

4. The Second Law of Thermodynamics

It can be started that, according to the first law of thermodynamics, **when a system undergoes a complete cycle then the net heat supplied is equal to the net work done.** This is based on the conservation of energy principle, which follows from observation of natural events. The second law came up as embodiment of real happenings while retaining the basic nature of the first law of thermodynamics. Feasibility of process, direction of process and grades of energy such as low and high are the potential answers provided by the 2nd law. The second law of thermodynamics is capable of indicating the maximum possible efficiencies of heat engines, coefficient of performance of heat pumps and refrigerators, defining a temperature scale independent of physical properties etc. The Second Law of thermodynamics, which is also a natural law, indicates that, although the net heat supplied in a cycle is equal to the net work done, **the gross heat supplied must be greater than the net work done;** some heat must always be rejected by the system. This law can be understood by considering the heat pump and heat engine.

Thermal Reservoir

A thermal reservoir is defined as a sufficiently large system in stable equilibrium to which and from which a finite amount of heat can be transferred without any change in its temperature.

Heat source: is a high temperature reservoir such as: boiler, furnace, combustion chamber, nuclear reactor, the sun, etc.

Heat sink: is a low temperature reservoir such as: condenser, atmospheric air, river water, ocean, etc.

Heat Engine

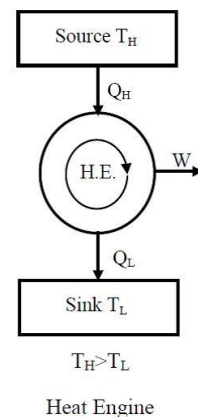
It is defined as the system operating in a complete cycle and developing a net work from a supply of heat. The second law implies a source of heat and sink of heat are both necessary. Let the heat supplied from the source be Q_H , let the heat rejected to the sink be Q_L and let the net work done by the engine be W . apply the first law of thermodynamics:

$$\sum dQ = \sum dW \quad \dots \dots \dots (4.1)$$

$$Q_H - Q_L = W \quad \dots \dots \dots (4.2)$$

According to the second law the gross heat supplied must be greater than the net work.

$$Q_H > W \quad \dots \dots \dots (4.3)$$



The thermal efficiency is defined as the ratio of the net work done during the cycle to gross heat supplied during the cycle.

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \quad \dots \dots \dots (4.4)$$

The thermal efficiency of a heat engine is always less than 100%.

It can be seen that a temperature difference is always required for heat to flow; therefore the source must be at higher temperature than the sink.

Heat Pump and Refrigerator

It is the inverse of heat engine. Work is done on the system. The net work done on the system equals the net heat rejected by the system. In the heat pump an amount of heat Q_L is supplied from cold reservoir and amount of heat Q_H is rejected to the hot reservoir. According to the first law of thermodynamics:

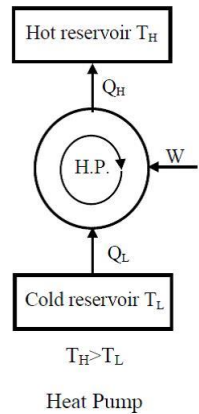
$$\sum dQ = \sum dW \quad \dots \dots \dots (4.5)$$

$$Q_H - Q_L = W$$

$$Q_H = Q_L + W \quad \dots \dots \dots (4.6)$$

Therefore, in order to transfer heat from a cold reservoir to a hot reservoir a work must be done.

$$W > 0 \quad \dots \dots \dots (4.7)$$



As heat a pump is not a work producing machine and also its objective is to maintain a body at higher temperature, so its performance can't be defined using efficiency as in the case of heat engines. Performance of a heat pump is quantified through a parameter called coefficient of performance (*C.O.P.*). Coefficient of performance is defined by the ratio of desired effect and net work done for getting the desired effect.

$$C.O.P. = \frac{\text{Desired effect}}{\text{Net work done}} \quad \dots \dots \dots (4.8)$$

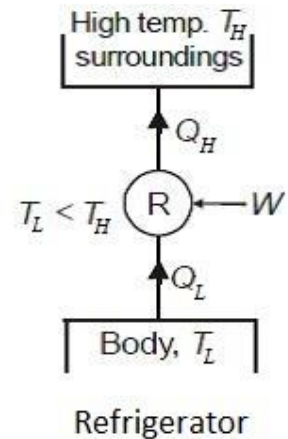
$$C.O.P. = \frac{Q_H}{W} \quad \dots \dots \dots (4.9)$$

$$W = Q_H - Q_L \quad \dots \dots \dots (4.10)$$

$$C.O.P. = \frac{Q_H}{Q_H - Q_L} \quad \dots \dots \dots (4.11)$$

A **Refrigerator** is a device similar to a heat pump but with reverse objective. It maintains a body at a temperature lower than that of the surroundings while operating in a cycle.

