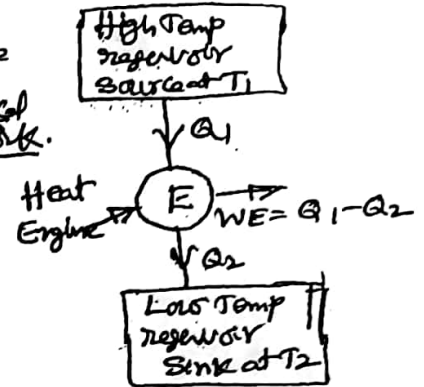


* Second Law of Thermodynamics

UNIT-III

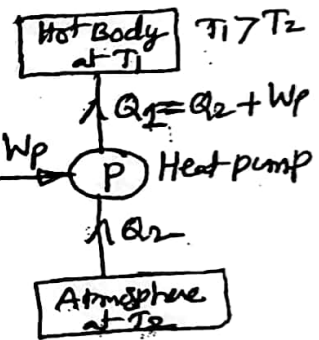
The second law of thermodynamics recognizes that the mutual conversion of heat into work during a process is impossible, while its opposite is possible [complete conversion of work into heat is possible].

Heat Engine:- A heat engine is a device used for converting heat energy into mechanical work.
 heat energy (Q_1) from high temperature reservoir at temperature T_1 is supplied to the engine. After doing work (W_E), a part of this heat energy is rejected to sink (or) low temperature reservoir.



$$\eta_{H-E} = \frac{\text{Maximum work obtained}}{\text{total heat supplied}} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

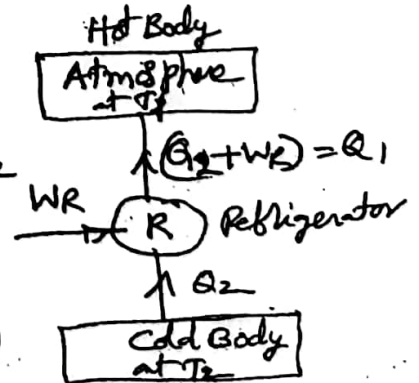
Heat pump:- A heat pump is device used for to transfer heat from atmosphere [Cold] at temperature T_2 to hot body (space at T_1), W_p with the help of mechanical pump.



The performance of heat pump is expressed by the coefficient of performance (COP).

$$(C.O.P)_P = \frac{\text{Amount of heat delivered } (Q_1)}{\text{Amount of work supplied to pump } (W_p)} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2}$$

Refrigerator:- A refrigerator is a reversed heat engine which either cool (or) maintain the temperature lower than the temperature of surroundings. This is done by extracting heat (Q_2) from cold body and rejecting heat to the atmosphere ($Q_1 + W_R$) with the help of mechanical work supplied to refrigerator.



$$(C.O.P)_R = \frac{\text{Amount of heat taken from cold body } (Q_2)}{\text{Amount of work required } (W_R)}$$

$$(COP)_{\text{pump}} = 1 + (COP)_{\text{refrigerator}} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2}$$

Statements of the Second Law of Thermodynamics

2

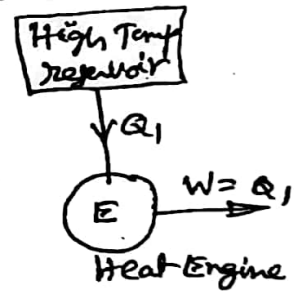
Kelvin-Planck Statement:- It relates the working of heat engines.

"It is impossible to construct an engine which while operating in a cycle, produces no other effect except to extract the heat from a single temperature reservoir and do equivalent amount of work."

According to the Kelvin-Planck statement, a heat engine can not be 100 percent efficient. In practice, no heat engine can convert all heat supplied to useful work. The heat engine receives heat from a high temperature reservoir and it must reject some amount of heat to a low-temperature reservoir. The work done by a cyclic heat engine is the difference between heat supplied and ~~heat~~ heat rejection.

Perpetual motion machine of the second kind (PMM-II):-

A 100% percent efficient machine, which is impossible to obtain in actual practice, because no machine can convert whole of the heat energy supplied to it, into its equivalent amount of work. A PMM-II is impossible.



