4

Entropy

Contents

4.1 Introduction

- The entropy is a thermodynamics property of a working substance and serves as a valuable tool in the second law analysis of engineering devices. We know that all heal is not equally valuable for converting into work.
- Entropy is a function of a quantity of heat which shows the possibility of conversion of that heat into work.
- The increase in entropy is lower when heat is added at a high temperature and the increase in entropy is higher when heat is added at a low temperature.
- The maximum entropy means, there is minimum availability for conversion into work and the minimum entropy means, there is maximum availability for conversion into work.

4.2 Characteristics of Entropy

- The characteristics of entropy in a summarised form are given below :
- Entropy is property of system.
- For reversible process between state 1 and 2, the change in entropy is given by,

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{Rev} \qquad \textit{Eq. (4.1)}$$

- The change in entropy for the system may be positive, negative or zero (depending on the heat absorption, rejection or absence)
- Entropy is point function, independent on path of the process.
- For a reversible process, the change in entropy for the surrounding is equal in magnitude but opposite in sign to the change in entropy for the system.so total or net change for system plus surrounding is equal to zero.
- The increase of entropy during the process is a measure of the loss of availability of the energy of the system.
- The entropy of a pure substance approaches zero at the absolute zero temperature.
- From the molecular point of view, entropy can .also be considered to be a measure of microscopic disorder.
- The entropy is a measure the lack of information about a system.
- The entropy of system is changed due to main three causes
    - Heat transfer - heat transfer to system increases the entropy of system, and heat transfer from system decreases the entropy of that system
    - Mass flow
    - Irreversibilities - such as friction, heat transfer due to finite temperature difference and fast expansion or compression.

4.3 Entropy is a Property

- Let us consider a system undergoing a reversible process from state 1 to state 2 along path A and then from state 2 to the original state 1 along path B as shown in *Fig.4.1 – P-v Diagram*. Applying the Clausius theorem to this reversible cyclic process, we have

$$\oint \frac{\delta Q}{T} = 0 \qquad \textit{Eq. (4.2)}$$

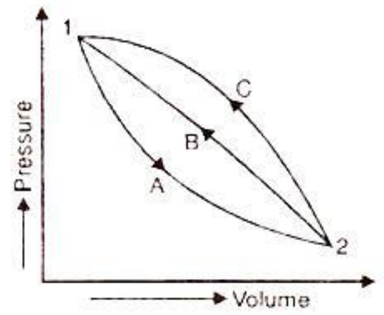

Fig.4.1 – P-v Diagram

- Hence when the system passes through the cycle 1-A-2-B-1, we have

$$\int_{1(A)}^{2} \frac{\delta Q}{T} + \int_{2(B)}^{1} \frac{\delta Q}{T} = 0 \tag*{Eq. (4.3)}$$

- Now consider another reversible cycle in which the system changes from state 1 to state 2 along path A, but returns from state 2 to the original state 1 along a different path C. For this reversible cyclic process, we have

$$\int_{1(A)}^{2} \frac{\delta Q}{T} + \int_{2(C)}^{1} \frac{\delta Q}{T} = 0 \tag*{Eq. (4.4)}$$

- From above equation we have,

$$\int_{2(B)}^{1} \frac{\delta Q}{T} = \int_{2(C)}^{1} \frac{\delta Q}{T} \tag*{Eq. (4.5)}$$

- Above equation indicates that no restriction is imposed on paths, except that they must be reversible, the quantity $(\frac{\delta Q}{T})$ is a function of the initial and final states of the system and is independent of the path of the process. Hence it represents a property of the system.