Refrigerator also performs a non-spontaneous process of extracting heat from low temperature body for maintaining it cool, therefore external work W is to be done for realizing it. The block diagram shows how refrigerator extracts heat Q_L for maintaining body at low temperature T_L at the expense of work W and rejects heat to high temperature surroundings.



Performance of refrigerator is also quantified by coefficient of performance, which could be defined as:

$$(C.O.P.)_{ref.} = \frac{\text{Desired effect}}{\text{Net work}} = \frac{Q_L}{W} \quad \dots \dots \dots (4.12)$$

$$W = Q_H - Q_L \quad \dots \dots \dots (4.13)$$

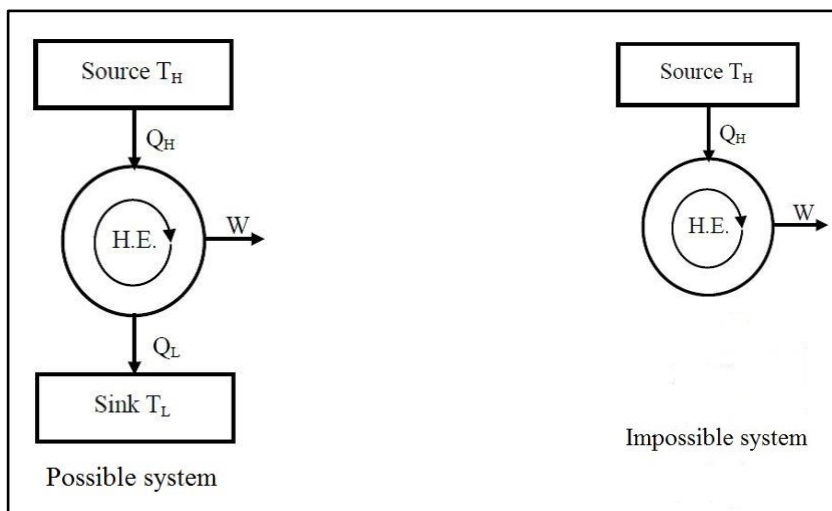
$$(C.O.P.)_{ref.} = \frac{Q_L}{Q_H - Q_L} \quad \dots \dots \dots (4.14)$$

(C.O.P.) values of a heat pump and a refrigerator can be interrelated as:

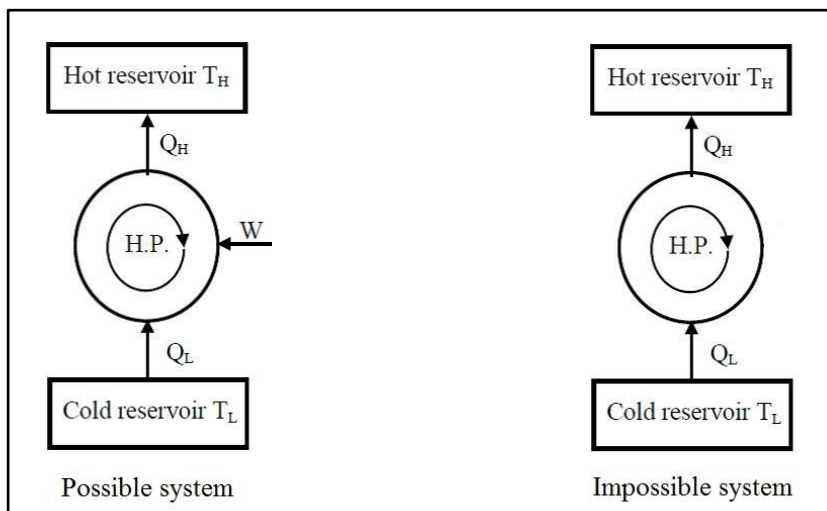
$$(C.O.P.)_{HP} = (C.O.P.)_{ref.} + 1 \quad \dots \dots \dots (4.15)$$

Statements of the Second Law of Thermodynamics

1. Kelvin-Planck statement: no process is possible whose sole effect is the removal of heat from a single thermal reservoir at a uniform temperature and the performance of an equal amount of work.