Clausius Statement:-

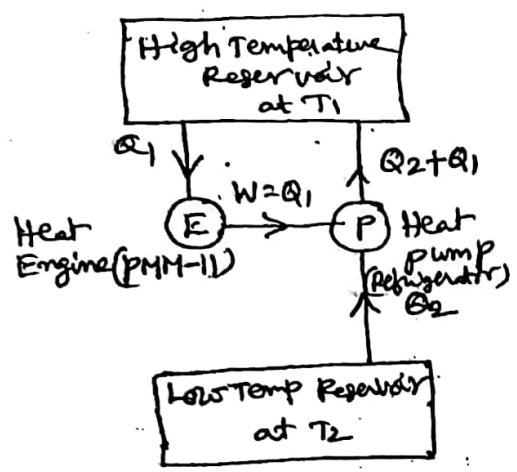
It relates the working of the refrigerators and heat pumps.

"It is impossible for any device that operates in a cycle, and produce no effect other than the transfer of heat energy from a lower temperature body to higher temperature body."

The heat energy can not flow by itself from a low-temperature body to a high-temperature body without addition of work.

Refrigerators and heat pumps transfer energy from a low-temperature region to a higher temperature region at the cost of work input to their compressors.

Equivalence of Kelvin-Planck and Clausius statements.



Any device that violates one statement also leads to violation of the other statement.

Consider a heat engine (PMM2) and an actual refrigerator, operating between a high temperature T_1 & low temperature T_2 . The heat engine is receiving heat Q_1 from high temperature reservoir at T_1 and it converts all heat in to net work $W=Q_1$. It does not reject any amount of heat to low temperature reservoir, thus violating the Kelvin-Planck statement of second law.

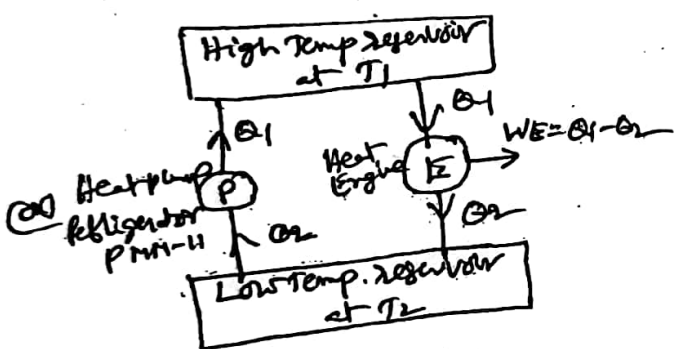


Figure (b)

This device

The work produced by heat engine is supplied to a refrigerator (Heat pump) that removes heat Q_2 and discharges (Q_1+Q_2) to high temperature reservoir. The refrigerator and heat engine together constitute a device, whose sole effect is to transfer heat energy Q_2 to a high temperature reservoir (Q_2+Q_1) . This device clearly violates Kelvin-Planck statement leads to violation of Clausius statement.

Figure (b) shows violation of Clausius statement leads to violation of Kelvin-Planck statement.

* Carnot cycle, (∞) Carnot Engine :-

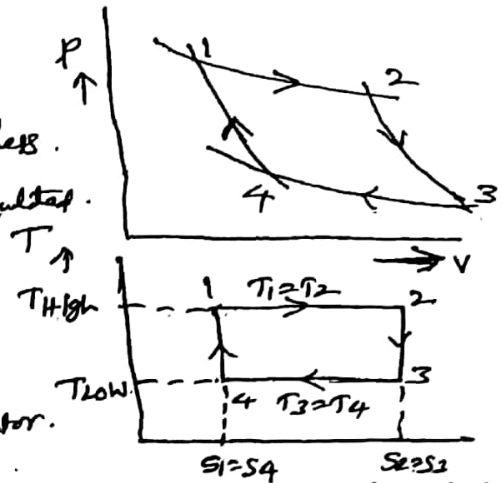
A French engineer, Sadi Carnot in 1824 proposed an engine which works on a reversed cycle. It is theoretically a heat engine that converts the maximum amount of energy in to mechanical work. Carnot showed that the efficiency of any engine depends on the difference between the highest temperature and lowest temperature reached during one cycle. The greater the temperature difference, higher the efficiency.

It comprises four reversible processes given below.