4.4 Clausius Theorem

- The cyclic integration of $\frac{\delta Q}{T}$ is equal to zero.
- For any reversible process,

$$\oint \left(\frac{\delta Q}{T}\right)_{Rev} = 0 \tag*{Eq. (4.6)}$$

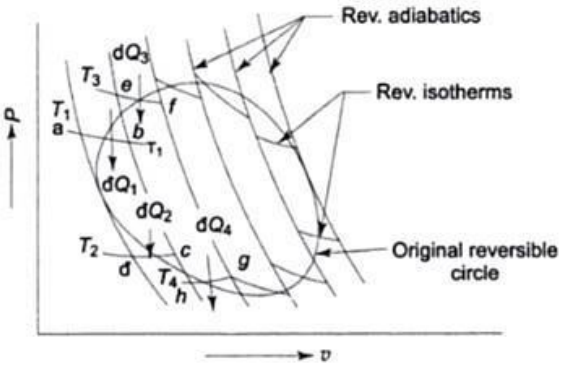

Fig.4.2 – P-v Diagram

- Consider a closed curve ABCDA representing a reversible cycle as shown in Fig. Let. closed cycle ABCDA is divided into a number of small Carnot cycles by drawing adiabatic and isothermal lines in such a way that, Algebraic sum of heat transferred during the sets of isothermal processes of Carnot cycles is equal to heat transferred during the original reversible cycle (ABCDA).

- Thus the original reversible cycle is replaced by number of Carnot cycles. If the adiabatic processes of Carnot cycles are close to one another (i.e. process 2-3 is adiabatic expansion while process 5-6 adiabatic compression, so process 2-3 is cancelled out) and the number of Carnot cycles is large, the saw toothed zig-zag line will coincide with the original cycle.
- For the elemental Carnot cycle 1-2-3-4 receives heat δQ_{H1} at temperature T_{H1} during reversible isothermal process 1-2 and rejects heat δQ_{L1} at temperature T_{L1} during reversible isothermal process 3-4,
- From kelvin temperature scale,

$$\frac{\delta Q_{H1}}{T_{H1}} = \frac{\delta Q_{L1}}{T_{L1}} \qquad \textit{Eq. (4.7)}$$

- If heal supplied is taken as positive and heal rejected as negative.

$$\left(\frac{\delta Q_{H1}}{T_{H1}}\right) + \left(\frac{\delta Q_{L1}}{T_{L1}}\right) = 0 \qquad \textit{Eq. (4.8)}$$

- Similarly, for the elemental Carnot cycle 5-6-7-8-5,

$$\left(\frac{\delta Q_{H2}}{T_{H2}}\right) + \left(\frac{\delta Q_{L2}}{T_{L2}}\right) = 0 \qquad \textit{Eq. (4.9)}$$

- If similar equations are written for all the elemental Carnot cycles, then for the whole original cycle.

$$\left(\frac{\delta Q_{H1}}{T_{H1}}\right) + \left(\frac{\delta Q_{L1}}{T_{L1}}\right) + \cdots = 0 \qquad \textit{Eq. (4.10)}$$

$$\oint \left(\frac{\delta Q}{T}\right)_{Rev} = 0 \qquad \textit{Eq. (4.11)}$$

4.5 Clausius Inequality

- When a system undergoes a complete cyclic process, the integral of $\frac{\delta Q}{T}$ around the cycle is less than zero or equal to zero.
- Mathematically,

$$\oint \left(\frac{\delta Q}{T}\right) \leq 0 \qquad \textit{Eq. (4.12)}$$

- Consider a reversible engine R and irreversible engine I working between two thermal reservoir at temperature T_H and T_L.
- Efficiency of reversible engine,

$$\eta_R = 1 - \frac{\delta Q_L}{\delta Q_H} = 1 - \frac{T_L}{T_H} \qquad \textit{Eq. (4.13)}$$

- Efficiency of irreversible engine,

$$\eta_I = 1 - \frac{\delta Q_L}{\delta Q_H} \neq 1 - \frac{T_L}{T_H} \qquad \textit{Eq. (4.14)}$$

- We know that efficiency of reversible engine is more than irreversible engine under same temperature limit.

