in Fig. 1(a) For this cycle, heat dQ_i enters at a particular part of the cycle. At this point the system is connected to a reservior which is at temperature T_i. The total work extracted from the cycle is ΔW, given by

$$\Delta W = \sum_{cycle} dQ_i \qquad\qquad ④$$

from the first law of thermodynamics, the sum here is taken around the whole cycle, indicated schematically by the dotted circle in Fig. 1(a).

Next we imagine that the heat at each point is supplied via a Carnot engine which is connected between a reservior at temperature T and the reservior at temperature T_i (see Fig. 1(b)). The reservior at T is common for all the Carnot engines connected at all points of the cycle. Each Carnot engine we know that

$$\frac{\text{heat from the reservior at } T}{T} = \frac{\text{heat to the reservior at } T_i}{T_i} \qquad ⑤$$

(a)

(b)

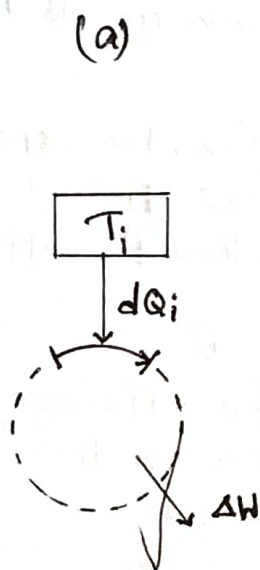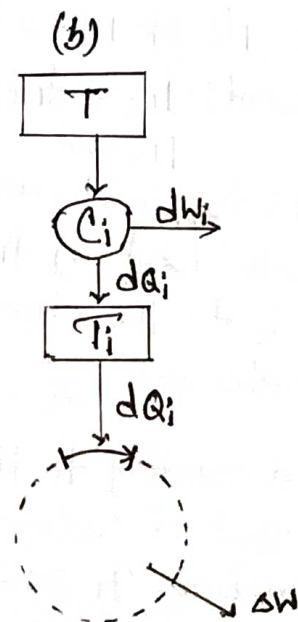

Fig. 1

and hence, $\dfrac{dQ_i + dW_i}{T} = \dfrac{dQ_i}{T_i}$

Rearranging, $dW_i = dQ_i \left(\dfrac{T}{T_i} - 1\right) \qquad\qquad ⑥$

The thermodynamic system in Fig. 1(b) looks at first sight to do nothing other than convert heat to work, which is not allowed according to Kelvin's statement of the second law of thermodynamics and hence we must insist that this is not the case.

Hence, total work produced per cycle $= \Delta W + \sum_{cycle} dW_i \leq 0$

Using equ. ④,⑥ we have,

$$\sum_{cycle} dQ_i + \sum_{cycle} dQ_i \left(\frac{T}{T_i} - 1\right) \leq 0 \qquad\qquad ⑦$$

$$T \sum_{cycle} \frac{dQ_i}{T_i} \leq 0 \qquad\qquad ⑧$$

Since $T > 0$, We have that,

$$\sum_{cycle} \frac{dQ_i}{T_i} \leq 0 \qquad\qquad ⑨$$

and replacing the sum by an integral, we can write this as

$$\oint \frac{dQ_i}{T_i} \leq 0 \qquad\qquad ⑩$$

which is known as the clausius inequality, embodied in the expression of clausius theorem.

⊞ Principle of increase of entropy :

Statement: The entropy of a system increases in all irreversible process.