- ① Reversible isothermal expansion
- ② Reversible adiabatic expansion
- ③ Reversible isothermal compression
- ④ Reversible adiabatic compression

Carnot Cycle Assumptions

- 1) Working substance is perfect gas.
- 2) piston movement in cylinder is frictionless.
- 3) Walls of cylinder & piston are perfectly insulated.
- 4) Heat supply and Heat rejection are at constant temperatures
- 5) cylinder head is very good conductor of heat and partially perfect insulator.



Working of a Carnot Engine:-

1. First Stage (isothermal expansion)

The hot body at a temperature T_1 is brought in contact with bottom (B) of the cylinder. The air expands isothermally at constant temperature process (1-2).

Heat supplied, $Q_{1-2} = \dots$ work done by air during isothermal expansion.

$$= P_1 V_1 \ln \frac{V_2}{V_1} = nRT_1 \ln \frac{V_2}{V_1} = nRT_1 \ln r$$

2. Second Stage [Adiabatic expansion]:- The hot body is removed from the bottom of the cylinder B and the insulating cap is brought in contact. The air now allowed to expand reversibly and adiabatically. process (2-3). no heat supplied. The temperature falls from T_2 to T_3 .

So, decrease in internal energy = work done by air during adiabatic expansion.

$$= \frac{P_2 V_2 - P_3 V_3}{\gamma - 1} = \frac{nR(T_2 - T_3)}{\gamma - 1} = \frac{nR(T_1 - T_3)}{\gamma - 1}$$

3. Third Stage [isothermal compression]

Remove the insulating cap from bottom of cylinder and bring the cold body in its contact. The air is compressed at constant temperature $T_3 = T_4$. During this process, heat is rejected to cold body.

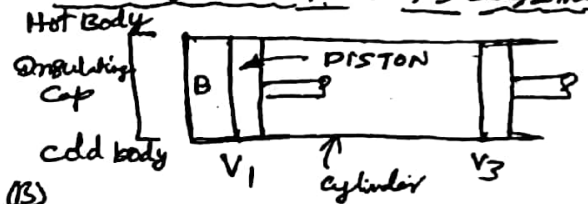
Heat rejected = work done on air during isothermal compression

$$Q_{3-4} = P_3 V_3 \ln \frac{V_3}{V_4} = nRT_3 \ln \frac{V_3}{V_4} = nRT_3 \ln r$$

where, $r =$ Compression ratio = Expansion ratio, $\frac{V_2}{V_1} = \frac{V_3}{V_4}$

4. Fourth Stage [Adiabatic compression]:- Now insulating cap is brought in contact with bottom of cylinder, and air is allowed to be compressed adiabatically. Increase in internal energy due to increase in temperature from T_4 to T_1 .

Carnot Cycle on P-V & T-S diagrams



increase in internal energy = work done on air during adiabatic compression.

$$= \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} = \frac{mR(T_1 - T_2)}{\gamma - 1} = \frac{mR(T_1 - T_3)}{\gamma - 1}$$

∴ Efficiency of Carnot cycle $\eta_{\text{Carnot}} = \frac{\text{Work done}}{\text{Heat supplied}} = \frac{\text{Heat supplied} - \text{Heat rejected}}{\text{Heat supplied}}$

$$= \frac{mR T_1 \ln \frac{V_2}{V_1} - mR T_3 \ln \frac{V_2}{V_1}}{mR T_1 \ln \frac{V_2}{V_1}}$$

$$= \frac{T_1 - T_3}{T_1} = 1 - \frac{T_3}{T_1} = 1 - \frac{T_{\text{Low}}}{T_{\text{High}}}$$

Alternative proof:-

Heat supplied during isothermal expansion 1-2, $Q_{1-2} = T_1 (S_2 - S_1)$

Heat rejection during isothermal compression 3-4, $Q_{3-4} = T_3 (S_2 - S_1)$

$$\eta_{\text{Carnot cycle}} = \frac{H.S - H.R}{H.S} = \frac{T_1 (S_2 - S_1) - T_3 (S_2 - S_1)}{T_1 (S_2 - S_1)} = 1 - \frac{T_3}{T_1}$$

For adiabatic expansion 2-3,

$$\frac{T_2}{T_3} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} \quad \text{or} \quad \frac{V_3}{V_2} = \left(\frac{T_2}{T_3}\right)^{\frac{1}{\gamma-1}}$$

