Exe #1

qur-1.   we have,

$$dS = \frac{dE}{T} + \frac{P}{T} d\Psi - \sum_i \frac{\mu_i}{T} dN_i \qquad —①$$

also $S = S(E, \Psi, N_i)$

$$\Rightarrow \quad dS = \frac{\partial S}{\partial E}\bigg|_{\Psi, N_i} dE + \frac{\partial S}{\partial \Psi}\bigg|_{E, N_i} d\Psi + \sum_i \frac{\partial S}{\partial N_i}\bigg|_{E, \Psi, N_{i \neq j}} dN$$

$$—②$$

Comparing ① and ②

$$\boxed{\frac{\mu_i}{T} = - \frac{\partial S}{\partial N_i}\bigg|_{E, \Psi, N_{i \neq j}}}$$

qur-⑥

(i.)   from ①,   (rewriting eqn ①),

$$dE = T dS - P d\Psi + \sum_i \mu_i dN_i \qquad —③$$

also $E = E(S, \Psi, N_i)$

$$dE = \frac{\partial E}{\partial S}\bigg|_{\Psi, N_i} dS + \frac{\partial E}{\partial \Psi}\bigg|_{S, N_i} d\Psi + \sum_i \frac{\partial E}{\partial N_i}\bigg|_{S, \Psi, N_{i \neq j}} dN_i \qquad —④$$

Comparing ③ and ④,

$$\boxed{\mu_i = \frac{\partial E}{\partial N_i}\bigg|_{S, \Psi, N_{i \neq j}}}$$

(ii.)

$$H = E + PV$$

$$dH = \underline{dE + PdV} + V\,dp$$

from eqn ③

$$\underline{\cancel{dH}} \quad PdV + dE = TdS + \sum_i \mu_i\, dN_i$$

$$\Rightarrow dH = TdS + V\,dp + \sum_i \mu_i\, dN_i \qquad — ⑤$$

Also $H = H(S, P, N_i)$

$$dH = \left.\frac{\partial H}{\partial S}\right|_{P, N_i} dS + \left.\frac{\partial H}{\partial P}\right|_{S, N_i} dp + \left.\frac{\partial H}{\partial N_i}\right|_{S, P, N_i \neq J} dN_i$$

$$— ⑥$$

from ⑤ and ⑥

$$\boxed{\mu_i = \left.\frac{\partial H}{\partial N_i}\right|_{S, P, N_i \neq J}}$$

(iii.)

$$G = H - TS$$

$$dG = dH - TdS + SdT$$

from eqn. ⑤

$$dH - TdS = V\,dp + \sum_i \mu_i\, dN_i \qquad — ⑦$$

$$\Rightarrow dG = SdT + V\,dp + \sum_i \mu_i\, dN_i$$

gibbs free energy.

Also $G = G(T, P, N_i)$.

$$dG = \frac{\partial G}{\partial T}\bigg|_{P, N_i} dT + \frac{\partial G}{\partial p}\bigg|_{T, N_i} dp + \sum \frac{\partial G}{\partial N_i}\bigg|_{T, P, M_i \neq J} dM_i^\circ$$

$$— ⑧$$

Comparing ⑦ and ⑧ ⇒

$$\boxed{\mu_i^\circ = \frac{\partial G}{\partial N_i}\bigg|_{T, P, N_J \neq i}}$$

(IV.) $\qquad F = E - TS \qquad$ (Helmoltz free energy.)

$$\Rightarrow dF = dE - TdS - SdT$$

from eqn ③,

$$dE - TdS = -Pd\forall + \sum_i \mu_i^\circ dM_i^\circ$$

$$dF = -Pd\forall - SdT + \sum_i \mu_i dM_i \qquad —⑨$$

Also $\qquad F = (T, \forall, N_i)$

$$dF = \frac{\partial F}{\partial T}\bigg|_{\forall, N_i} dT + \frac{\partial F}{\partial \forall}\bigg|_{T, M_i} d\forall + \sum_i \frac{\partial F}{\partial N_i}\bigg|_{\forall, T, N_J \neq i} dN_i$$

$$—⑩$$

comparing ⑨ and ⑩,

$$\boxed{\mu_i = \frac{\partial F}{\partial N_i}\bigg|_{\forall, T, N_J \neq i}}$$

(a) we have,

$$T dS = dE + P d\forall - \sum_i \frac{\mu^i}{T} dN_i$$

for any cyclic process

$$T_{ini} = T_{final}$$

$$\forall_{ini} = \forall_{final}$$

$$N_i_{ini} = N^i_{final}$$

$$E_{in} = E_{final}$$

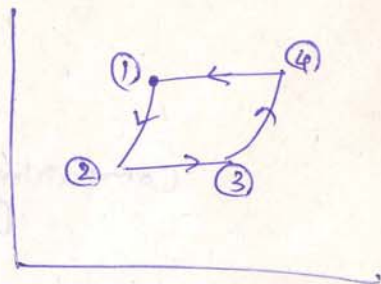$$\therefore dE \Big|_{cyclic} = 0$$

$$d\forall \Big|_{cyclic} = 0$$

$$\sum_i dN_i \Big|_{cyclic} = 0.$$

$$\therefore \text{ from the above eqn } T dS = 0$$

$$\text{Since } T \neq 0$$

$$\Rightarrow \boxed{dS = 0}$$

(b) Here by thermodynamics we are commenting only on initial stage and final stage of the process. if both are same then ΔS will be zero for initial and final stage only.

we are not considering kinetics here, ∴ we are not talking about the entire path of the process.

Reverse of the cycle is only possible if ∆S is $=0$ ~~kept constant~~ during entire path, Not just initial and the final stages.

ⓑ [Alternative Answer]

$$\Delta S_{total} = \Delta S|_{system} + \Delta S|_{universe}$$

$$\underbrace{\phantom{\Delta S|_{system}}}_{\substack{\downarrow \\ =0}} \qquad \underbrace{\phantom{\Delta S|_{universe}}}_{\substack{\downarrow \\ time}}$$

for Cyclic process

for each cycle $\Delta S|_{universe}$ is increasing as we are taking heat from the source and dumping it into the sink but during this process the ~~heat~~ entropy change for the system remains zero.

ⓒ a cyclic process can occur spontaneously in nature if and only if $\Delta S_{total} = \Delta S|_{system} + \Delta S|_{surrounding} \geqslant 0$.

Exercise # 1

Que # 4:

a.)

We have,

$$Tds = EdT + pdv + \sum(\mu/T)\, dN \qquad (1)$$

For single specie and assuming there is no chemical change we can ignore the summation term in the above equation.