$$\therefore \eta_R > \eta_I \qquad \textit{Eq. (4.15)}$$

$$\therefore \left(1 - \frac{\delta Q_L}{\delta Q_H}\right)_R > \left(1 - \frac{\delta Q_L}{\delta Q_H}\right)_I \qquad \textit{Eq. (4.16)}$$

$$\therefore \left(1-\frac{T_L}{T_H}\right)_R > \left(1-\frac{\delta Q_L}{\delta Q_H}\right)_I \qquad \text{Eq. (4.17)}$$

$$\therefore \left(\frac{T_L}{T_H}\right) < \left(\frac{\delta Q_L}{\delta Q_H}\right)_I \qquad \text{Eq. (4.18)}$$

$$\therefore \left(\frac{\delta Q_H}{T_H}\right) < \left(\frac{\delta Q_L}{T_L}\right) \qquad \text{Eq. (4.19)}$$

$$\therefore \left(\frac{\delta Q_H}{T_H}\right) - \left(\frac{\delta Q_L}{T_L}\right) < 0 \qquad \text{Eq. (4.20)}$$

- We know heat added should be positive and heat rejected should be negative.

$$\therefore \left(\frac{\delta Q_H}{T_H}\right) - \left(\frac{-\delta Q_L}{T_L}\right) < 0 \qquad \text{Eq. (4.21)}$$

$$\therefore \left(\frac{\delta Q_H}{T_H}\right) + \left(\frac{\delta Q_L}{T_L}\right) < 0 \qquad \text{Eq. (4.22)}$$

- Considering complete original irreversible cycle,

$$\therefore \left[\left(\frac{\delta Q_{H1}}{T_{H1}}\right) + \left(\frac{\delta Q_{L1}}{T_{L1}}\right) + \left(\frac{\delta Q_{H2}}{T_{H2}}\right) + \left(\frac{\delta Q_{L2}}{T_{L2}}\right)\right] + \cdots < 0 \qquad \text{Eq. (4.23)}$$

$$\oint \left(\frac{\delta Q}{T}\right)_I < 0 \qquad \text{Eq. (4.24)}$$

- According to Clausius theorem, $\oint \left(\frac{\delta Q}{T}\right)_{Rev} = 0$ for reversible cycle. combing results for reversible and irreversible cycle,

$$\oint \left(\frac{\delta Q}{T}\right) \leq 0 \qquad \text{Eq. (4.25)}$$

- This expression known as Clausius inequality.

$$\oint \left(\frac{\delta Q}{T}\right)_{Reversible} = 0 \qquad \text{Eq. (4.26)}$$

$$\oint \left(\frac{\delta Q}{T}\right)_{Irreversible} < 0 \qquad \text{Eq. (4.27)}$$

$$\oint \left(\frac{\delta Q}{T}\right)_{Impossible} > 0 \qquad \text{Eq. (4.28)}$$

4.6 Principle of increase of entropy or change in entropy of the universe

- The entropy of an isolated system during a process always increases or in the limiting case of reversible process remains constant.
- Mathematically,

$$\Delta S_{isolated} \geq 0 \qquad \text{Eq. (4.29)}$$

- Now, consider any system and its surrounding within a single boundary as shown in *Fig.4.9 - T-s diagram Adiabatic process*. The combination of system and surrounding within a single boundary is called the universe.

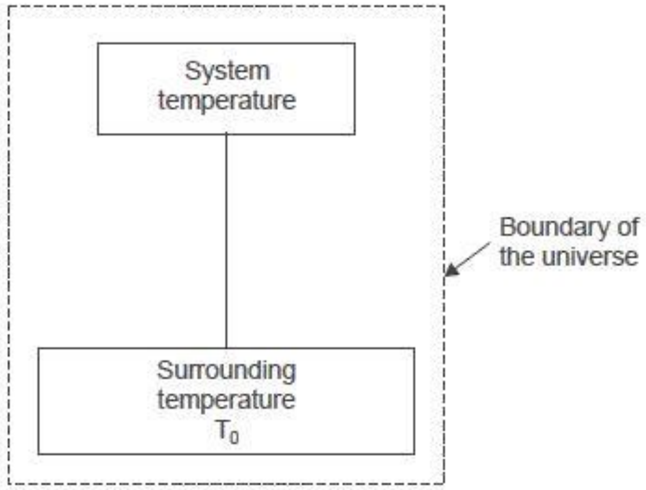

Fig.4.3 - Entropy change of universe

- Applying the principle of increase in entropy.