2. Clausius statement: no process is possible whose sole effect is the removal of heat from a reservoir at a lower temperature and the absorption of equal amount of heat by a reservoir at a higher temperature.



Entropy

Entropy is the outcome of the second law of thermodynamics and is a thermodynamic property. It is a thermodynamic quantity representing the unavailability of a system's thermal energy for conversion into mechanical work, often interpreted as the degree of disorder or randomness in the system. This property has immense significance in thermodynamic process analysis.

Clausius Inequality

The inequality of Clausius is a corollary or a consequence of the second law of thermodynamics. It is valid for all possible cycles, including both reversible and irreversible heat engines and refrigerators.

$$\oint \frac{\delta Q}{T} \leq 0 \quad \dots \dots \dots (4.16)$$

$$\oint \frac{\delta Q}{T} = 0, \quad \text{for reversible cycle}$$

$$\oint \frac{\delta Q}{T} < 0, \quad \text{for irreversible cycle}$$

$$\oint \frac{\delta Q}{T} > 0, \quad \text{for impossible cycle}$$

Entropy a Property of System

From Clausius inequality it is shown that for a reversible cycle:

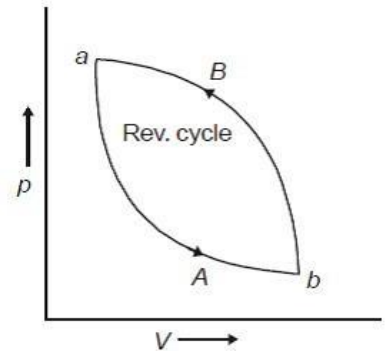
$$\oint \frac{\delta Q}{T} = 0$$

Let us take a reversible cycle comprising of two processes A and B as shown and apply Clausius inequality.

$$\int_a^b \frac{\delta Q}{T}_{path A} + \int_b^a \frac{\delta Q}{T}_{path B} = 0 \quad \dots \dots \dots (4.17)$$

$$\int_a^b \frac{\delta Q}{T}_{path A} = - \int_b^a \frac{\delta Q}{T}_{path B} \quad \dots \dots \dots (4.18)$$

$$\int_a^b \frac{\delta Q}{T}_{path A} = \int_a^b \frac{\delta Q}{T}_{path B} \quad \dots \dots \dots (4.19)$$



Since $\oint \frac{\delta Q}{T}$ is the same for all reversible paths between state a and state b. It can be concluded that this quantity is independent on path and is a function of end states. Therefore, it is a property of the system. This property is called **entropy** and given the symbol "S".

$$dS = \left(\frac{\delta Q}{T}\right)_{rev.} \quad \dots \dots \dots (4.20)$$

Entropy is an extensive property. The change in the entropy of the system as it undergoes a change of state may be found as:

$$\int_1^2 dS = \int_1^2 \frac{\delta Q}{T} \quad \dots \dots \dots (4.21)$$

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} \quad \dots \dots \dots (4.22)$$

To perform this integration the relation between Q and T must be known. Since Q is a path function therefore, δQ is an exact differential.

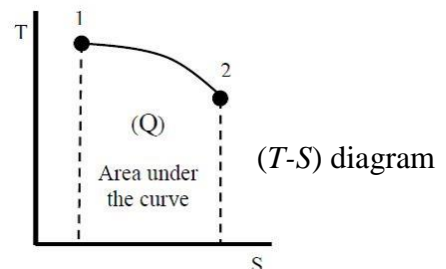
$$dS = \left(\frac{dQ}{T}\right)_{rev.} \quad \dots \dots \dots (4.23)$$

$$dQ = TdS \quad \dots \dots \dots (4.24)$$

Therefore, there is a diagram on which area to represents the heat flow in a reversible process. This diagram is called (T-S) diagram.

$$\int_1^2 dQ = \int_1^2 TdS \quad \dots \dots \dots (4.25)$$

$$Q = \int_1^2 TdS \quad \dots \dots \dots (4.26)$$



Therefore, the heat flow is a reversible process and can be represented as the area under the curve on the (T - S) diagram.