Therefore we will have, $\qquad Tds = Edt + pdv \qquad (2)$

$$Tds = CvdT + pdv \qquad (3)$$

Also we have, $\qquad\qquad pdv + vdp = RdT \qquad (4)$

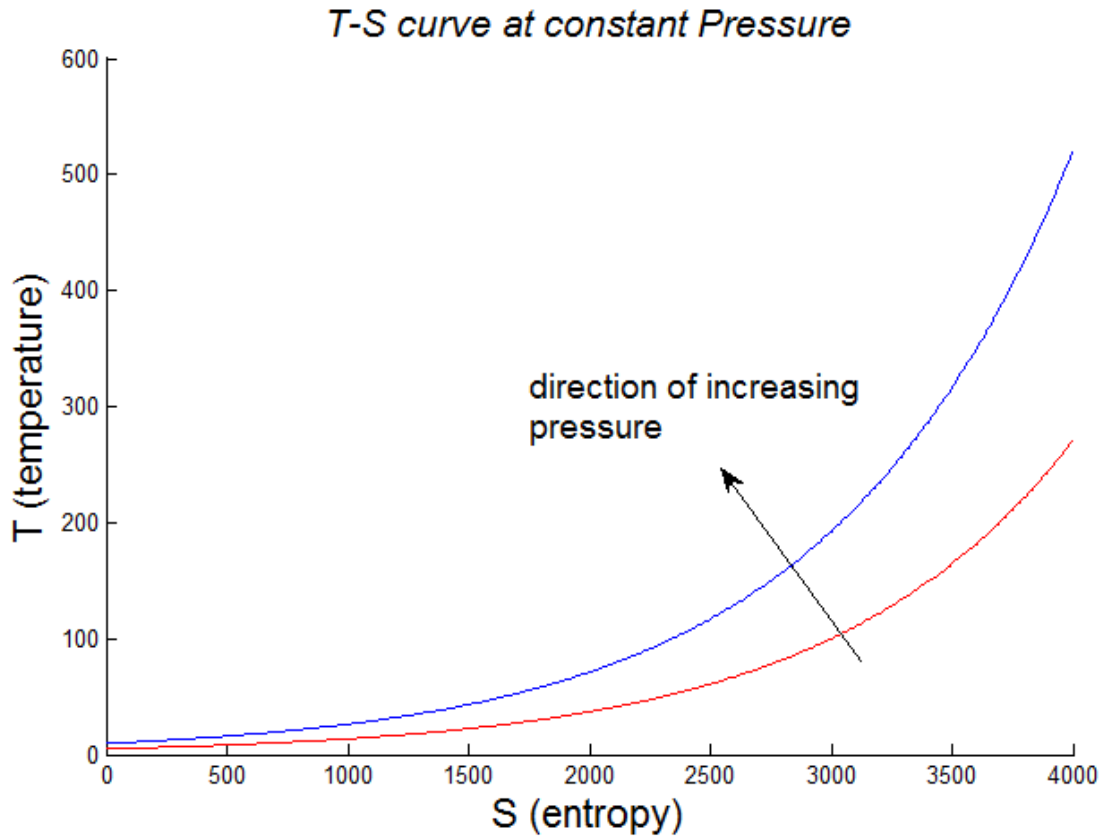From these two equations we will be having,

$$Tds = CpdT - vdp \qquad (5)$$

For constant pressure, dp = 0. The above equation will become,

$$Tds = CpdT$$

Integrating the above equation and putting starting values as T_{ref} and S_{ref} for T and S respectively. We will get,

$$T = Tref * \exp\left((S - Sref)/Tref\right)$$

The plot will look like as following,

T-S curve at constant Pressure

In the above figure, there are two line plotted for the two different reference values and the arrow shows the direction of increasing pressure.
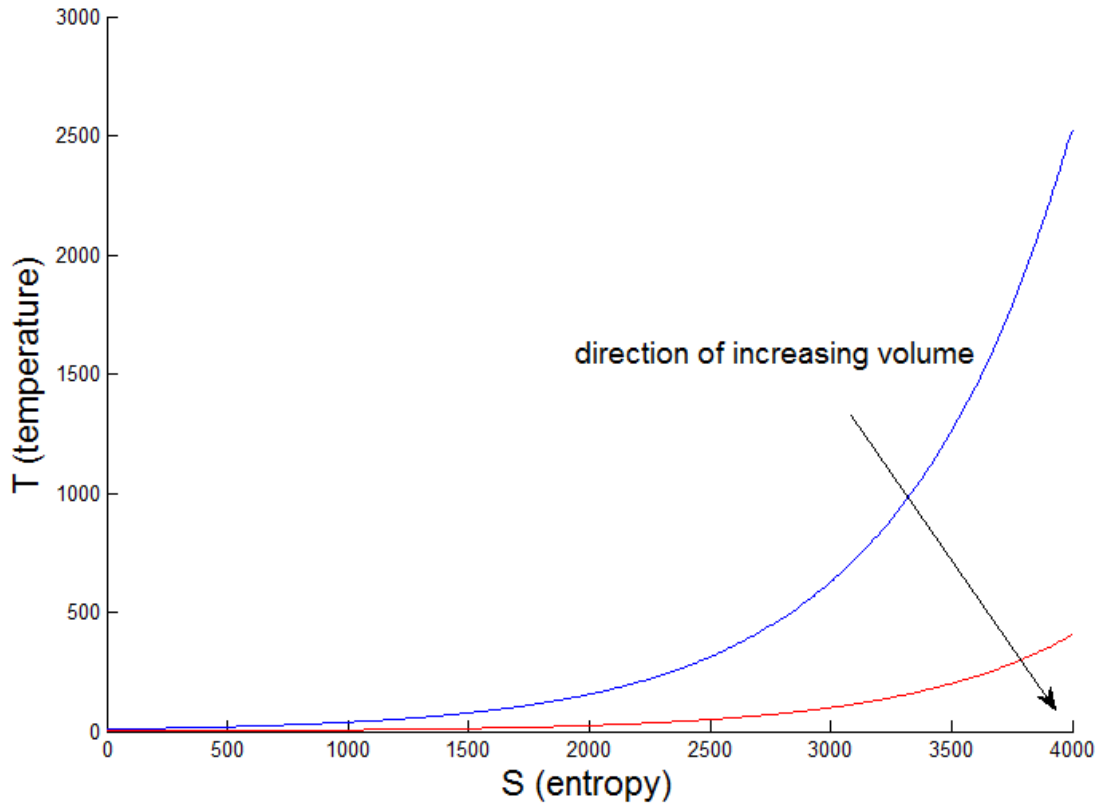
For constant volume dv=0. The equation (3) will become,

