^3 = \left(\frac{1}{2\sqrt{2}}\right)^2$

$300 \times 300 \times 300 \times 8 = T_2^3$

$T_2 = 600K$

$w = \frac{nR\Delta T}{x-1}$

$= \frac{1\times R\times(600-300)}{2}$

$= 150R$

13. **Ans. (3)**

For process $(1 \rightarrow 2)$

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

$= -1 \times 2 \times 300\ln\left(\frac{20}{10}\right)$ (R = 2 cal/mol K)

$= -600 \times \ln_2$

$= -600 \times 0.7$

$= -420$ cal

For process $(2 \rightarrow 3)$

$w = -p(V_2 - V_1)$

$= \frac{-nRT_1}{V_1}(V_2 - V_1) = \frac{-1\times2\times300}{20}(40-20)$

$w = -600$ cal

For process $(3 \rightarrow 4)$

$V_1 = 40$ L, $V_2 = 10$ L, T = 600 K

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

$w = -1 \times 2 \times 600 \times \ln\left(\frac{10}{40}\right)$

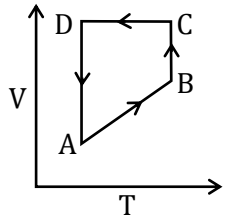
$w = 1200 \times 2\ln 2 = 1680$ cal

For process $(4 \rightarrow 1)$ (isochoric)

$w = 0$

Net work = $-420 + 1680 - 600 = 660$ cal

14. Ans. (3)



Process $A \rightarrow B$ = Isobaric

Process $B \rightarrow C$ = Isothermal

Process $C \rightarrow D$ = Isochoric

Process $D \rightarrow A$ = Isothermal

Ongoing $A \rightarrow B$, Volume increases

Hence '3' is the correct diagram.

15. Ans. (2)

$P_A \times T_A = P_B \times T_B$

$P_A \times T_A = 2P_A \times 300$

$T_A = 600K$

For the process A–B. it's given that

PT = constant

Differentiating above equation partially we have

PdT + TdP =0

Equation of state for two moles of a gas

$PV = nRT \text{ or } P = \frac{2RT}{V}$ ...(ii)

After differentiating Eq. (ii)

PdV + VdP = 2RdT ...(iii)

from eq. (ii)

$\left(\frac{2RT}{V}\right)dT + TdP = 0$

2RTdT + VTdP = 0

Vdp = – 2RdT ...(iv)

Now from eq. (iii) and (iv), we have

– 2RdT + PdV = 2RdT

PdV = 4RdT

The work done in the process AB

$W_{AB}\int PdV = \int_{600}^{300} 4RdT$

$= 4R(300 - 600)$

$= -1200R$

$W_{AB} = -1200R$

$\Delta U_{AB} = nC_vdT$

$= 2\times\frac{3}{2}\times R\times(300-600)$

$\Delta U_{AB} = -900R$

$Q = \Delta U - \Delta W$

$= -900R - 1200R$

$Q = -2100R$

16. Ans. (3)

moles of $H_2O(\ell) = \frac{500}{18}$ moles

$C_m(H_2O(l)) = 75.6$ J/mole k

$H_2O(l)$ loss heat and its temperature decreases from 20°C to 0°C

mass of one ice cube = 9 gm

moles of 1 ice cube = $\frac{9}{18}$ moles ; $\Delta H_{fussion}$(ice) = 6 kJ/mole

Let N number of ice cubes required (at 0°C) to convert $H_2O(l)$ from 20°C to 0°C

So, Heat gain by ice cubes (0°C ice to 0°C $H_2O(l)$) = Heats loss by $H_2O(l)$

[20°C $H_2O(l)$ to 0°C $H_2O(l)$

$\Rightarrow N \times n_1 \times \Delta H_{fussion} = n_2C_m.\Delta T$

[n_1 = moles of H_2O in each ice cube = 1/2, n_2 = moles of liquid water = $\frac{500}{18}$]

$\Rightarrow N\times\frac{9}{18}\times 6\text{ kJ} = \frac{500}{18}\times 75.6(20-0)\text{kJ}$

$\Rightarrow N = \frac{500\times75.6\times20}{9\times6\times1000} = 14$

$\Rightarrow \boxed{N=14}$

17. Ans. (3)

work = $\pi ab/4$

$=\frac{22}{7}\times\frac{14}{4}\times10$

$=\frac{440}{4}$ bar litre

= 110 bar Litter 1 bar litre = 100 J

= 110 × 100 J

= 11000J

= 11 kJ (Expanding at lower pressure)

18. Ans. (3)

Area under in the curve

$$=\frac{1}{2}\times 2V_1\times 5P_1$$

$= 5P_1V_1$

19. Ans. (2)

Work depends upon path so area under the PV curve is maximum in 3 and minimum in 1.