(T - S) Diagram for Vapor

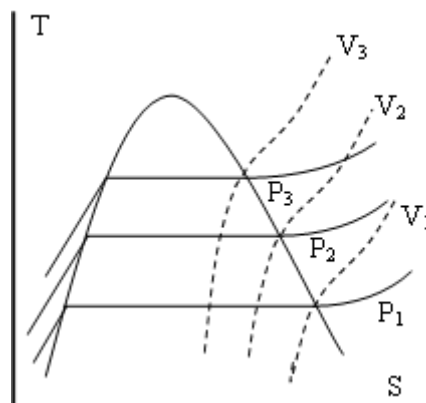
The (T - S) diagram of a vapor is shown in figure below. Lines $P_1, P_2, P_3 \dots P_n$ are lines of constant pressure. These lines are incident with the saturated liquid line in the liquid region. The constant pressure lines are horizontal in the mixture phase region and curve upward in the superheated region. The lines of constant volume are concave down in the mixed phase region and concave up in the superheated region. The slop of the constant volume lines is greater than the slop of constant pressure lines in the superheated region.

The entropy of saturated liquid is given the symbol s_f and the entropy of saturated vapor is given the symbol s_g . s_f and s_g are found from the tables according to the quality of vapor. The entropy of wet vapor is calculated as follows:

$$s = s_f + xs_{f,g}$$

For isentropic processes:

$$\Delta s = 0$$



Example (4.1): A rigid cylinder of volume 0.025 m^3 contains steam at 80 bar and 350°C . The cylinder is cooled until the pressure is 50 bar. Calculate the quality of steam after cooling, the amount of heat rejected during the process and the change in entropy. Sketch the (T - S) diagram indicating the area which represents the heat flow.

Solution:

At 80 bar and 350°C the steam is superheated because $T > T_{sat}$.

From superheated steam tables at (80 bar = 8 MPa) and 350°C :

$$s_1 = 6.1301 \text{ kJ/kg}\cdot\text{K}, u_1 = 2750 \text{ kJ/kg}, v_1 = 0.02995 \text{ m}^3/\text{kg}$$

$$v_2 = v_1 = 0.02995 \text{ m}^3/\text{kg}$$

From saturated steam tables at 50 bar ($v_f = 0.001286 \text{ m}^3/\text{kg}$, $v_g = 0.03944 \text{ m}^3/\text{kg}$)

Since $v_f < v_2 < v_g$, so the steam is in the wet phase

$$v_2 = x \cdot v_g \rightarrow x = \frac{v_2}{v_g} = \frac{0.02995}{0.03944}$$

$x = 0.758$ Ans.

From saturated steam tables at 50 bar ($u_f = 1147.81 \text{ kJ/kg}$, $u_{fg} = 1449.3 \text{ kJ/kg}$)

$$(s_f = 2.9202 \text{ kJ/kg. K}, s_{fg} = 3.0532 \text{ kJ/kg. K})$$

$$u_2 = u_f + x \cdot u_{fg} = 1147.81 + 0.758 \times 1449.3 = 2247 \text{ kJ/kg}$$

$$s_2 = s_f + x \cdot s_{fg} = 2.9202 + 0.758 \times 3.0532 = 5.2345 \text{ kJ/kg. K}$$

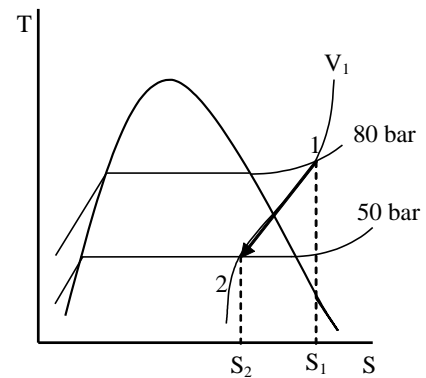
$$m = \frac{V_1}{v_1} = \frac{0.025}{0.02995} = 0.835 \text{ kg}$$

$$Q = m(u_2 - u_1) + W = 0.835 \times (2247 - 2750) + 0$$

$Q = -420 \text{ kJ}$ Ans.

$$\Delta S = m(s_2 - s_1) = 0.835 \times (5.2345 - 6.1301)$$

$\Delta S = -0.7478 \text{ kJ/K}$ Ans.