$$Tds = CvdT$$

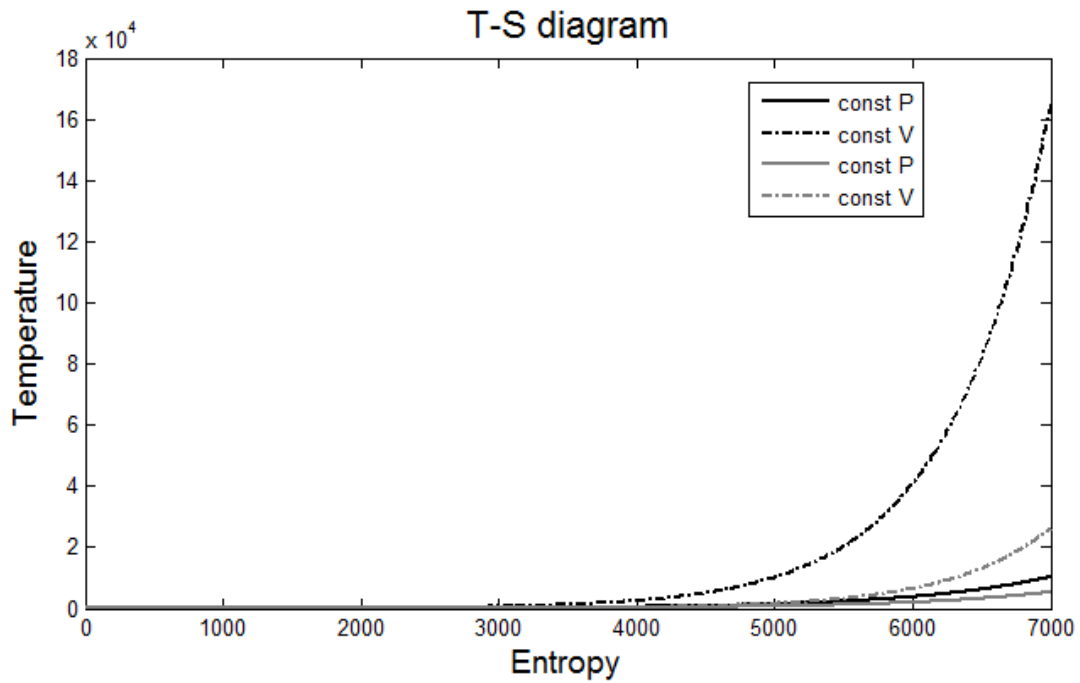Integrating this equation will lead to the following solution,

$$T = Tref * \exp\left((S - Sref)/Cv\right)$$

The plot will look like as following,

T-S curve at constant Volume

The combined plot for constant P and constant V on T-S diagram is given below,

T-S diagram

In the above figure there are black and gray lines are for two different reference values of temperature and entropy.

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b.)

For the constant T, dT = 0. Here in this particular case we can use the direct ideal gas equation,

$$pv = RT$$

Right hand side will be a constant value and therefore it will be a rectangular hyperbola. The plot is shown below,
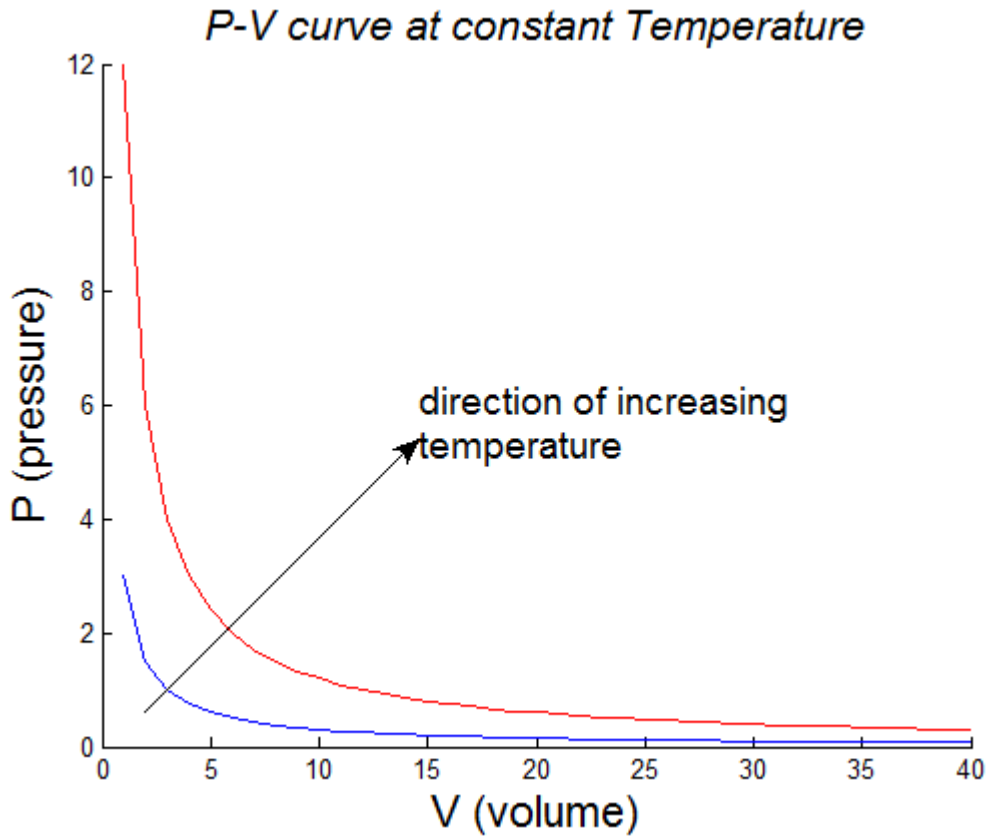
Now for the constant entropy, ds = 0. From the equation (3) and (4), by putting dT from (4) into (3) we will have,