For adiabatic compression 4-1,

$$\frac{T_1}{T_4} = \left(\frac{V_4}{V_1}\right)^{\gamma-1} \quad \text{or} \quad \frac{V_4}{V_1} = \left(\frac{T_1}{T_4}\right)^{\frac{1}{\gamma-1}}$$

Since $T_1 = T_2$ and $T_3 = T_4$
 so, $\frac{V_3}{V_2} = \frac{V_4}{V_1}$ (or) $\frac{V_2}{V_1} = \frac{V_3}{V_4}$

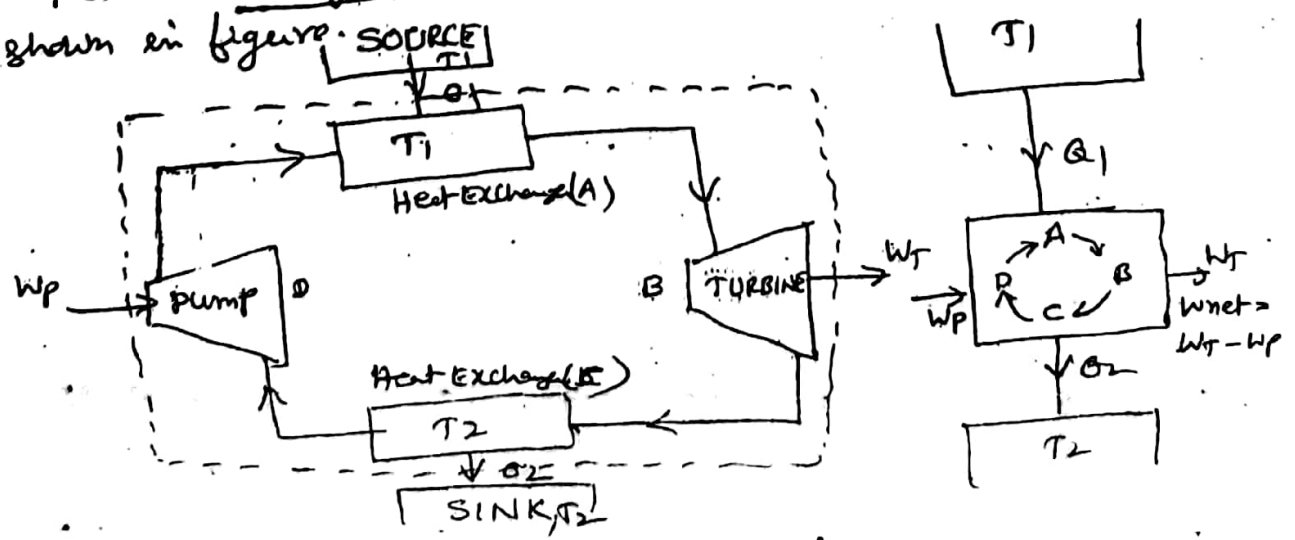
$$\frac{T_1}{T_4} = \frac{T_1}{T_3} = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

$$\eta_{\text{Carnot}} = 1 - \frac{T_3}{T_1} = 1 - \frac{1}{\left(\frac{V_2}{V_1}\right)^{\gamma-1}}$$

Carnot Heat Engine:-

A cyclic heat engine operating on the Carnot cycle is called a Carnot heat engine.

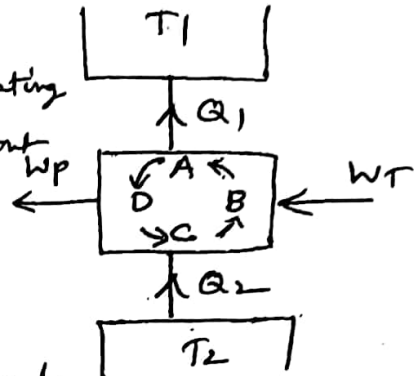
For a steady flow system, the Carnot cycle is represented as shown in figure.