Entropy Change for Perfect Gas

The first law of thermodynamics for non-flow reversible and irreversible processes and in the absence of potential and kinetic energies is:

$$\delta Q - \delta W = dU$$

If the process is reversible, then:

$$(\delta Q)_{rev.} - \delta W = dU \quad \dots \dots \dots (4.27)$$

Also from the second law of thermodynamics, for reversible processes $dS = \left(\frac{dQ}{T}\right)_{rev.}$ so:

$$T \cdot dS = P \cdot dV + dU \quad \dots \dots \dots (4.28)$$

$$T \cdot dS = P \cdot dV + d(H - PV) = P \cdot dV + dH - V \cdot dP - P \cdot dV$$

$$T \cdot dS = dH - V \cdot dP$$

$$dS = \frac{dH}{T} - \frac{V \cdot dP}{T} \quad \dots \dots \dots (4.29)$$

Integrating equations (4.28) and (4.29), we get:

$$S_2 - S_1 = \int_1^2 \left(\frac{P \cdot dV}{T} \right) + \int_1^2 \frac{dU}{T} \quad \dots \dots \dots (4.30)$$

$$S_2 - S_1 = \int_1^2 \frac{dH}{T} - \int_1^2 \frac{V \cdot dP}{T} \quad \dots \dots \dots (4.31)$$

For a perfect gas:

$$dU = mC_v dT, dH = mC_p dT, \frac{P}{T} = \frac{mR}{V}, \frac{V}{T} = \frac{mR}{P}$$

Hence, equations (4.30) and (4.31) become:

$$S_2 - S_1 = mR \int_1^2 \frac{dV}{V} + mC_v \int_1^2 \frac{dT}{T} \quad \dots \dots \dots (4.32)$$

$$S_2 - S_1 = mC_p \int_1^2 \frac{dT}{T} - mR \int_1^2 \frac{dP}{P} \quad \dots \dots \dots (4.33)$$

$$S_2 - S_1 = mR \ln \left(\frac{V_2}{V_1} \right) + mC_v \ln \left(\frac{T_2}{T_1} \right) \quad \dots \dots \dots (4.34)$$

$$S_2 - S_1 = mC_p \ln \left(\frac{T_2}{T_1} \right) - mR \ln \left(\frac{P_2}{P_1} \right) \quad \dots \dots \dots (4.35)$$

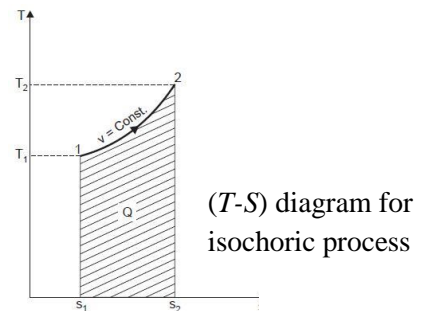
Equations (4.34) and (4.35) can be used to calculate the entropy change for any reversible thermodynamic process as follows:

1. Constant volume (isochoric) process: during such processes $dV = 0$, so equation (4.34) becomes:

$$S_2 - S_1 = mC_v \ln \left(\frac{T_2}{T_1} \right) \quad \dots \dots \dots (4.36)$$

For unit mass:

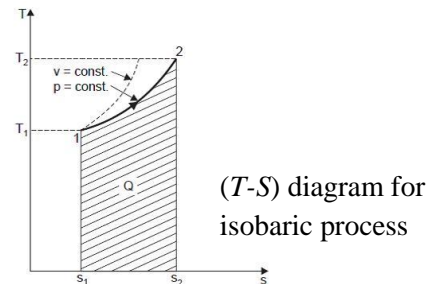
$$s_2 - s_1 = C_v \ln \left(\frac{T_2}{T_1} \right) \quad \dots \dots \dots (4.37)$$



2. Constant pressure (isobaric) process: during such processes $dP = 0$, so equation (4.35) becomes:

$$S_2 - S_1 = mC_p \ln \left(\frac{T_2}{T_1} \right) \quad \dots \dots \dots (4.38)$$

For unit mass:



$$s_2 - s_1 = C_p \ln \left(\frac{T_2}{T_1} \right) \quad \dots \dots \dots (4.39)$$