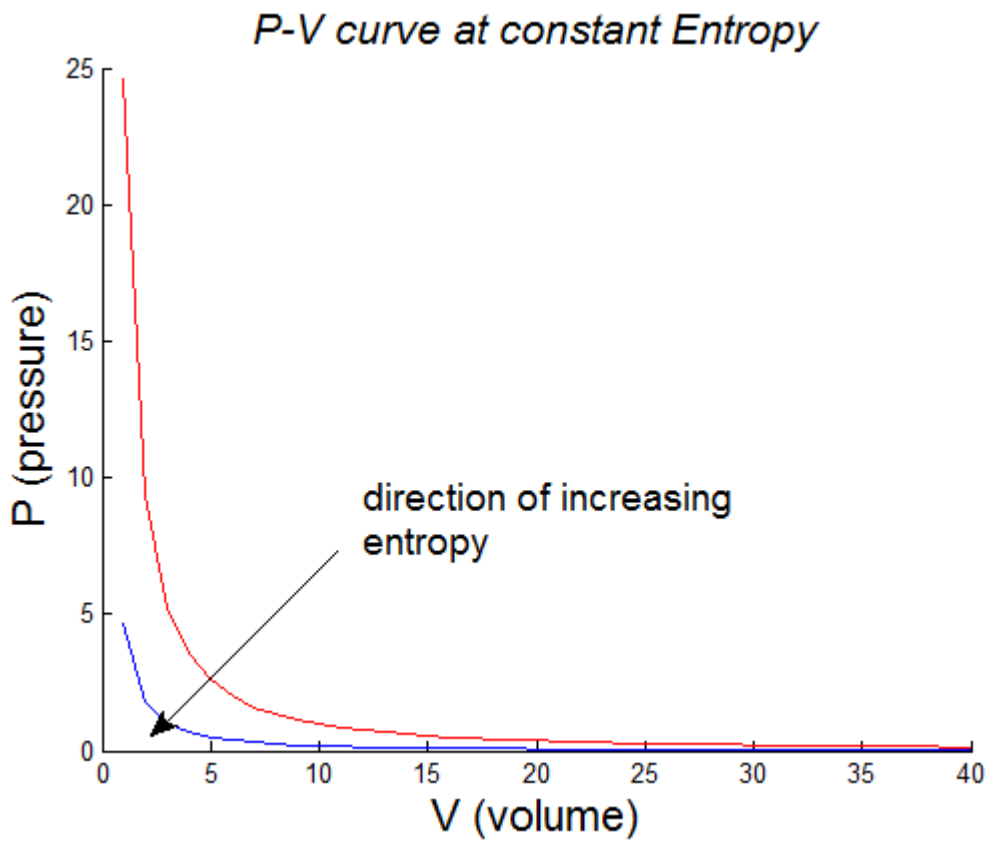$$Tds = \left(\left(Cv * \frac{p}{R} \right) + p \right) dv + \left(Cv * \frac{v}{R} \right) dp$$

4

For constant entropy ds = 0, we will be left with,

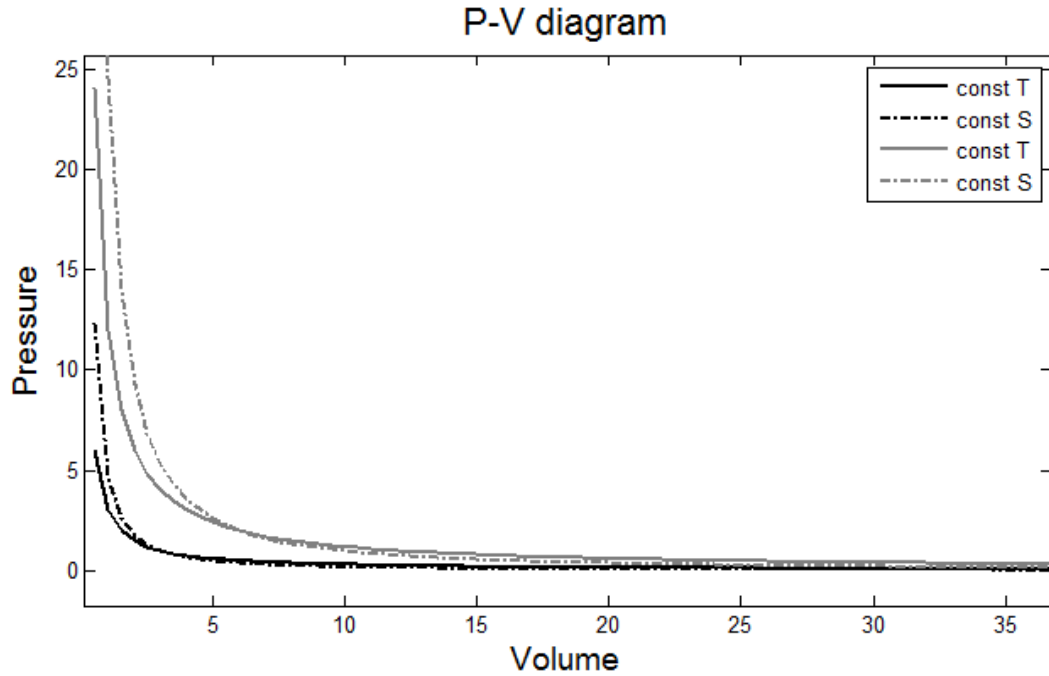$$\left(\frac{Cv}{R} + 1\right) * pdv = -\left(\frac{Cv}{R}\right) * vdp$$

Integrating above equation from the reference point, we will have the following relation,

