

In terms of pressure & volume.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{T_2}{T_1} = \frac{P_2}{P_1} \times \frac{V_2}{V_1}$$

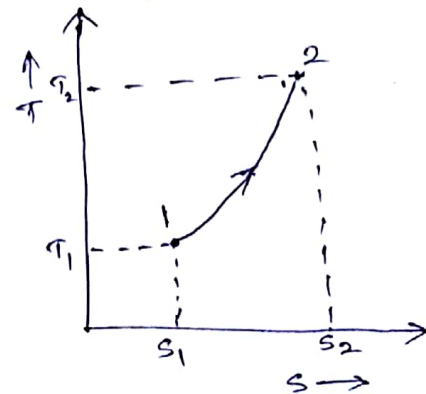
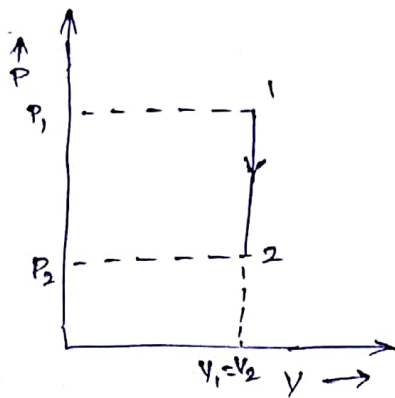
Substituting this value in equation (2)

$$\begin{aligned} ds &= mR \ln \left[\frac{V_2}{V_1} \right] + mC_v \ln \left[\frac{P_2}{P_1} \times \frac{V_2}{V_1} \right] \\ &= mR \ln \left[\frac{V_2}{V_1} \right] + mC_v \ln \left[\frac{P_2}{P_1} \right] + mC_v \ln \left[\frac{V_2}{V_1} \right] \\ &= m(C_p - C_v) \ln \left[\frac{V_2}{V_1} \right] + mC_v \ln \left[\frac{P_2}{P_1} \right] + mC_v \ln \left[\frac{V_2}{V_1} \right] \\ &= mC_p \ln \left[\frac{V_2}{V_1} \right] - mC_v \ln \left[\frac{V_2}{V_1} \right] + mC_v \ln \left[\frac{P_2}{P_1} \right] + mC_v \ln \left[\frac{V_2}{V_1} \right] \\ &= mC_p \ln \left[\frac{V_2}{V_1} \right] + mC_v \ln \left[\frac{P_2}{P_1} \right] \end{aligned}$$

Change in Entropy for different process :-

(a) constant Volume process :-

A system undergoing a change of state from 1 to 2 at $V=c$ process is shown in P-V & T-S diagram.



We have already seen that change in entropy,

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

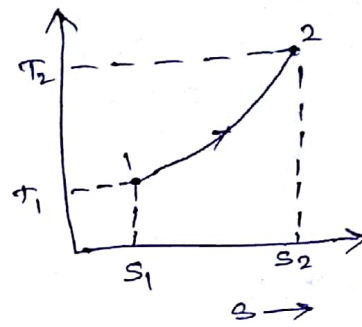
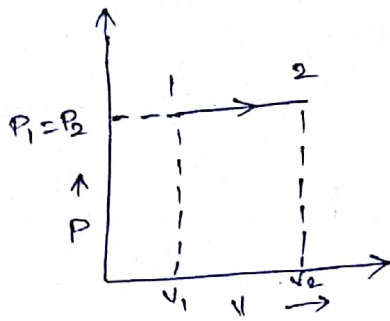
$$\because V=c \Rightarrow V_1 = V_2 \quad \ln \left(\frac{V_2}{V_1} \right) = 0 \Rightarrow \ln(1) = 0$$

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

$$\because \frac{T_2}{T_1} = \frac{P_2}{P_1}$$

$$ds = mC_v \ln \left(\frac{T_2}{T_1} \right) \quad (\text{or}) \quad mC_v \ln \left(\frac{P_2}{P_1} \right)$$

(b) constant pressure process :-



From equation (2)

$$ds = mR \ln\left(\frac{v_2}{v_1}\right) + mC_v \ln\left(\frac{T_2}{T_1}\right)$$

$$P = C \Rightarrow \frac{v_2}{v_1} = \frac{T_2}{T_1}$$

$$ds = mR \ln\left(\frac{v_2}{v_1}\right) + mC_v \ln\left(\frac{v_2}{v_1}\right)$$