3. Constant temperature (isothermal) process: during such processes $dT = 0$, so equations (4.34) and (4.35) become:

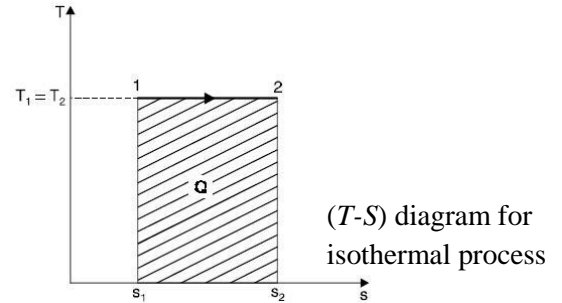
$$S_2 - S_1 = mR \ln \left(\frac{V_2}{V_1} \right) \quad \dots \dots \dots (4.40)$$

$$S_2 - S_1 = mR \ln \left(\frac{P_1}{P_2} \right) \quad \dots \dots \dots (4.41)$$

For unit mass:

$$s_2 - s_1 = R \ln \left(\frac{V_2}{V_1} \right) \quad \dots \dots \dots (4.42)$$

$$s_2 - s_1 = R \ln \left(\frac{P_1}{P_2} \right) \quad \dots \dots \dots (4.43)$$



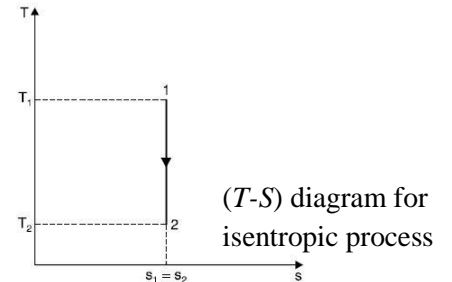
4. Reversible adiabatic (isentropic) process: for these processes $dQ = 0$. Hence:

$$\Delta S = S_2 - S_1 = 0 \quad \dots \dots \dots (4.44)$$

$$S_2 = S_1 \quad \dots \dots \dots (4.45)$$

For irreversible adiabatic processes:

$$\Delta S = (S_2 - S_1) > 0 \quad \dots \dots \dots (4.46)$$



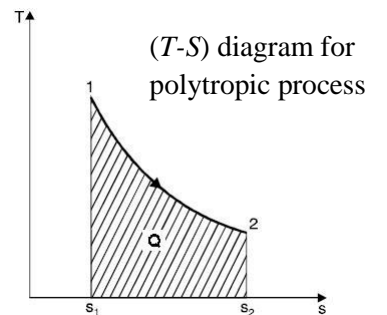
5. Polytropic process: these processes follow the law $PV^n = C$. Using equation (4.34):

$$S_2 - S_1 = mR \ln \left(\frac{V_2}{V_1} \right) + mC_v \ln \left(\frac{T_2}{T_1} \right)$$

Substituting the relation $\left(\frac{V_2}{V_1} \right) = \left(\frac{T_1}{T_2} \right)^{\frac{1}{n-1}}$ into the above equation gives:

$$S_2 - S_1 = mR \ln \left(\frac{T_1}{T_2} \right)^{\frac{1}{n-1}} + mC_v \ln \left(\frac{T_2}{T_1} \right) \quad \dots \dots \dots (4.47)$$

$$S_2 - S_1 = \frac{mR}{n-1} \ln \left(\frac{T_1}{T_2} \right) + mC_v \ln \left(\frac{T_2}{T_1} \right) \quad \dots \dots \dots (4.48)$$



For a perfect gas, $R = C_p - C_v$, $\gamma = \frac{C_p}{C_v}$

So, $R = \gamma \cdot C_v - C_v = C_v(\gamma - 1)$

Substituting R in equation (4.48):

$$S_2 - S_1 = mC_v \ln \left(\frac{T_2}{T_1} \right) + \frac{mC_v(\gamma - 1)}{n - 1} \ln \left(\frac{T_1}{T_2} \right) \dots \dots \dots (4.49)$$

$$S_2 - S_1 = mC_v \ln \left(\frac{T_2}{T_1} \right) \left\{ 1 - \left(\frac{\gamma - 1}{n - 1} \right) \right\} \dots \dots \dots (4.50)$$

$$S_2 - S_1 = mC_v \ln \left(\frac{T_2}{T_1} \right) \left(\frac{n - \gamma}{n - 1} \right) \dots \dots \dots (4.51)$$

For unit mass:

$$s_2 - s_1 = C_v \ln \left(\frac{T_2}{T_1} \right) \left(\frac{n - \gamma}{n - 1} \right) \dots \dots \dots (4.52)$$

Example (4.2): Air at 15°C and 1.05 bar occupies 0.02 m³. The air is heated at constant volume until the pressure is 4.2 bar and then cooled at constant pressure to the original temperature. Calculate the net heat flow to or from the air and the net entropy change.