$$dS_{Universe} \geq 0 \qquad \text{Eq. (4.30)}$$

Where,

$$dS_{Universe} = dS_{System} + dS_{Surrounding} \qquad \text{Eq. (4.31)}$$

- In the combined closed system, the heat δQ transferred from the system to surrounding.
- For reversible process,

$$dS_{system} = \frac{-\delta Q}{T_{Sys}} \qquad \text{Eq. (4.32)}$$

$$dS_{surr} = \frac{\delta Q}{T_{Surr}} \qquad \text{Eq. (4.33)}$$

- Total change in entropy for the combined system,

$$dS_{system} + dS_{surr} = \delta Q\left(\frac{-1}{T_{sys}} + \frac{1}{T_{surr}}\right) \qquad \text{Eq. (4.34)}$$

$$\therefore dS_{Universe} = \delta Q\left(\frac{1}{T_{surr}} - \frac{1}{T_{sys}}\right) \qquad \text{Eq. (4.35)}$$

- But, $T_{sys} > T_{Surr}$,

$$\therefore \delta Q\left(\frac{1}{T_{surr}} - \frac{1}{T_{sys}}\right) > 0 \qquad \text{Eq. (4.36)}$$

$$\therefore dS_{Universe} \geq 0 \qquad \text{Eq. (4.37)}$$

- Above equation states that the process involving the integration of a system and the surroundings, net entropy of universe increases or remains constant.
- Since all natural processes are irreversible, the entropy is increasing continuously. The entropy becomes maximum value when the system reaches a stable equilibrium state from non-equilibrium state.

4.7 Applications of Entropy Principle

- Mixing of two fluid
- Heat transfer through a finite temperature difference
- Maximum work obtained from two finite bodies
- Minimum work required for refrigerator operates between two finite bodies

- Isothermal dissipation of work
- Adiabatic dissipation of work

4.8 Entropy and Irreversibility

- We know that change in entropy in a reversible process is equal to $\frac{\delta Q}{T}$. Let us now find the change in entropy in an irreversible process.
- Consider a closed system undergoing a change from state 1 to state 2 by a reversible process 1-L-2 and returns from state 2 to the initial state 1 by an irreversible process 2-M-1 as *Fig.4.9 - T-s diagram Adiabatic process* on the thermodynamic coordinates, pressure and volume.

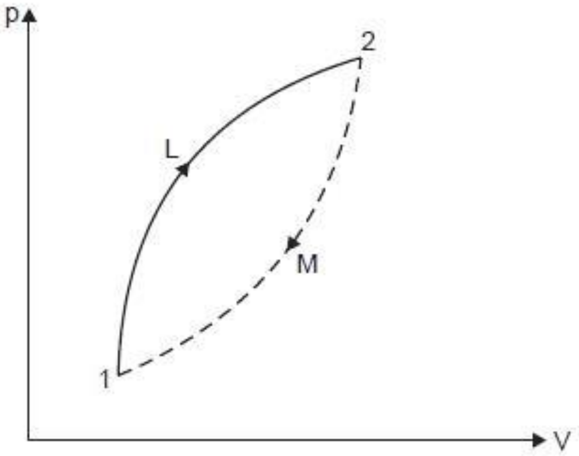

Fig.4.4 - Entropy change for an irreversible process.

- Since entropy is a thermodynamic property, we can write

$$\oint ds = \int_{1(L)}^{2} ds_R + \int_{2(M)}^{1} ds_I = 0 \qquad \text{Eq. (4.38)}$$

- Now for a reversible process, from equation, we have

$$\int_{1(L)}^{2} ds_R = \int_{1(L)}^{2} \left(\frac{\delta Q}{T}\right)_R \qquad \text{Eq. (4.39)}$$

- From above equation,

$$\int_{1(L)}^{2} \left(\frac{\delta Q}{T}\right)_R + \int_{2(M)}^{1} ds_I = 0 \qquad \text{Eq. (4.40)}$$

- Again, since in above equation the processes 1-L-2 and 2-M-1 together form an irreversible cycle, applying Clausius equality to this expression, we get

$$\oint \frac{\delta Q}{T} = \int_{1(L)}^{2} ds_R + \int_{2(M)}^{1} ds_I < 0 \qquad \text{Eq. (4.41)}$$

- This for infinitesimal changes in states can be written as

$$(ds) \geq \frac{\delta Q}{T} \qquad \text{Eq. (4.42)}$$

- Where equality sign stands for the reversible process and inequality sign stands for the irreversible process. It may be noted here that the effect of irreversibility is always to increase the entropy of the system.