$$P = Pref * \left(\frac{v}{vref}\right)^{\wedge}(-\gamma)$$

The plot is as following,

P-V curve at constant Entropy

The P-V curve for the constant Temp and constant Entropy is shown below,
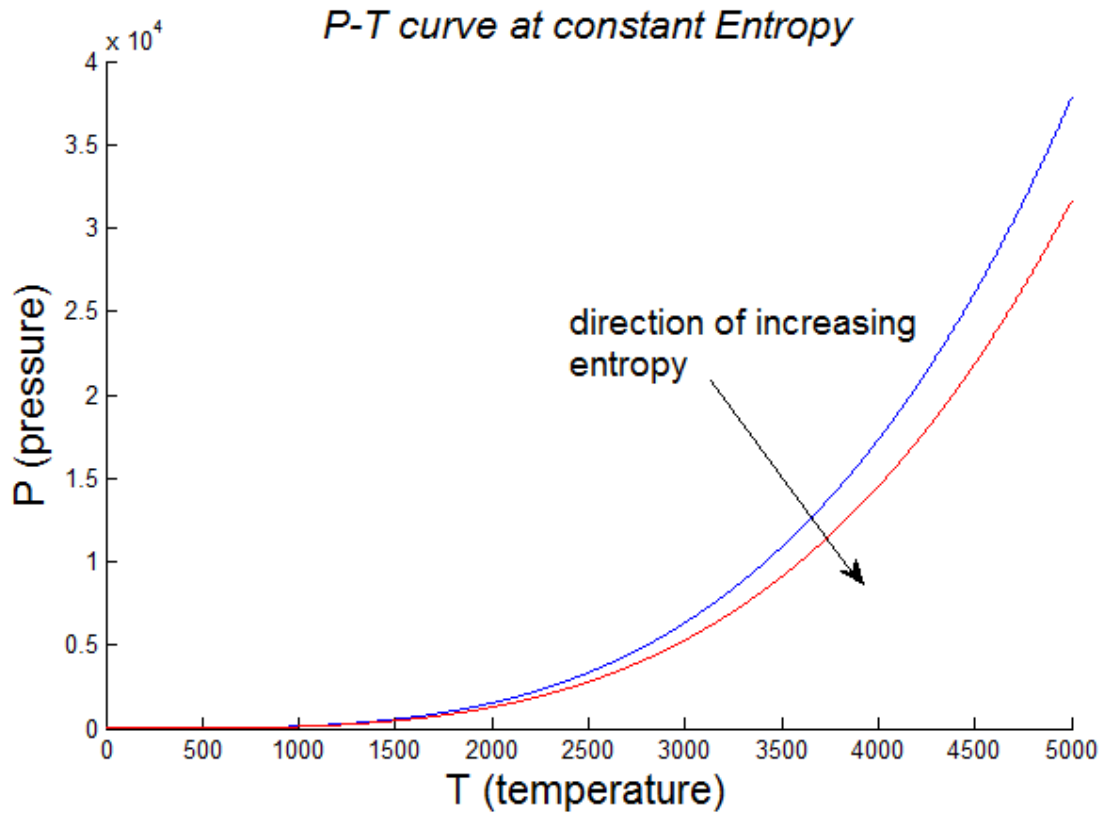
P-V diagram

c.)

Putting ds = 0 in equation (3) and using the value of 'dv' from the equation (4), we will have,

$$C_p dT = v dp$$

Integrating the above equation from the reference values of T and P, we will get the following relation,

$$p = pref * (\frac{T}{Tref})^\wedge(\gamma/(\gamma - 1))$$
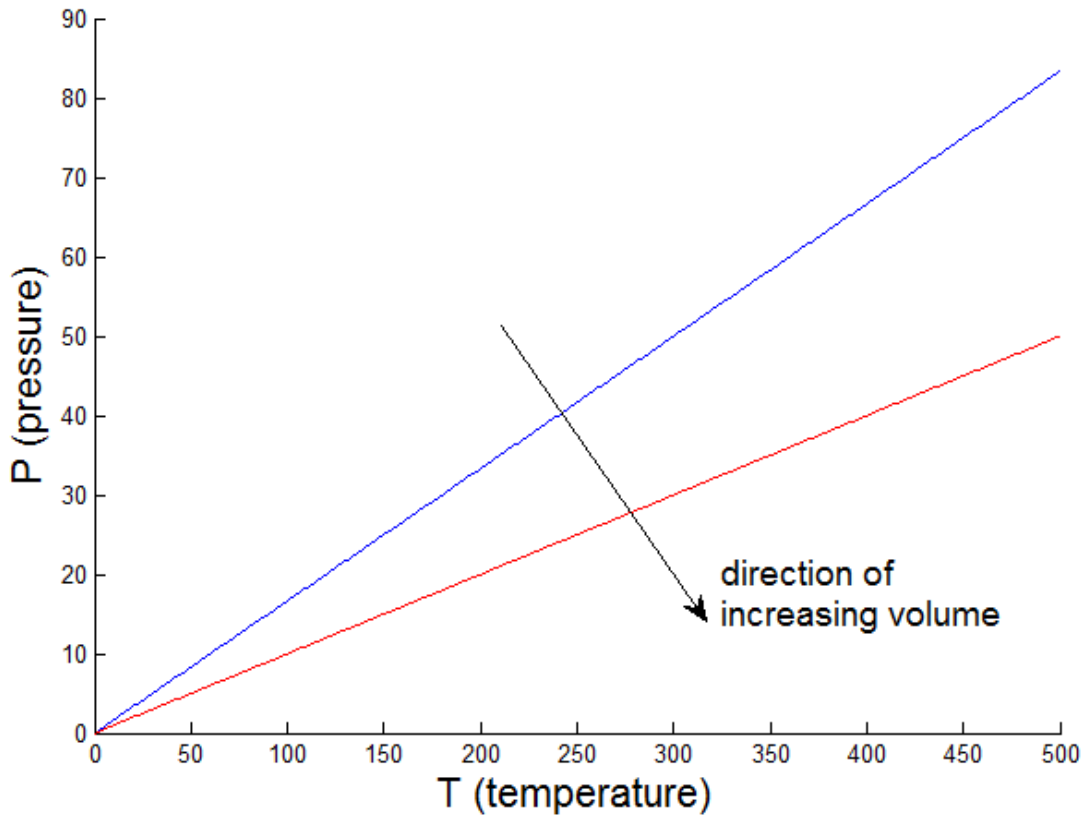
The plot is given below,

P-T curve at constant Entropy

Now for the case of constant volume, dv = 0. Here we can directly use the ideal gas equation,
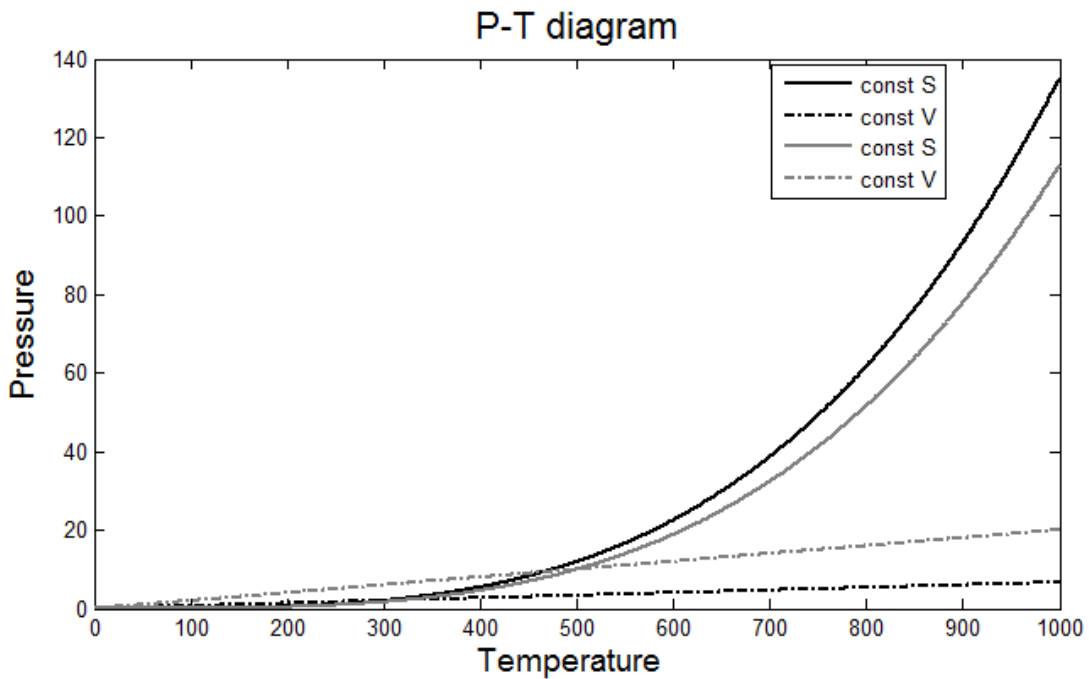
$$p = \left(\frac{R}{v}\right) * T$$