Proof: Suppose, in an irreversible heat engine, the working substance absorbs heat Q_1 from source at temperature T_1 and rejects heat Q_2 to the sink at temperature T_2, then the efficiency of the engine is,

$$\eta' = 1 - \frac{Q_2}{Q_1} \qquad\qquad ①$$

But according to the carnot's theorem, this efficiency is less than that of reversible engine working between the same two temperatures T_1 and T_2, then the efficiency is,

$$\eta = 1 - \frac{T_2}{T_1} \qquad\qquad ②$$

Thus, $\eta > \eta'$

$$\Rightarrow 1 - \frac{T_2}{T_1} > 1 - \frac{Q_2}{Q_1}$$

$$\Rightarrow - \frac{T_2}{T_1} > - \frac{Q_2}{Q_1}$$

$$\Rightarrow \frac{T_2}{T_1} < \frac{Q_2}{Q_1}$$

$$\Rightarrow \frac{Q_1}{T_1} < \frac{Q_2}{T_2}$$

$$\Rightarrow \frac{Q_2}{T_2} - \frac{Q_1}{T_1} \geq 0$$

Here, the source loosens the entropy $= \frac{Q_1}{T_1}$

and the sink gains the entropy $= \frac{Q_2}{T_2}$

$\therefore$ Net entropy change of the whole system $= \frac{Q_2}{T_2} - \frac{Q_1}{T_1}$, which is clearly greater than zero. Thus there is an increase in entropy in all irreversible process. This is known as the law or principle of increase in entropy.

All natural process taking place in the universe are <u>irreversible</u>. It means the entropy of the universe increases.

$$\therefore dS(universe) \geq 0.$$

☐ <u>Entropy change for an ideal gas:</u>

Let us consider n moles of an ideal gas occupying volume v at pressure P and temperature T. If the system absorbs dQ heat reversibly then increase in entropy is given by.

$$dS = \frac{dQ}{T} \qquad\qquad\text{①}$$

According to the first law of thermodynamics,

$$dQ = du + Pdv \qquad\qquad\text{②}$$

Putting the value of equ.② in equ.① ;

$$dS = \frac{du + Pdv}{T} \qquad\qquad\text{③}$$

The equation of ideal gas for 1 mole,

$$PV = RT \qquad\qquad\text{④}$$

$$du = C_v dT \qquad\qquad\text{⑤}$$

Substituting equ.④ and ⑤ in equ.③ ;

$$dS = \frac{C_v dT + \frac{RTdv}{v}}{T} \qquad\qquad\text{⑥}$$

$$dS = C_v \frac{dT}{T} + R \frac{dv}{v}$$

Integrating,

$$dS = C_v \frac{dT}{T} +$$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \qquad\qquad\text{⑧}$$

$$\Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \quad\text{——— ⑧}\qquad \boxed{P_1 V_1 = P_2 V_2}$$

Case-1: At constant temperature for an isothermal process. In this case $T_1 = T_2$;

$$\Delta S_T = R \ln \frac{V_2}{V_1} \quad\text{——— ⑨}$$

$$\Delta S_T = R \ln \frac{P_1}{P_2} \quad\text{——— ⑩}$$

Case-2: At constant pressure (Isobaric process). In this case $P_1 = P_2$

$$\Delta S_p = C_p \ln \frac{T_2}{T_1} \quad\text{——— ⑪}$$

Case-3: At constant volume for an isobaric process. In this case $V_1 = V_2$.