Solution:

$$m = \frac{PV}{RT} = \frac{1.05 \times 10^5 \times 0.02}{287 \times (15 + 273)} = 0.0254 \text{ kg}$$

$$\frac{T_2}{T_1} = \frac{P_2}{P_1} \rightarrow T_2 = (15 + 273) \times \frac{4.2}{1.05} \rightarrow T_2 = 1152 \text{ K}$$

$$Q_{1-2} = mC_v(T_2 - T_1) = 0.0254 \times 0.718 \times (1152 - 288) = 15.75 \text{ kJ}$$

$$Q_{2-3} = mC_p(T_3 - T_2) = 0.0254 \times 1.005(288 - 1152) = -22.05 \text{ kJ}$$

$$Q_{net} = Q_{1-2} + Q_{2-3} = 15.75 + (-22.05)$$

$Q_{net} = -6.3 \text{ kJ}$ Ans.

$$\Delta S = S_3 - S_1 = (S_2 - S_1) + (S_3 - S_2)$$

$$(S_2 - S_1) = mC_v \ln \left(\frac{T_2}{T_1} \right) = 0.0254 \times 0.718 \times \ln \left(\frac{1152}{288} \right) = 0.0253 \text{ kJ/K}$$

$$(S_3 - S_2) = mC_p \ln \left(\frac{T_3}{T_2} \right) = 0.0254 \times 1.005 \times \ln \left(\frac{288}{1152} \right) = -0.0354 \text{ kJ/K}$$

$$\Delta S = 0.0253 + (-0.0354)$$

$\Delta S = -0.0101 \text{ kJ/K}$ Ans.

Example (4.3): Calculate the change of entropy per kg of air expanding polytropically in a cylinder behind a piston from 6.3 bar and 550°C to 1.05 bar according to the law $PV^{1.3} = C$.

Solution:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} \rightarrow T_2 = (550 + 273) \times \left(\frac{1.05}{6.3}\right)^{\frac{1.3-1}{1.3}} = 544 \text{ K}$$

$$s_2 - s_1 = C_v \ln\left(\frac{T_2}{T_1}\right) \left(\frac{n-\gamma}{n-1}\right) = 0.718 \times \ln\left(\frac{544}{823}\right) \times \left(\frac{1.3-1.4}{1.3-1}\right)$$

$$\Delta s = 0.1 \text{ kJ/kg. K} \quad \text{Ans.}$$

Exercises

Problem (4.1): Determine the change in entropy of 0.5 kg of air compressed polytropically from 1.013×10^5 Pa to 0.8 MPa and 800 K, following an index of 1.2. Take $C_v = 0.71$ kJ/kg.K.

Ans. (-122.27 J/K)

Problem (4.2): 1 m^3 of air is heated reversibly at constant pressure from 15°C to 300°C , and is then cooled reversibly at constant volume back to the initial temperature. The initial pressure is 1.03 bar. Calculate the net heat flow and the overall change of entropy. Sketch the processes on a (T - S) diagram.

Ans. (101.5 kJ, 0.246 kJ/K)

Problem (4.3): 1 kg of air is allowed to expand reversibly in a cylinder behind a piston in such a way that the temperature remains constant at 260°C while the volume is doubled. The piston is then moved in and heat is rejected by the air reversibly at constant pressure until the volume is the same as it was initially. Calculate the net heat flow and the overall change of entropy. Sketch the processes on a (T - S) diagram.

Ans. (-161.9 kJ/kg, -0.497 kJ/kg.K)

Problem (4.4): 1 kg of air at 1.02 bar and 20°C , undergoes a process in which the pressure is raised to 6.12 bar and the volume becomes 0.25 m^3 . Calculate the change of entropy and mark the initial and final states on a (T - S) diagram.

Ans. (0.087 kJ/kg.K)