HW-5

Name - SUSNATA CHATTOPADHYAY
Roll - 22MS077
PH2202

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(5) From Maxwell's Relation we have,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Now, $P = f(V)\,T$

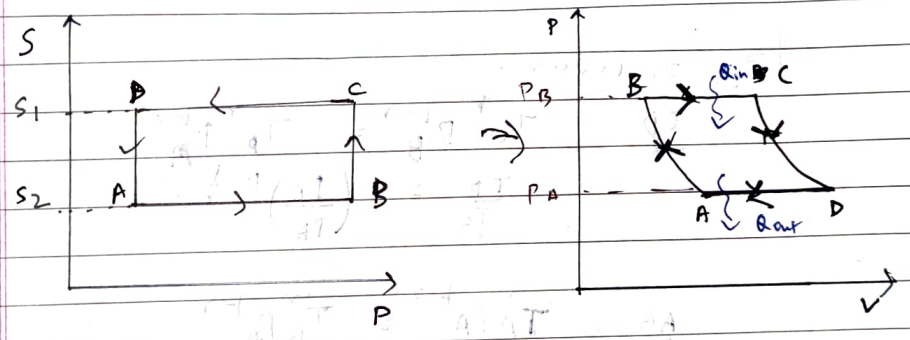
$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = f(V) = \frac{P}{T}$$

$$\therefore \left(\frac{\partial S}{\partial V}\right)_T = \frac{P}{T} > 0 \quad (\because P, T > 0) \quad \forall\, V$$

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T > 0$$

Entropy increases with volume.

(6) (7)



A

~~DA, BC~~
~~BA, DC~~ → Isobaric Process.
~~CB, AD~~
AB, CD → Adiabatic Process.
$(\because \Delta S = 0 \rightarrow Q_{rev} = 0)$

$$\eta = \frac{|W|}{Q_{in}}$$

Since, it's a cycle

$$\therefore \Delta U_{cycle} = W_{tot} + Q_{tot} = 0$$

$$\Rightarrow W_{tot} = -(Q_{in} + Q_{out}) \Rightarrow |W_{tot}| = |Q_{in} + Q_{out}|$$

Now,

$Q_{in} = nC_p (T_C - T_B) > 0.$

$Q_{out} = nC_p (T_A - T_D) < 0.$

$\therefore \eta = \frac{|Q_{in} - Q_{out}|}{Q_{in}}.$

$= \frac{nC_p (T_C - T_B) + nC_p (T_A - T_D)}{nC_p (T_C - T_B)}$

$= 1 + \left(\frac{T_A - T_D}{T_C - T_B}\right)$

Now, for adiabatic process.

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

$\therefore$ In Process.

CD $\Rightarrow T_C^\gamma P_B^{1-\gamma} = T_D^\gamma P_A^{1-\gamma}$

$\frac{T_D}{T_C} = \left(\frac{P_A}{P_B}\right)^{1-\frac{1}{\gamma}}.$

AB $\Rightarrow T_A^\gamma P_A^{1-\gamma} = T_B^\gamma P_B^{1-\gamma}$

$\frac{T_A}{T_B} = \left(\frac{P_B}{P_A}\right)^{\frac{1-\gamma}{\gamma}} = \left(\frac{P_A}{P_B}\right)^{1-\frac{1}{\gamma}}.$

$\therefore (T_A - T_D) = T_B \left(\frac{P_A}{P_B}\right)^{1-\frac{1}{\gamma}} - T_C \left(\frac{P_A}{P_B}\right)^{1-\frac{1}{\gamma}}$

$= -(T_C - T_B) \left(\frac{P_A}{P_B}\right)^{1-\frac{1}{\gamma}}.$

So, $\boxed{\eta = 1 - \left(\frac{P_A}{P_B}\right)^{1-\frac{1}{\gamma}}}$ D.

(6) $U = AT^4V$

$P = \frac{1}{3}AT^4$

Find $S = ?$

Ans From fundamental eqn of thermodynamics

$$dU = TdS - pdV$$

since Volume V = const

we have $dU = TdS$

$$\therefore \frac{dU}{dS} = T = \left(\frac{U}{AV}\right)^{1/4}$$

$$\therefore \int \frac{dU}{U^{1/4}} = \left(\frac{1}{AV}\right)^{1/4} \int dS$$

Integ.

$$\frac{4}{3} U^{3/4} = \left(\frac{1}{AV}\right)^{1/4} S + C$$

Now,

At $T=0 \rightarrow U = 0$ (follows from given expression)

$\searrow S = 0$ (By 3rd Law of Thermodynamics)

$\therefore U = 0 \Rightarrow S = 0$

$\therefore C = 0$

$$\therefore S = \frac{4}{3}(AV)^{1/4} U^{3/4}$$

Ans

Entropy of system $= \frac{4}{3}(AV)^{1/4}(AV)^{3/4} T^3 = \boxed{\frac{4}{3} AV T^3}$

(4) The eqn of state of a thermodynamic syst. is $p = \frac{AT^3}{V}$

$$U = BT^n \ln\left(\frac{V}{V_0}\right) + f(T)$$

For a reversible path, 1st Law gives us.

$$dQ = TdS = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(p + \left(\frac{\partial U}{\partial V}\right)_T\right) dV$$

Further

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Thus using property of partial differentials we arrive at,

$$\left(\frac{\partial U}{\partial V}\right)_T = T^2 \left[\frac{\partial}{\partial T}\left(\frac{p}{T}\right)_V\right]_V$$

$$\frac{p}{T} = \frac{AT^2}{V} \quad \therefore T^2 \left(\frac{\partial}{\partial T}\left(\frac{p}{T}\right)\right)_V = \frac{2AT^3}{V}$$

& $\left(\frac{\partial U}{\partial V}\right)_T = \frac{BT^n}{V}$

comparing, Since, B, n are constant

$$\therefore \frac{BT^n}{V} = \frac{2A}{V} T^3$$

$$\boxed{\begin{aligned} 2A &= B \\ n &= 3 \end{aligned}}$$ Ans

Q.3) Given.