$$\Delta S_V = C_V \ln \frac{T_2}{T_1} \quad\text{——— ⑫}$$
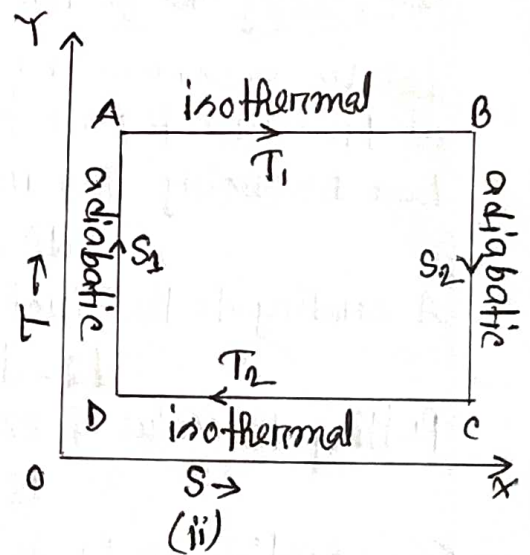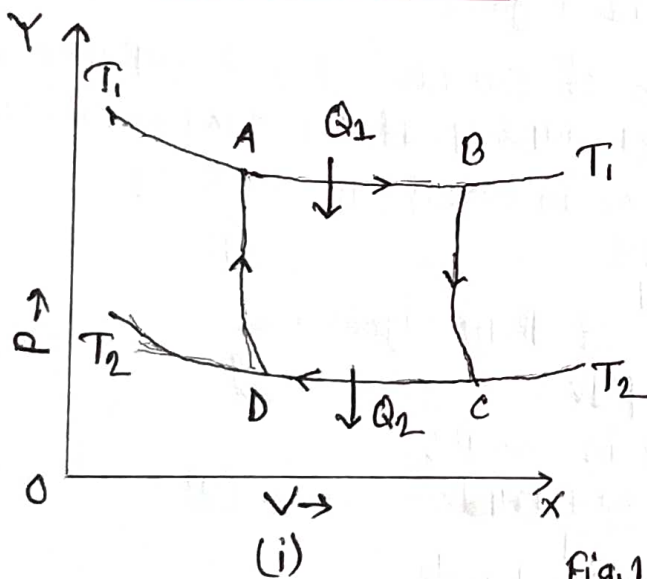
Entropy-temperature diagram:

Fig.1.

Thermodynamic changes in the state of a substance can be represented by plotting entropy (S) along horizontal axis and temperature (T) along perpendicular axis. Such a diagram is called temperature-entropy (T-S) diagram for the substance.

Consider a Carnot's reversible cycle. ABCDA as shown in p-v diagram which composed of two isothermals AB and CD at constant temperature T_1 and T_2 respectively. Consider a Carnot's reversible cycle on T-S diagram as shown in Fig.1 (ii), which is a rectangle ABCD.

Suppose S_1 be the entropy of working substance in state A, S_2 be the entropy in state B, Q_1 be the heat absorbed along AB and Q_2 be the rejected along CD.

In going from A to B, along isothermal expansion AB, the gain in the entropy of the working substance is given by,

$$S_2 - S_1 = \frac{Q_1}{T_1} \qquad\qquad\qquad ①$$

In going from B to C, along adiabatic expansion BC, there is no change in the entropy

In going from C to D, along isothermal compression CD, the loss in entropy of the working substance is given by,

$$S_2 - S_1 = \frac{Q_2}{T_2} \qquad\qquad\qquad ②$$

In going from D to A, along abi adiabatic compression DA, there is no change in the entropy.

From equ. ① and ② we get,

$$Q_1 = T_1(S_2 - S_1)$$

$$Q_2 = T_2(S_2 - S_1)$$

$$\therefore Q_1 - Q_2 = (T_1 - T_2)(S_2 - S_1)$$

The quantity $(Q_1 - Q_2)$ represents the external workdone in the cycle and $(T_1 - T_2)(S_2 - S_1)$ is the area of the rectangle on the T-S diagram. Thus, the area of the rectangle on the T-S diagram represents the external workdone in a reversible Cannot's cycle.