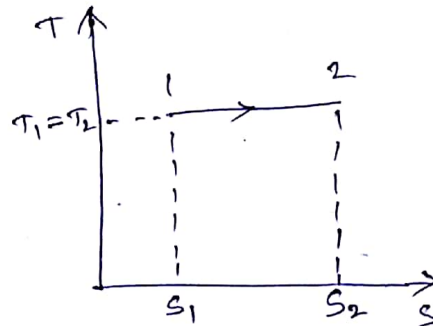
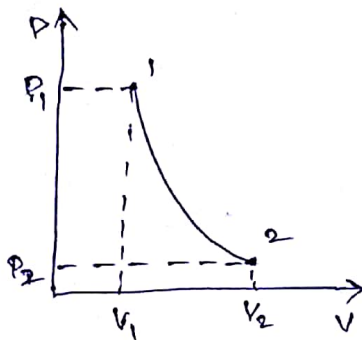
$$ds = m(C_p - C_v) \ln\left(\frac{v_2}{v_1}\right) + mC_v \ln\left(\frac{v_2}{v_1}\right)$$

Taking $m \ln\left(\frac{v_2}{v_1}\right)$ commonly.

$$ds = m \ln\left(\frac{v_2}{v_1}\right) (C_p - C_v + C_v)$$

$$ds = m C_p \ln\left(\frac{v_2}{v_1}\right) \quad (\text{or}) \quad ds = m C_p \ln\left(\frac{T_2}{T_1}\right)$$

(c) constant temperature pressure :-



from equation (2)

$$ds = mR \ln\left(\frac{v_2}{v_1}\right) + mC_v \ln\left(\frac{T_2}{T_1}\right)$$

$$T = C \quad T_1 = T_2$$

$$ds = mR \ln\left(\frac{v_2}{v_1}\right) + mC_v \ln\left(\frac{T_2}{T_2}\right)$$

$$\therefore \ln(1) = 0$$

$$ds = mR \ln\left(\frac{v_2}{v_1}\right)$$

multiplying & dividing by T on right hand side -

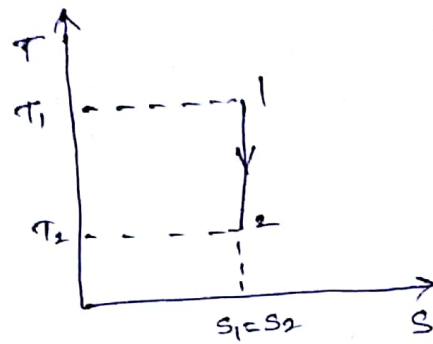
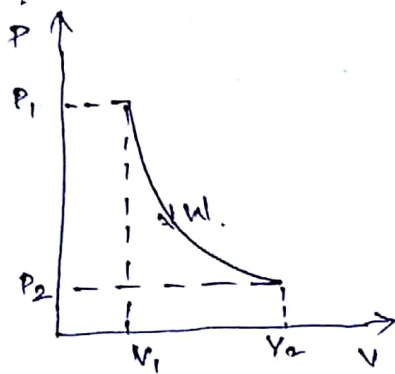
$$ds = \frac{mRT \ln\left(\frac{v_2}{v_1}\right)}{T}$$

$$\therefore Q = mRT \ln\left(\frac{v_2}{v_1}\right)$$

$$ds = \frac{Q}{T}$$

(A) Adiabatic (or) Isentropic process :-

Adiabatic process is the process in which the heat is neither received nor rejected. Simply there is no transfer during the process.

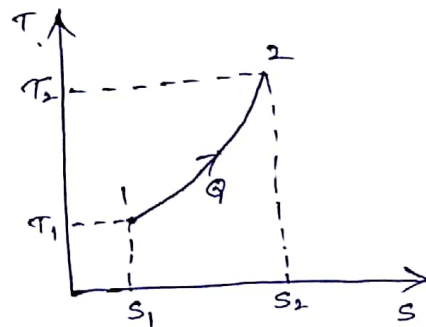
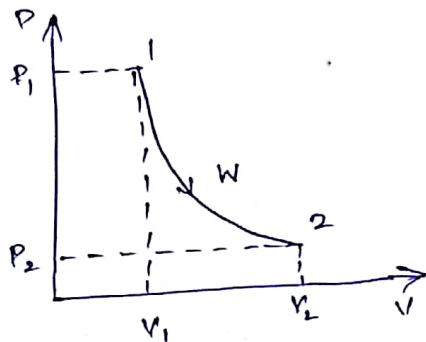


No heat transfer during process.

Change in entropy is zero, $ds = 0$.

(B) Polytropic process :-

During the polytropic process, there being heat transfer between system & its surrounding. There will be always a change in specific entropy.



From equation 9.

$$ds = mR \ln\left(\frac{V_2}{V_1}\right) + m \cdot C_v \cdot \ln\left(\frac{T_2}{T_1}\right) \text{ KJ/K}$$

Another expression may be derived.