Plot is given as following,

P-T curve at constant Volume

The combined plot for constant entropy and volume for two different reference values of pressure and temperature is given below,
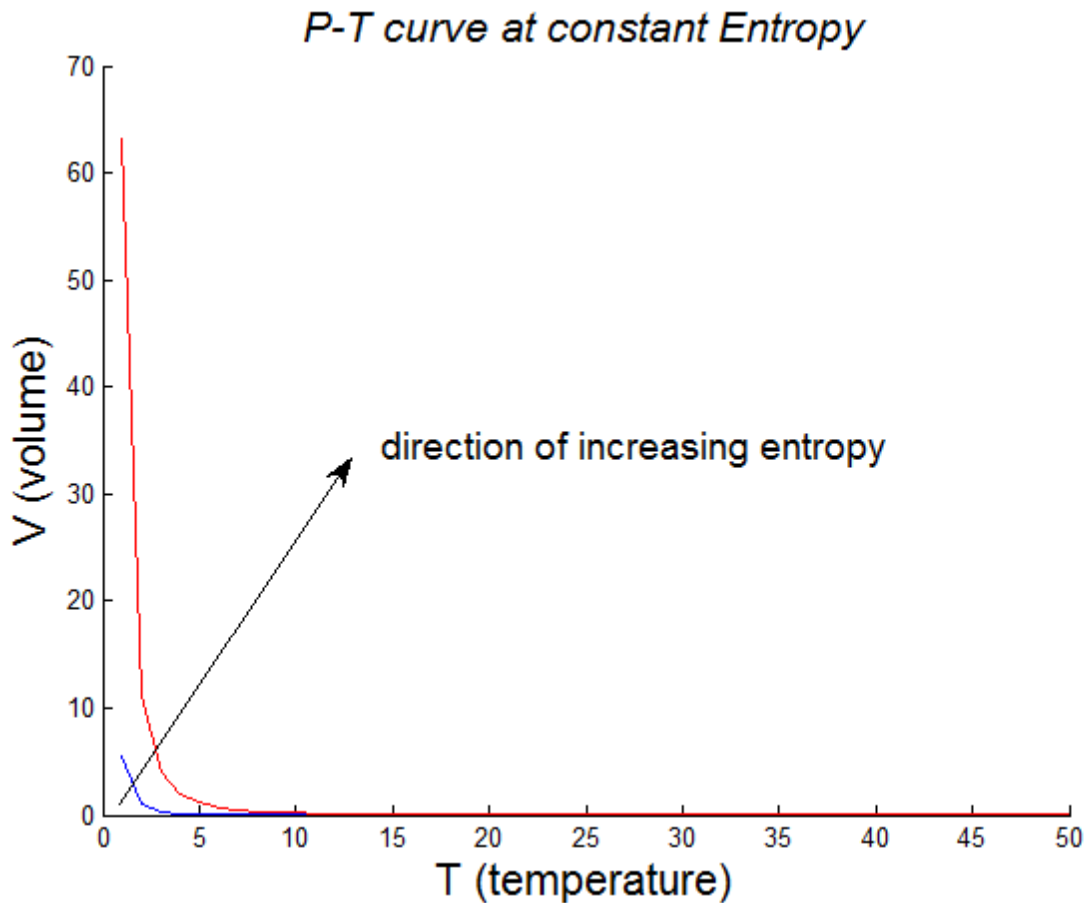

P-T diagram

d.)

Putting ds = 0 in the equation (3) and eliminating p from ideal gas equation, we will get,

$$CvdT + \left(\frac{RT}{v}\right)dv = 0$$

Integrating the above equation from the reference point in (v,T) plane, we will end up with the following solution,