4.9 Change of Entropy in a Reversible Process

- Let,
- S_1 = Entropy at the initial state 1, and
- S_2 = Entropy at the final state 2.
- The change in entropy of a system, as it undergoes a change from state 1 to 2,

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right) \qquad \textit{Eq. (4.43)}$$

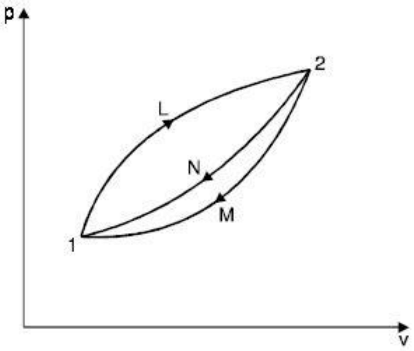

Fig.4.5 - Reversible cyclic process between two fixed end states.

- If the two equilibrium states 1 and 2 are infinitesimal near to each other, the integral sign may be omitted and $S_2 - S_1$ becomes equal to dS.
- Hence equation may be written as

$$dS = \int_1^2 \left(\frac{\delta Q}{T}\right) \qquad \textit{Eq. (4.44)}$$

- Thus, from equation, we find that the change of entropy in a reversible process is equal to $\frac{\delta Q}{T}$. This is the mathematical formulation of the second law of thermodynamics.
- Equation indicates that when an inexact differential δQ is divided by an integrating factor T during a reversible process, it becomes an exact differential.

4.10 Entropy Changes for a Closed System

4.10.1 Heating a Gas at Constant Volume

- Let 1 kg of gas be heated at constant volume and let the change in entropy and absolute temperature be from S_1 to S_2 and T_1 to T_2 respectively.

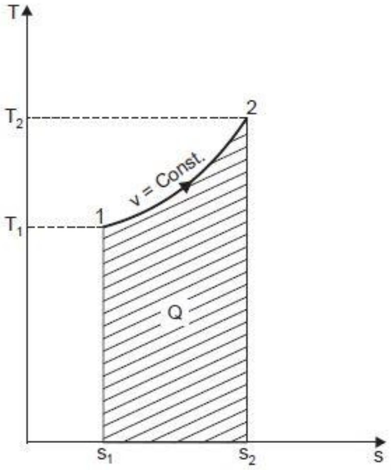

Fig.4.6 - T-s diagram Constant volume process

$$Q = C_v(T_2 - T_1) \qquad \textit{Eq. (4.45)}$$

- Differentiating to find small increment of heat dQ corresponding to small rise in temperature dT.

$$dQ = C_v dT \qquad \textit{Eq. (4.46)}$$

- Dividing both sides by T, we get

$$\frac{dQ}{T} = C_v \frac{dT}{T} \qquad \textit{Eq. (4.47)}$$

$$dS = C_v \frac{dT}{T} \qquad \textit{Eq. (4.48)}$$

- Integrating both sides, we get

$$\int_{s_1}^{s_2} dS = C_v \int_{T_1}^{T_2} \frac{dT}{T} \qquad \textit{Eq. (4.49)}$$

$$s_2 - s_1 = C_v ln\left(\frac{T_2}{T_1}\right) \qquad \textit{Eq. (4.50)}$$

4.10.2 Heating a Gas at Constant Pressure

- Let 1 kg of gas be heated at constant pressure, so that its absolute temperature changes from T_1 to T_2 and entropy S_1 to S_2.