Heat transfer during polytropic process.

$$dQ = \left(\frac{\gamma - n}{\gamma - 1}\right) \times W$$

$$dQ = \left[\frac{\gamma - n}{\gamma - 1}\right] \times P dV$$

γ - adiabatic index,
 n - polytropic index,
 W - Work done.

Dividing both sides by 'T'.

$$\frac{dq}{T} = \left[\frac{\gamma - n}{\gamma - 1} \right] \times \frac{P}{T} \cdot dV.$$

$$ds = \left[\frac{\gamma - n}{\gamma - 1} \right] \times \frac{mR}{V} \cdot dV.$$

$$\Rightarrow PV = mRT.$$

$$\frac{P}{T} = \frac{mR}{V}.$$

Integrating both sides from initial to final.

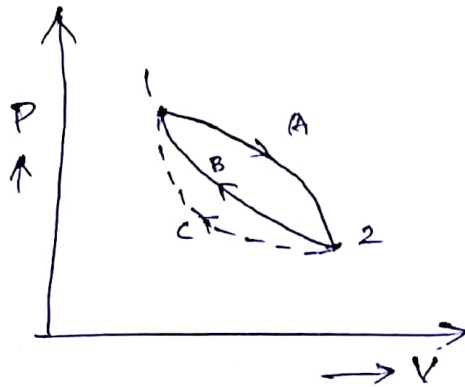
$$\int_1^2 ds = \left[\frac{\gamma - n}{\gamma - 1} \right] \times mR \int_1^2 \frac{dV}{V}.$$

$$s_2 - s_1 = \left[\frac{\gamma - n}{\gamma - 1} \right] \times mR \left[\ln V \right]_1^2.$$

$$ds = \left[\frac{\gamma - n}{\gamma - 1} \right] \times mR \ln \left[\frac{V_2}{V_1} \right].$$

Principle of increase of Entropy:-

change of entropy for reversible process is given by the expression, $ds = \frac{dq}{T}$, Now we will examine the entropy change for an irreversible process.



Reversible cycle 1-A-2-B-1.

$$\int_{1A}^{2A} \frac{dq}{T} + \int_{2A}^{1B} \frac{dq}{T} = 0 \quad \text{--- (1)}$$

Irreversible cycle 1-A-2-C-1.

$$\int_{1A}^{2A} \frac{dq}{T} + \int_{2C}^{1C} \frac{dq}{T} \leq 0 \quad \text{--- (2)}$$

subtracting equation (1) from (2) \Rightarrow (2)-(1).

$$\int_{2C}^{1C} \frac{dQ}{T} - \int_{2B}^{1B} \frac{dQ}{T} \leq 0 \quad \text{--- (3)}$$

on reversing the limit and rearranging equation (3).

$$\int_{1B}^{2B} \frac{dQ}{T} \geq \int_{1C}^{2C} \frac{dQ}{T} \quad \text{--- (4)}$$

Since the process 2-B-1 is reversible

$$ds = \frac{dQ}{T}.$$

substituting this value in equation (4).

$$\int_{1B}^{2B} ds \geq \int_{1C}^{2C} \frac{dQ}{T}.$$

(or)

$$ds \geq \frac{dQ}{T} \quad \text{--- (5)}$$

$ds = 0$ for reversible process.

$ds > 0$ for irreversible process

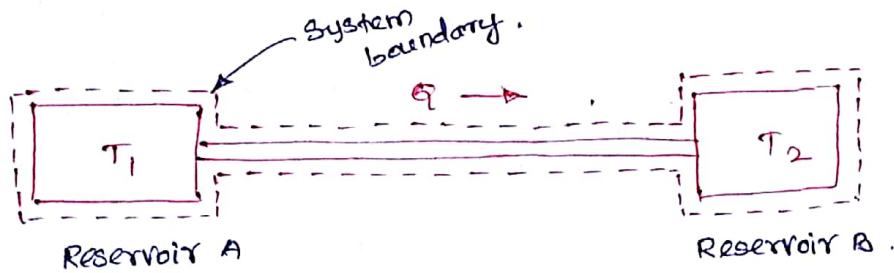
$ds < 0$ for impossible process.

Applications of Entropy:-

1. Transfer of heat through a finite temperature difference.
2. Mixing of two fluids.
3. Maximum work obtainable from two finite bodies of temperature T_1 and T_2 .
4. Maximum work obtainable from a finite body and a FER.
5. Processes Exhibiting External Mechanical Irreversibility.
 - a) Isothermal dissipation of work.
 - b) Adiabatic dissipation of work.