$$v = vref * (\frac{T}{Tref})^\wedge(-1/(\gamma - 1))$$
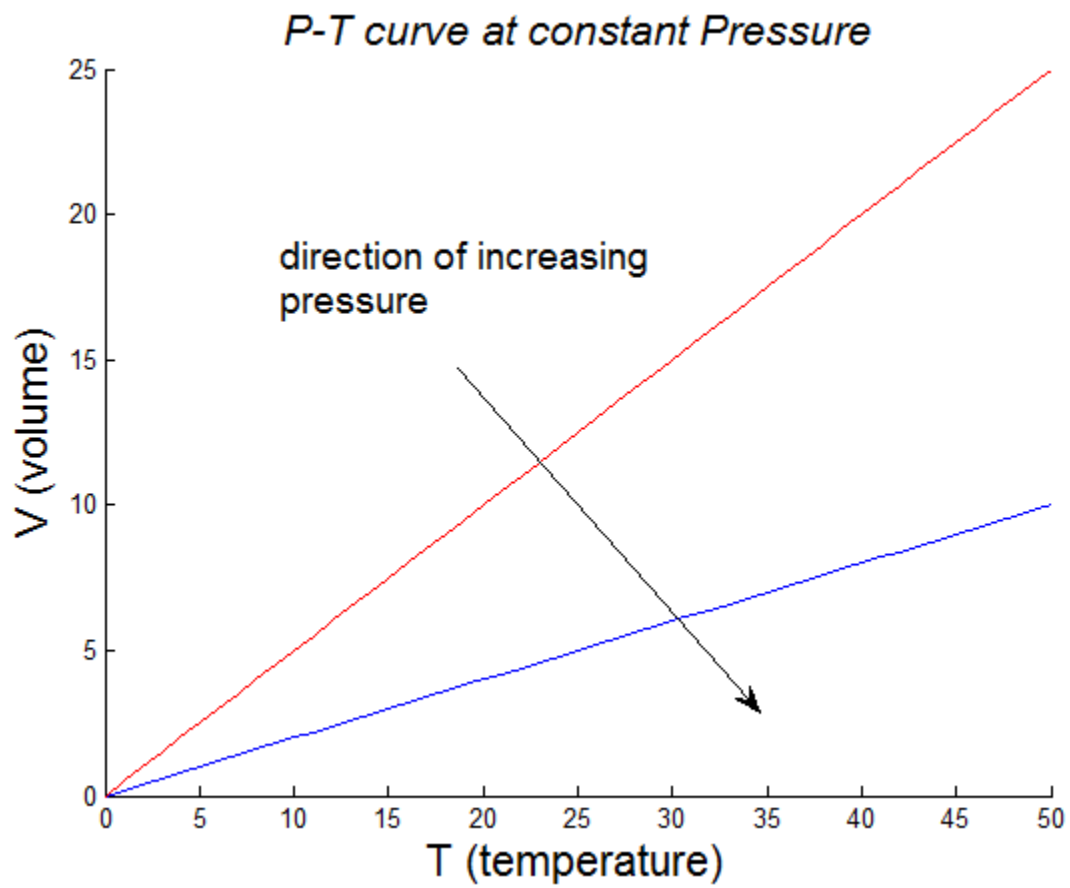
The plot is as following,
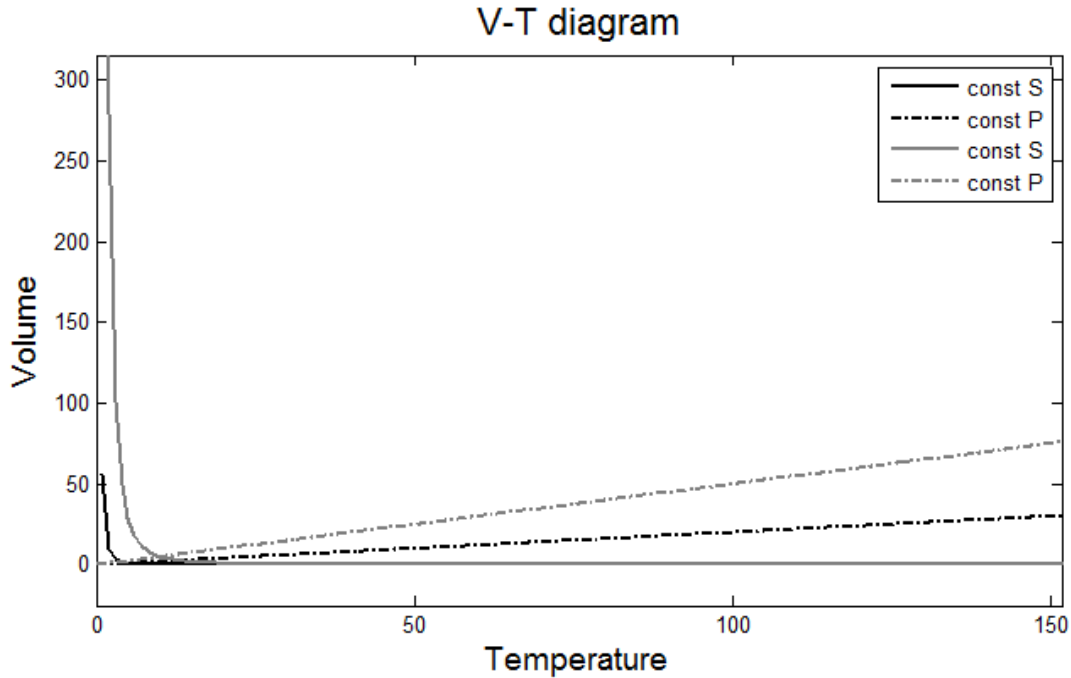

For constant pressure dp = 0, by using the ideal gas equation we get,

$$v = vref * \left(\frac{T}{Tref}\right)$$

The plot is given below,

The combined figure for constant entropy and constant pressure for two different reference values of volume and temperature is given below,

V-T diagram

Que # 3

Let's assume that the system goes from state 1 to 2, we will have,

$$U2 - U1 = q - w \qquad (1)$$

Here U is internal energy and q is heat supplied to the system and w is the work done by the system.

The relation between heat taken and by the system in terms of entropy is,

$$\frac{dq}{T} \leq ds$$

Integrating the above equation we get,

$$q \leq T(S2 - S1) \qquad (2)$$

The expression for the change of Gibbs free energy can be written as,

$$G2 - G1 = (U2 - U1) + (p2V2 - p1V1) - (T2S2 - T1S1)$$

11

By using (1) the above expression can be simplified to the fllowing,

$$G2 - G1 = q - w + (p2V2 - p1V1) - (T2S2 - T1S1) \qquad (3)$$

If the only heat transferred to the system is from a heat reservoir which remains at the constant temperature T and also the initial and the final temperatures, T1 and T2, of the system are equal, and equal to the temperature T of the reservoir. Apart from the system, the only other body which has undergone a change of volume at the end of the process is at a constant pressure p. The initial and the final pressures p1 and p2 are equal and equal to p.

Putting T1 = T2 = T and p1 = p2 = p, we get following from the equation (2) and (3),

$$w - p(V2 - V1) \leq -(G1 - G2) \qquad (4)$$

The term p(V2-V1) is the work done by the system in displacing its environment at the steady pressure p. This is not necessarily the whole of work 'w' done by the system. Therefore we define an additional work time "w' " by the relation,

$$w = w' + p(V2 - V1) \qquad (5)$$

This w' is the useful work we can get out of any process. From equations (4) and (5) we get,

$$w' \leq -(G1 - G2)$$

The above relation remains unchanged even if the system passes through intermediate temperatures and pressures which are different from T and p respectively, provided that the only heat intake is from the reservoir at T and that the only body, other than the system itself, which has undergone a volume change at the end of the process is the environment at the pressure p.

The inequality sign refers to an irreversible path and equality sign to a reversible one but in both the cases the value of (G2-G1) is the same. The useful work which can be extracted by any process will be less than or equal to (G2-G1), e.g. Galvanic cell.

So the maximum what we can get out of any process will be equal to the change in the Gibb's free energy.