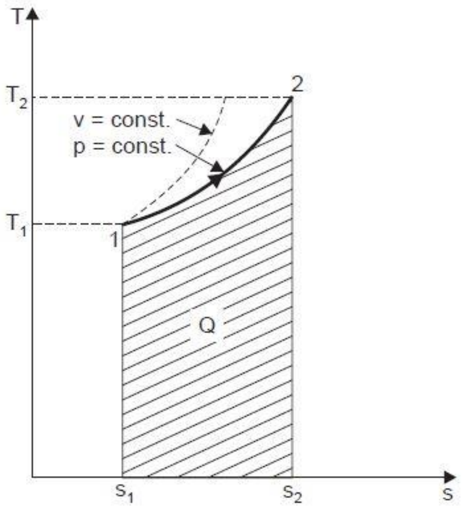

Fig.4.7 - T-s diagram Constant pressure process

$$Q = C_p(T_2 - T_1) \qquad \textit{Eq. (4.51)}$$

- Differentiating to find small increment of heat dQ corresponding to small rise in temperature dT.

$$dQ = C_p dT \qquad \textit{Eq. (4.52)}$$

- Dividing both sides by T, we get

$$\frac{dQ}{T} = C_p \frac{dT}{T} \qquad \textit{Eq. (4.53)}$$

$$dS = C_p \frac{dT}{T} \qquad \textit{Eq. (4.54)}$$

- Integrating both sides, we get

$$\int_{s_1}^{s_2} dS = C_p \int_{T_1}^{T_2} \frac{dT}{T} \qquad \textit{Eq. (4.55)}$$

$$s_2 - s_1 = C_p ln\left(\frac{T_2}{T_1}\right) \qquad \textit{Eq. (4.56)}$$

4.10.3 Isothermal Process

- An isothermal expansion 1-2 at constant temperature T is shown in *Fig.4.9 - T-s diagram Adiabatic process*. Entropy changes from S_1 to S_2 when gas absorbs heat during expansion. The heat taken by the gas is given by the area under the line 1-2 which also represents the work done during expansion.