Q1. Transfer of heat through a finite temperature difference :-

Consider two small reservoir of 1 at T_1 , and 2 at T_2 . It exchanges heat Q from reservoir 1 to reservoir 2.



From reservoir 1,

$$\text{change in entropy } \Delta S_1 = \frac{-Q}{T_1}$$

[-ve sign indicates that the heat is transferred from 1.]

From reservoir 2,

$$\text{change in entropy } \Delta S_2 = \frac{Q}{T_2}$$

Heat transfer from reservoir 1 and 2 to the surrounding is considered as negligible.

$$\begin{aligned} \text{Total entropy } \Delta S &= \Delta S_1 + \Delta S_2 \\ &= -\frac{Q}{T_1} + \frac{Q}{T_2} \\ &= Q \left[\frac{T_1 - T_2}{T_1 T_2} \right] \end{aligned}$$

- i) $\Delta S > 0$ (or) $T_1 > T_2$, Irreversible process
- ii) $\Delta S = 0$ (or) $T_1 = T_2$, Reversible process
- iii) $\Delta S < 0$ (or) $T_1 < T_2$, process is impossible.

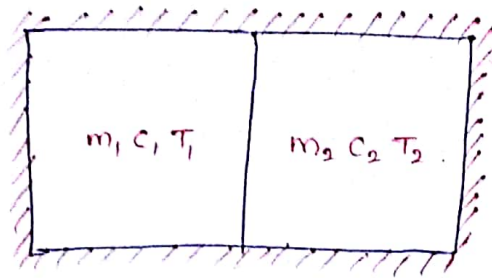
Q2. Mixing of Two fluids :-

Consider a system having two subsystem.

⇒ system 1 contains fluid of mass m_1 , specific heat at constant pressure of C_1 , and temperature of T_1 .

⇒ system 2 contains fluid of mass m_2 , specific heat at constant pressure of C_1 , and temperature of T_2 .

These two subsystems are separated by the partition in an adiabatic enclosure. When the partition is removed, then the two fluids will mix with each other. After mixing, it will attain the thermal equilibrium at temperature T_f .



T_f should always be lesser than T_1 but greater than T_2 .

By energy balance,

$$m_1 c_1 (T_1 - T_f) = m_2 c_2 (T_f - T_2)$$

$$T_f = \frac{m_1 c_1 T_1 + m_2 c_2 T_2}{m_1 c_1 + m_2 c_2}$$

change in entropy fluid contained in the subsystem 1,

$$\Delta S_1 = \int_{T_1}^{T_f} \frac{dq}{T} = \int_{T_1}^{T_f} \frac{m_1 c_1 dT}{T}$$

$$\Delta S_1 = m_1 c_1 \ln \frac{T_f}{T_1} \quad \text{--- (1)}$$

By, subsystem 2,

$$\Delta S_2 = \int_{T_2}^{T_f} \frac{dq}{T} = \int_{T_2}^{T_f} m_2 c_2 \frac{dT}{T}$$

$$\Delta S_2 = m_2 c_2 \ln \frac{T_f}{T_2} \quad \text{--- (2)}$$

from (1) & (2),

$$\text{total entropy } \Delta S = \Delta S_1 + \Delta S_2$$

$$= m_1 c_1 \ln \frac{T_f}{T_1} + m_2 c_2 \ln \frac{T_f}{T_2}$$

$$\text{If } m_1 = m_2 = m$$

$$c_1 = c_2 = c$$

$$\Delta S = m c \ln \frac{T_f}{T_1} \times \frac{T_f}{T_2}$$

$$\Delta S = m c \ln \frac{T_f^2}{T_1 T_2}$$

$$\text{and also, } T_f = \frac{T_1 + T_2}{2}$$

$$\Delta S = m c \ln \frac{(T_1 + T_2)^2}{4 T_1 T_2}$$

$$\Delta S = m c \ln \left(\frac{T_1 + T_2}{2\sqrt{T_1 T_2}} \right)^2$$

(15)

$$\Delta S = 2 m c \ln \frac{(T_1 + T_2)/2}{\sqrt{T_1 T_2}}$$

Absolute Entropy :-

The entropy of a pure crystalline substance at ~~an~~ absolute zero temperature is zero. This is the statement of third law of thermodynamics. This law provides an absolute reference point is called as "ABSOLUTE ENTROPY".

It is very much useful in thermodynamic analysis of chemical reactions.

$$\text{Absolute entropy, } \Delta S = S_1 - S_0$$

where,

S_1 = entropy of system at state 1.

S_0 = entropy of system at standard state denoted '0'.