⊞ Calculate the change of entropy in reversible cycle / reversible isothermal process:
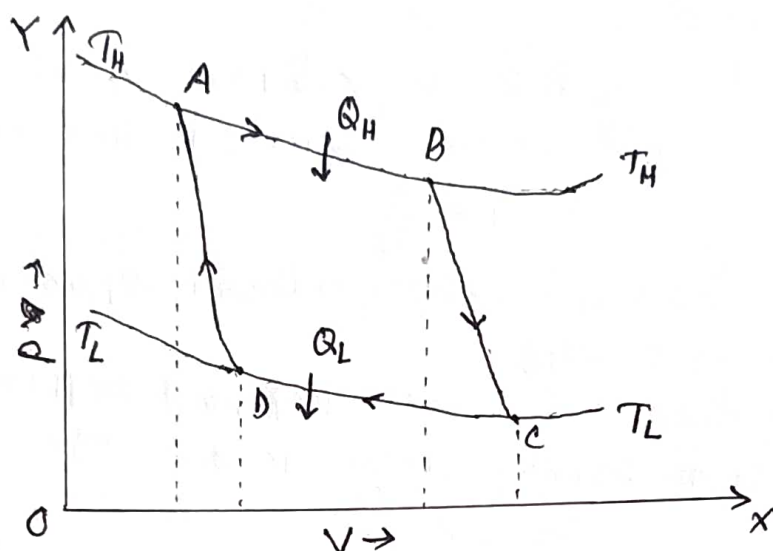
Consider, a complete reversible Carnot's cycle ABCD for an ideal gas formed by two isothermals AB and CD and two adiabatics BC and DA.

1. **Isothermal expansion AB:** Let, Q_H be the heat absorbed by the working substance in going from A to B during isothermal expansion AB at constant temperature T_H. The increase in entropy of the working substance is given by,

$$\therefore \int_A^B dS = \frac{Q_H}{T_H}$$

2. **Adiabatic expansion BC:** In going from state B to C along the adiabatic expansion BC, there is no change in entropy of the working substance but the temperature falls from T_H to T_L.

$$\therefore \int_B^C dS = 0.$$

3. **Isothermal compression CD:** In going from state C to D during isothermal compression, the working substance rejects heat Q_L to the sink at temperature T_L. The decrease in entropy of the working substance is given by,

$$\therefore \int_C^D dS = -\frac{Q_L}{T_L}$$

4. **Adiabatic Compression DA:** In going from D to A along the adiabatic compression, the working substance has no change in entropy but temperature rises from T_L to T_H.

$$\therefore \int_D^A dS = 0$$

$\therefore$ The net change in entropy of the working substance for the whole cycle ABCDA is,

$$\oint dS = \int_A^B dS + \int_B^C dS + \int_C^D dS + \int_D^A dS$$

$$= \frac{Q_H}{T_H} + 0 - \frac{Q_L}{T_L} + 0$$

$$\therefore \oint dS = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} \underline{\hspace{4cm}} ①$$

But for reversible Carnot's cycle, $\dfrac{Q_H}{T_H} = \dfrac{Q_L}{T_L}$

$$\Rightarrow \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

Substituting the value in equ. ① ;

$$\therefore \oint dS = 0$$

Thus, in a cycle of reversible process, the entropy of the system remains unchanged or constant. In other words, the total change in entropy is always zero.

➡ Calculate the increase in entropy when one gram molecular weight of ice at 0°C melts to from water. Latent heat of fusion of ice = 80 calories.

Sol^n: Here,

mass $m = 1$ gm
Latent heat of ice, $L = 80$ cal/gm
Temperature, $T = 273 + 0 = 273$ k

$\therefore$ The change in entropy, $dS = \dfrac{dQ}{T} = \dfrac{mL}{T} = \dfrac{1 \times 80}{273}$

$$= 0.293 \text{ Cal/k}$$
$$= 0.29 \times 4.2 \text{ J/k}$$
$$= 1.218 \text{ J/k}.$$

Calculate the entropy change involved in thermodynamic expansion of 2 moles of a gas from a volume of 5 litre to a volume of of 50 litres at 303 K.

Sol^n : Here, $n = 2$ moles

$V_1 = 5$ litre

$V_2 = 50$ litre

$T_1 = 273$ K

$T_2 = (273 + 303)K$

$= 576$ K

We know that,

$$\Delta S = C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$= C_v \ln \frac{576}{273} + 2 \times 8.31 \ln \frac{50}{5}$$

$$=$$

Calculate the entropy change when 2 moles of an ideal gas is allowed to expand itself isothermally at 293K from a pressure of 10 atm to a pressure of 2 atm.

Sol^n : Here,

$n = 2$ moles