Que # 5

Let's take the following cycle as shown in the figure below; here the heat addition is at the highest pressure,

P-V curve at constant Entropy
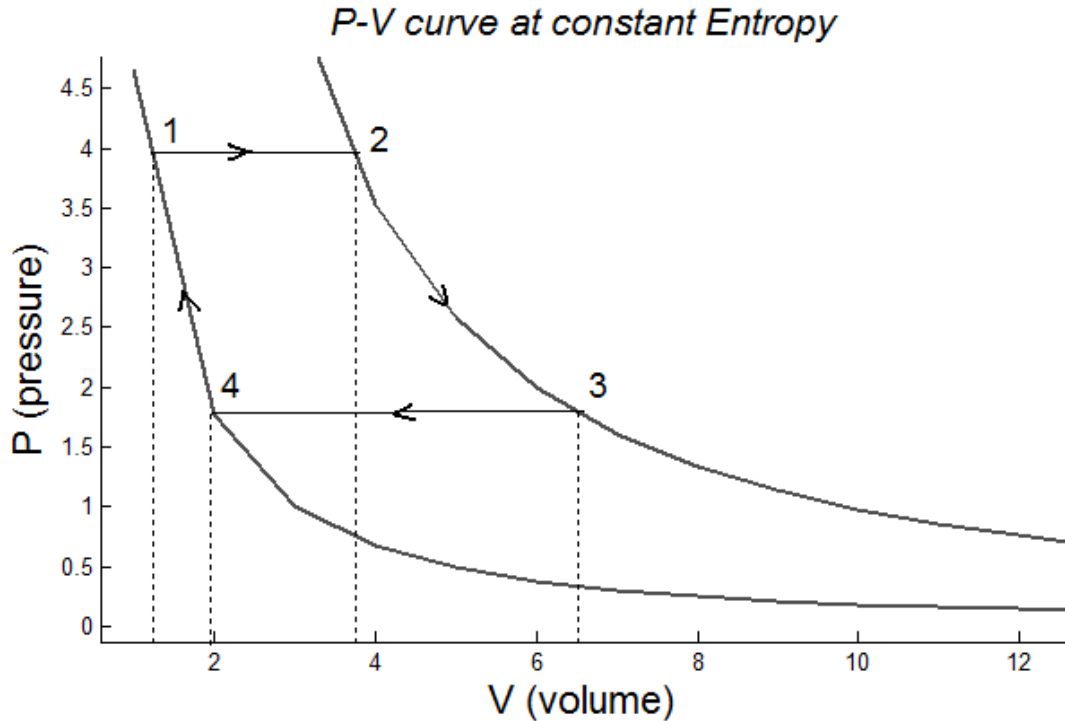
We are going to calculate the work done by the gas in the above process.

$W(1\rightarrow2) = P1\ (V2-V1)$
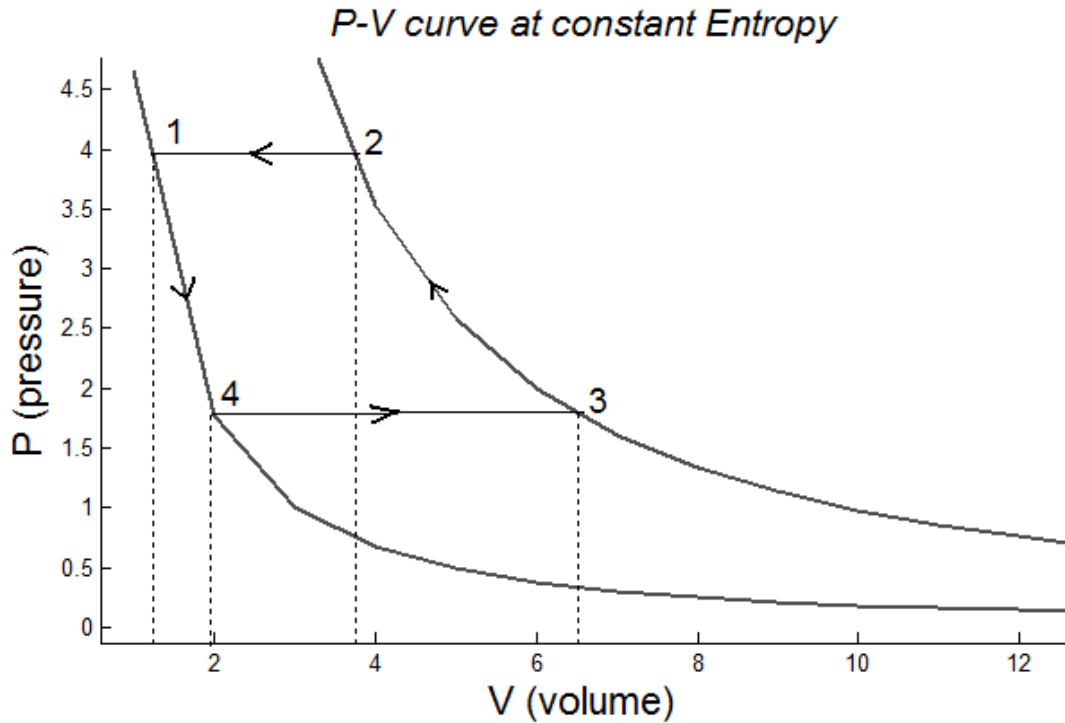
$W(2\rightarrow3) = (1/(\gamma-1))*(P2V2 - P3V3)$

$W(3\rightarrow4) = P3\ (V4-V3)$

$W(4\rightarrow1) = (1/(\gamma-1))*(P4V4 - P1V1)$

$W(I)\ net\ = W(1\rightarrow2) + W(2\rightarrow3) + W(3\rightarrow4) + W\ (4\rightarrow1)$

Now we consider the case when the heat addition is not done at the maximum pressure as shown in the figure. The heat addition is done from $4\rightarrow3$ isentropic process,

P-V curve at constant Entropy

$W(2\rightarrow1) = P1\ (V1-V2)$

$W(1\rightarrow4) = (1/(\gamma-1))*(P1V1 - P4V4)$

$W(4\rightarrow3) = P3\ (V3-V4)$

$W(3\rightarrow2) = (1/(\gamma-1))*(P3V3 - P2V2)$

$W(II)\ net = W(2\rightarrow1) + W(1\rightarrow4) + W(4\rightarrow3) + W(3\rightarrow2)$

It can be shown easily from the P-V diagram that the work done (which is also equal to Area under the curve in P-V diagram) in the 1st cycle will be more than the 2nd one, i.e. W(I) net > W(II) net.

Therefore we prefer heat addition at maximum pressure in a cycle in order to get maximum work done by the gas.