So, $\boxed{w_1 < w_2 < w_3}$

20. Ans. (2)

$$\Delta U = 10\text{KJ} - \frac{2\times 20\times 101.3}{1000}$$

$= 10$ KJ $- 4.052$

$= 5.942$ KJ

$= 5948$ J

SECTION-B

1. Ans. (5)

(i), (iv), (viii), (ix), (x)

At constant pressure, $w = -P\Delta V$ (work on system w = +ve, ΔV = –ve)

2. Ans. (–45)

Heat released has negative sign thus q = – 65J

The work lone on the system has w = 20J

The expression for the change in the internal energy is

$\Delta E = q + w$

$= -65$ J $+ 20$ J

$\Delta E = -45$ J

3. Ans. (4)

No. of moles n = 2 moles (ideal gas)

V = Constant

$$C_V = (16.5 + 10^{-2}\,T)\ \frac{J}{mol.K}$$

$T_1 = 300$ K; $T_2 = 400$ K

Since $dU = n\,C_{Vm}dT$ (for ideal gas)

$$\int dU = n\int_{T_1}^{T_2} C_{vm}.dT$$

$$\Delta U = 2\int_{300}^{400}(16.5+10^{-2}T)dT$$

$$= 2\left[16.5T+\frac{10^{-2}}{2}.T^2\right]_{300}^{400}$$

$$= 2\left[16.5(400-300)+\frac{10^{-2}}{2}(400^2-300^2)\right]=4000J$$

$\Delta U = 4$ kJ

4. **Ans. (75)**

$2H_2O_{(l)} \rightarrow 2H_2O_{(g)}$

$\Delta n_g = 2$

$\Delta H_{Vap} = \Delta U + \Delta n_g rT$

$\Delta H_{Vap} = 2 \times 40.66 = 81.32 KJ\ mol^{-1}$

$81.32 = \Delta U + 2 \times 8.314 \times 10^{-3} \times 373$

$\Delta U = 81.32 - 6.202$

$\Delta U = 74.118$ KJ

Hence when 2 mole liquid water vaporises at 100°C, ΔU will be 75KJ

5. **Ans. (4)**

Q = 1 Kcal

P = 1 atm

$w = -\int P.dV = -\int dV = -P\Delta V$

$= -1(1.5 - 1.2) = -0.3$ Litre-atm

$= -0.03$ KJ

$1J = \frac{1}{4.18} cal$

$-\frac{0.03}{4.18} Kcal = -7.18 \times 10^{-3} Kcal$

$\Delta E = Q + w$

$= 1$ Kcal $- 7.8 \times 10^{-3}$ Kcal

$= 0.993$ Kcal

$= 0.993 \times 4.184$

$= 4.15$ KJ ≈ 4 KJ

6. **Ans. (–10)**

The work done = – Pext dv = – $P\Delta V$

V_{final} = Volume of ice = 1.1 L

$V_{initial}$ = Volume of water = 1.0 L

$\Delta V = V_{final} - V_{inital} = 1.1 - 1.0 = 0.1$ L

Work done = – $P\Delta V$

$= -[1.0 \times 0.1]$

$= -0.1$ L atm (1 L atm = 101.32 J)

$= -10.1$ J

7. **Ans. (–39)**

$w_{done} = -$ Pext (ΔV)

$w_{done} = -$ Pext ΔV

ΔV = Area of piston x length covered by piston

$\Delta V = 500\ cm^2 \times 50cm$

$= 25000 cm^3$

$\Delta V = 25L$ $(1000 cm^3 = 1L)$

$w = -1atm \times 25$ Litre

= – 25 Litre atm

w = – 2.5 KJ (1 L atm = 101.3J)

Heat released to surrounding = 36.5 KJ

q = – 36.5 KJ (lose of heat)

$\Delta E = q + w$

= – 36.5 – 2.5

ΔE = – 39 KJ

8. Ans. (8)

$W_{irr} = -P_{ext}\Delta V = -P_{ext}(V_2 - V_1)\ \frac{5\times R\times 300}{4}$

$W_{irr} = -1\left(\frac{3}{4}\times 1500R\right) = -9.33$ kJ

$W_{rev} = -nRT\ln\frac{P_1}{P_2}$ (P_1 = 1 atm, P_2 = 4 atm for reversible composition process)