$PV = f(T)$

$U = g(T)$

T.F Eqⁿ of state.

Let

From class Notes, we have

$$\left(\frac{\partial U}{\partial V}\right)_T = T^2 \left[\frac{\partial}{\partial T}\left(\frac{P}{T}\right)\right]_V$$

for any system.

Since $U = g(T)$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\Rightarrow T^2 \left[\frac{\partial}{\partial T}\left(\frac{P}{T}\right)_V\right] = 0$$

Putting P

$$-\frac{1}{V}\left[\frac{\partial}{\partial T}\left(\frac{f(T)}{T}\right)\right]_V = 0$$

$\therefore \frac{f(T)}{T} = \text{constant}$

$= \alpha$ (say) $\in \mathbb{R}$

Now, $P = \frac{f(T)}{V}$, $V = \frac{f(T)}{P}$

$\therefore f(T) = \alpha T$

Q1) $V_1 = 11L$ | $C_V = \frac{3R}{2}$.

$P_1 = 20$ atm.

$V_2 = 31L$.

$P_2 = ?$

(i) change in Internal energy.

$$\Delta U = \int_{T_1}^{T_2} C_V \, dT = C_V (T_2 - T_1)$$

$$= \frac{3R}{2} \frac{1}{R} (P_2V_2 - P_1V_1)$$

$P_1V_1 = RT_1$

$P_2V_2 = RT_2$

$K = P_1V_1^3 = P_2V_2^3$

$$= \frac{3}{2}\left(-P_1V_1 + P_1\left(\frac{V_1}{V_2}\right)^3 V_2\right)$$

$$\Delta U = \frac{3}{2}\left(-11 \times 20 + \frac{20\,(11)^3}{(31)^2}\right)$$

$$= -288.45 \text{ L-atm}$$

From 1st law

$$dQ = dU - dW$$

$$= dU + P\,dV$$

(ii) $$\therefore Q = \Delta U + \int_{V_1}^{V_2} P\,dV = \Delta U + K \int_{V_1}^{V_2} \frac{dV}{V^3}$$

$$= \Delta U + \frac{K}{2}\left[\frac{1}{V_2^2} - \frac{1}{V_1^2}\right]$$

$$= \Delta U + \frac{1}{2}\left[\frac{P_2V_2^3}{V_2^2} - \frac{P_1V_1^3}{V_1^2}\right]$$

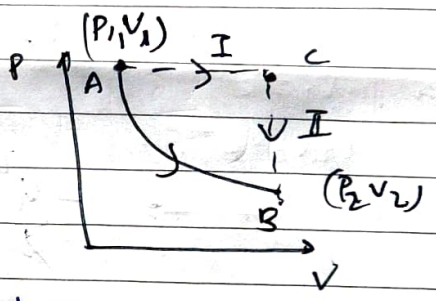
$$Q = -288.45 - \frac{1}{2}\left[P_1\left(\frac{V_1}{V_2}\right)^3 V_2 - P_1V_1\right]$$

$$= -288.45 - \frac{1}{2}\left[20\left(\frac{11}{13.1}\right)^3 - 20\times 11\right]$$

$$Q = -288.45 + 96.1498 = -192.3 \text{ L-atm}$$

Ans

Total Heat absorbed -



(iv) Change in Entropy

To calculate entropy, we construct a isobaric and isochoric path

$$dU = dQ - pdV$$

I.) $dP = 0$

$$dS_I = \frac{dQ}{T} = \frac{C_p dT}{T} \therefore \Delta S_I = C_p \ln\left(\frac{T_C}{T_A}\right)$$

$$= C_p \ln\left(\frac{V_C}{V_A}\right)$$

(II) $dV = 0$

$$dS_{II} = \frac{dQ}{T} = \frac{C_v dT}{T} \therefore \Delta S_{II} = C_v \ln\left(\frac{T_B}{T_C}\right)$$

$$= C_v \ln\left(\frac{P_B}{P_C}\right)$$

$$\therefore \Delta S = \Delta S_I + \Delta S_{II} = C_p \ln\left(\frac{V_C}{V_A}\right) + C_v \ln\left(\frac{P_B}{P_C}\right)$$

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$$= C_p \ln\left(\frac{V_B}{V_A}\right) + C_v \ln\left(\frac{P_B}{P_A}\right)$$

$$= C_p \ln\left(\frac{V_B}{V_A}\right) + C_v \ln\left(\left(\frac{V_B}{V_A}\right)^3\right)$$

$$\Delta S = \ln(V_B/V_A)\,(C_p - 3C_v)$$

$$C_v = \frac{3R}{2} \quad \therefore \quad C_p = \frac{5R}{2}$$

$$\Delta S = \ln\left(\frac{3}{11}\right)\left(\frac{5R}{2} - \frac{9R}{2}\right)$$

$$= -\frac{4}{2} \times 0.0821 \ln\left(\frac{3}{11}\right) \text{ L-atm}$$

$$= -0.1701 \text{ L-atm}$$