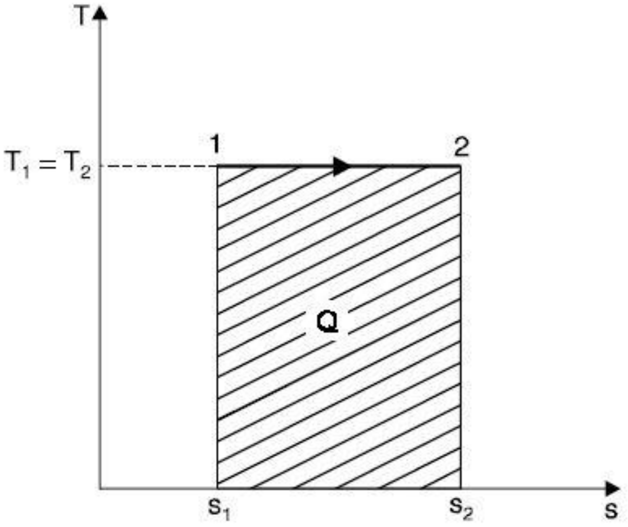

Fig.4.8 - T-s diagram Isothermal process

- For unit mass of substance,

$$dq = du + dw \qquad \textit{Eq. (4.57)}$$

$$dq = C_v\, dT + dw \qquad \textit{Eq. (4.58)}$$

$$dq = C_v\, dT + pdv \qquad \textit{Eq. (4.59)}$$

- For isothermal process du = 0

$$dq = pdv \qquad \textit{Eq. (4.60)}$$

- Divided by T both the sides,

$$\frac{dq}{T} = \frac{p}{T} dv \qquad \textit{Eq. (4.61)}$$

- For unit mass

$$pv = RT \qquad \textit{Eq. (4.62)}$$

$$\frac{p}{T} = \frac{R}{v} \qquad \textit{Eq. (4.63)}$$

$$\frac{dq}{T} = \frac{R}{v} dv \qquad \textit{Eq. (4.64)}$$

$$\int_1^2 dS = R \int_1^2 \frac{dv}{v} \qquad \textit{Eq. (4.65)}$$

$$S_2 - S_1 = Rln\left(\frac{v_2}{v_1}\right) \qquad \textit{Eq. (4.66)}$$

4.10.4 Adiabatic Process (Reversible)

- During an adiabatic process as heat is neither supplied nor rejected,

$$dQ = 0 \qquad \textit{Eq. (4.67)}$$

$$\frac{dQ}{dT} = 0 \qquad \textit{Eq. (4.68)}$$

$$dS = 0 \qquad \textit{Eq. (4.69)}$$

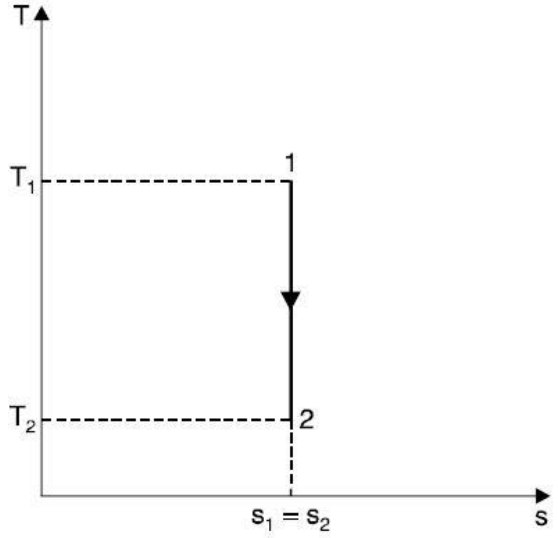

Fig.4.9 - T-s diagram Adiabatic process

- This shows that there is no change in entropy and hence it is known as isentropic process. *Fig.4.9 - T-s diagram Adiabatic process* represents an adiabatic process. It is a vertical line (1-2) and therefore area under this line is nil ; hence heat supplied or rejected and entropy change is zero.

4.10.5 Polytropic Process

- For unit mass of substance,

$$dq = du + dw \qquad \text{Eq. (4.70)}$$

$$dq = C_v\, dT + dw \qquad \text{Eq. (4.71)}$$

$$dq = C_v\, dT + pdv \qquad \text{Eq. (4.72)}$$

- Divided by T both the sides,

$$\frac{dq}{T} = C_v \frac{dT}{T} + \frac{p}{T} dv \qquad \text{Eq. (4.73)}$$

- For unit mass

$$pv = RT \qquad \text{Eq. (4.74)}$$

$$\frac{p}{T} = \frac{R}{v} \qquad \text{Eq. (4.75)}$$

$$\frac{dq}{T} = C_v \frac{dT}{T} + \frac{R}{v} dv \qquad \text{Eq. (4.76)}$$

- Integrating both the sides between initial and final states,

$$\int_1^2 dS = C_v \int_1^2 \frac{dT}{T} + R \int_1^2 \frac{dv}{v} \qquad \text{Eq. (4.77)}$$

$$S_2 - S_1 = C_v ln\left(\frac{T_2}{T_1}\right) + Rln\left(\frac{v_2}{v_1}\right) \qquad \text{Eq. (4.78)}$$

4.11 Third Law of Thermodynamics (Nernst Law)

- From a statistical point of view, entropy is a measure of molecular randomness (the uncertainty about the positions of molecules at any instant). At absolute zero temperature molecules become completely motionless. Therefore, the entropy of a pure crystalline substance at absolute zero temperature is zero since there is no uncertainty about the state of the molecules at that instant.
- This is third law of thermodynamics which states that “The entropy of all perfect crystalline substance (solid) is zero at absolute zero temperature.”

- If a system exists in its equilibrium crystalline state, its atoms are arranged in a pattern that represents the maximum degree of order, and if it also at absolute zero temperature, there must be a minimum of disordering thermal motion. Thus, it seems logical to assign zero absolute entropy to any system exhibiting its maximum state of order and minimum thermal motion.
- The third law of thermodynamics provides an absolute reference point for the determination of entropy. The entropy determined relative to this reference point is called absolute entropy. Application of Third law of thermodynamics
  - Provides an absolute reference point for the determination of entropy
  - Explaining the behavior of solids at very low temperature.
  - Measurement of action of chemical forces of the reacting substances.
  - Analyzing the chemical and phase equilibrium.

4.12 Reference Books

1. Thermal Science and Engineering by D. S. Kumar
2. Engineering Thermodynamics by R. K. Rajput