$= -5 \times 8.3 \times 300\ln\frac{1}{4}$

= 17.43 kJ

W_{total} = –9.33 + 17.43

= –8.1 kJ

9. Ans. (60)

Given q_{ACB} = +80 J (Heat flow into system)

w_{ACB} = –30 J (system work)

So internal energy change

$\Delta U_{ACB} = q_{ACB} + w_{ACB}$

= 80 J – 30 J

= 50 J

w_{ADB} = –10 J (work done by system)

$\Delta U_{ADB} = \Delta U_{ACB}$ = 50 J (U is state function)

and $\Delta U_{ADB} = q_{ADB} + W_{ADB}$

50 J = q_{ADB} – 10 J $\Rightarrow$ q_{ADB} = +60 J

10. Ans. (18)

Total DOF = 3N

N = number atoms

X = 3 × 2 = 6 (for O_2)

Y = 3 × 1 = 3 (for Ne)

Z = 3 × 3 = 9 (for H_2O)

$\left(\frac{X}{Y}\right)Z = \frac{6}{3} \times 9 = 18$

JEE (Advanced) Practice Paper

1. Ans. (C)

Boiling point, PH & density are intensive properties because these properties are independent of mass of sample.

2. Ans. (C)

$C_{v,m} = \frac{5}{2}R$

$C_{P,m} = C_{V,m} + R \quad \Rightarrow \quad \frac{5}{2}R + R = \frac{7}{2}R$

$\gamma = \frac{C_P}{C_V} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5}$

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

$T_iV_i^{\gamma-1} = T_f.V_f^{\gamma-1}$

$600 \times 1 = T_f \times (32)^{\frac{7}{5}-1}$

$T_f = \frac{600}{(32)^{\frac{2}{5}}} = \frac{600}{4} = 150k$

$\Delta H = nC_p\Delta T = 1 \times \frac{7}{2}R(150-600)$

$= -1575R$

3. Ans. (A)

In this cyclic process, net work done is zero because one part is in clockwise cyclic process and another part is in anticlockwise cyclic process

4. Ans. (A)

$\Delta U = q + w$ w = work done by gas = $\frac{Q}{2}$

$\Delta U = Q - \frac{Q}{2}$ Q = heat added

$\Delta U = Q - \frac{Q}{2} = \frac{Q}{2}$

For monoatomic ideal gas

$\Delta U = \frac{3}{2}nR\Delta T$

$Q = 3nR\Delta T$

$nC_P\Delta T = 3nR\Delta T$

$\boxed{C_P = 3R}$

5. Ans. (C)

Enthalpy of ideal gas depends on temperature

$\Delta H = nC_P\Delta T$

So, in Isothermal condition $\Delta H = 0$

6. **Ans. (B)**

for adiabatic expansion $\Rightarrow$ (w = –Ve)

$\Delta U = q + w$

$\Delta U = w$

$nC_v(T_2 - T_1) = w = -ve$

So, T_2 should be lesser than T_1

7. **Ans. (A,B,C)**

$$\frac{P_B}{T_B} = \frac{P_C}{T_C}$$

$$P_B = \frac{1 \times 500}{250} = 2 \text{ bar}$$

For process CD

$$nC_V\left(T_D - T_C\right) = -Pext\left[\frac{nrT_D}{P_D} - \frac{nRT_C}{P_C}\right]$$

$$2 \times \frac{3}{2}\left(T_B - T_C\right) = -3\left[T_B - T_C\right] = -3\left[\frac{T_D}{3} - \frac{T_C}{1}\right]$$

$T_D = 450K$

Also, $\Delta H_{CD} = nC_p\Delta T = 2 \times \frac{5}{2}R \times 200 = 1000R$

8. **Ans. (A,B,C,D)**

Enthalpy is a function of Pressure & temperature for a substance.

Absolute value of enthalpy can't be determined because it is not possible to find the exact value of constituent energies i.e. vibrational, rotational, translational etc.

The heat absorbed during isothermal expansion of an ideal gas against vacuum is zero because $\Delta T = 0$ & work done is zero.

Applying Charles's law, at constant P V α T.

9. **Ans. (BD)**

(A) In adiabatic process

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

(B) $w = nc_v\Delta T$ $\Delta T \Rightarrow$ same

So, w $\Rightarrow$ same in reversible as well as Irreversible process.

(C) $q = 0$, $\Delta U = W$

$Ne(T_2 - T_1) = w = -$ ve

$T_2 - T_1 = -ve$

$T_2 < T_1$

In isobaric expansion temperature increases U increase $\Delta U = +ve$

In adiabatic expansion temperature decrease U decreases $\Delta U = -ve$

(D) For ideal gas, if ΔV = same

then, $\Delta V_{(\text{adiabatic expansion})} < \Delta U_{(\text{isobaric expansion})}$

if initial state are same

10. Ans. (BC)

Fusion of ice into water $\Rightarrow$ Melting point

i.e. $\Delta T = 0$

ΔH & ΔU are nearly equal

Molar heat capacity is the heat required to increase the temperature of one mole of substance by 1°C. So, it is independent of temperature.

11. Ans. (BD)

Volume of ideal gas double

E_1 = Change in average. K.E. of molecules for isothermal expansion.

E_3 = Change in average K.E. of molecules for free expansion in insulated condition.

$E_1 = E_3$

E_4 = Change in average K.E. of molecules for expansion at constant pressure

then, $E_4 > E_3$

12. Ans. (A)

Work done reversible Isothermal process

$$W = P_{ext.}\int_{v_1}^{v_2} dv$$

$PV = nRT$

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

$$W = -nRT\int_{v_1}^{v_2}\frac{dv}{v} = -nRT[\ell nv]_{v_1}^{v_2}$$

$$= -nRT[\ell nv_2 - \ell nv_1]$$

$$= -nRT\,\ell n\,\frac{v_2}{v_1}$$

$$W = -2.303\ nRT\log\frac{v_2}{v_1}$$

At constant temperature

$$V \propto \frac{1}{P}$$

$$W = -2.303\ nRT\log\frac{P_1}{P_2}$$

i.e. $$w = 2.303\ nRT\log\frac{P_2}{P_1}$$

Work done for reversible adiabatic process/irreversible adiabatic process.

$$w = -P_{ext.}\int_{v_i}^{v_f} dv$$

$w = nC_v\Delta T = nC_v(T_2 - T_1)$

work done for Irreversible Isothermal process

$$w = -P_{ext.}\int_{v_i}^{v_f} dv$$

(P) $\rightarrow$ (1,3,4) ; (Q) $\rightarrow$ (2, 4) ; (R) $\rightarrow$ (2, 4) ; (S) $\rightarrow$ (4)

13. Ans. (A)

(P) Isothermal vapourisation of water at

100°C & 1atm $\Rightarrow$ Boiling point $\Rightarrow \Delta T = 0$

(Q) Isothermal reversible expansion of an ideal gas

$\Delta T = 0$

$\Delta U = nC_v\Delta T = 0$

$\Delta H = nC_p\Delta T = 0$

(R) Adiabatic free expansion of ideal gas

$\Delta T = 0$

So, $\Delta U = 0$

$\Delta H = 0$

$q = 0$

$w = 0$

(S) Isochoric heating of an ideal gas

i.e. $\Delta V = 0$

So, $w = 0$

14. Ans. (B)

(P) Isothermal process (reversible)

$\Delta U = q + w$

$\Delta U = 0$

$q = -w$

$$q = 2.303\ nRT \log \frac{P_1}{P_2}$$

(Q) Adiabatic process (reversible)

PV^{γ} = constant

(R) For isochoric process i.e. $\Delta V = 0$

$w = 0$

i.e. Area under PV curve = 0

(S) Isothermal process (Irreversible)

$q = -w$

$q = P_{ext.}(v_2 - v_1)$

15. Ans. (B)

In Isobaric process

$\Delta H = nC_P\Delta T$

$\Delta U = nC_V\Delta T$

$C_P\Delta T = C_V\Delta T + \Delta w$

$\Delta w = (C_P - C_V)\Delta T$ $\{C_P - C_V = R\}$

$\Delta w = R\Delta T$

$= 8.3 \times 72 = 597.6J = 0.59 \simeq 0.60KJ$

16. Ans. (A)

$\Delta U = \Delta Q - \Delta w = 1.60 - 0.60 = 1.0KJ$

17. Ans. (C)

$\Delta U = C_V\Delta T$

$$C_V = \frac{1.0}{72} = 0.0138KJ/molK = 13.8J/molK$$

$$\gamma = \frac{C_P}{C_V} = \frac{22.2}{13.8} = 1.60$$

18. Ans. (2.00)

$q = -10$ J

$W = -0.6\ (300 - 500) = 0.6 \times 200 \times 10^{-3} \times 101.3$ J

$\Delta U = -10 + 12.156$

$\Delta U = 2.156$

19. Ans. (2.00)

$w = -P_{ext}\Delta V = -1$ atm $(22 - 2) = -20$ Litre-atm (1 litre-atm = 101.3 J)

$= -2000$ J $= 2$kJ