- $Q_1 \rightarrow$ heat transferred to system reversibly and isothermally
- $W_T \rightarrow$ Workdone by turbine
- $Q_2 \rightarrow$ heat rejected to sink at temp T_2
- $W_P \rightarrow$ Work is done on the system by pump.
- \therefore Net Workdone by system, $W_{net} = W_T - W_P$

Reversed Heat Engine:-

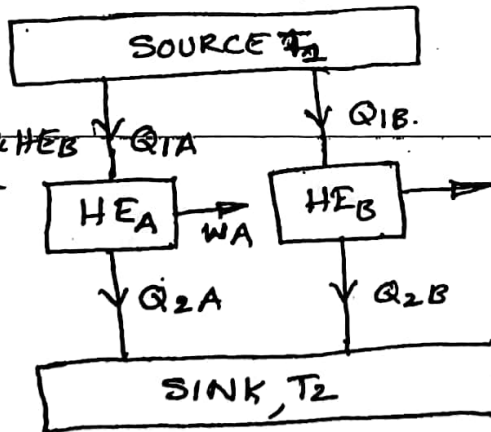
A reversed heat engine is operating reversibly (reversed direction) without any friction.



Carnot's Theorem (or) Carnot principle:

- ① No engine can be more efficient than a reversible engine operating between the same two reservoirs
(or) Carnot (reversible) engine among all the engines is the most efficient.
- ② The efficiency of all reversible heat engines operating between the same two temperatures & reservoirs are the same.

Two cyclic heat engines HEA & HEB operating between the source and sink, of which HEB is reversible.



HEA & HEB are two engines operating between the given source at temp T_1 and sink at temp T_2 .

Let HEA be any heat engine and HEB be any reversible heat engine. We have to prove efficiency of HEB is more than that of HEA. Let us assume that $\eta_A > \eta_B$.
Let the rate of working of the engines be such that

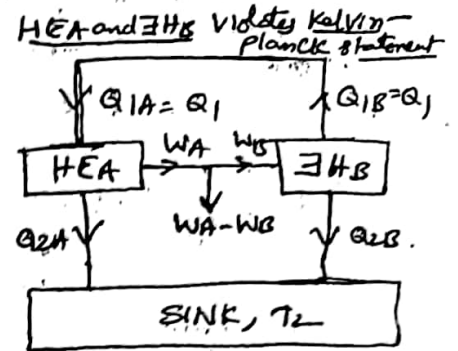
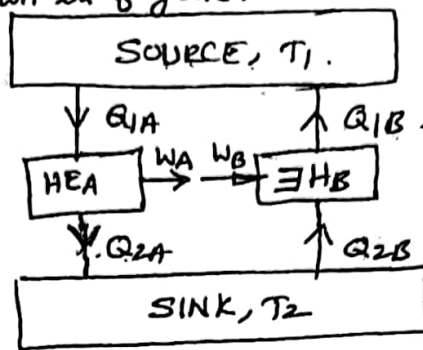
$$Q_{1A} = Q_{1B} = Q_1$$

since $\eta_A > \eta_B$

$$\frac{W_A}{Q_{1A}} > \frac{W_B}{Q_{1B}}$$

$$W_A > W_B \quad \left[\text{since } Q_{1A} = Q_{1B} \right]$$

Now, let HEB be reversed. Since HEB is a reversible heat engine, the magnitudes of heat and work transfer quantities will remain the same, but their directions will be reversed as shown in figure.



Since $W_A > W_B$, some part of W_A (equal to W_B) may be fed to drive the reversed heat engine HEB . Since $Q_{1A} = Q_{1B} = Q_1$, the heat discharged by HEB may be supplied to HEA . The source may therefore, be eliminated. The net result is that HEA and HEB together constitute a heat engine which operating in a cycle produces net work $W_A - W_B$ while exchanging heat with a single reservoir at T_2 . This violates the Kelvin-Planck statement of the second law. Hence the assumption that $\eta_A > \eta_B$ is wrong.

Corollaries of Carnot Theorem:-

- ① All reversible heat engines operating between the same constant temperature limits will have the same efficiency. None have higher than other.
- ② The efficiency of the reversible Carnot cycle engine does not depend on the working medium. It depends only on the temperature limits.
- ③ No engine can be more efficient than a reversible Carnot engine which operating between the same temperature limits.

Absolute Thermodynamic Temperature Scale:-

A temperature scale that is independent of the properties of the substances that are used to measure temperature is called Thermodynamic temperature scale.

The efficiency of any heat engine cycle receiving heat Q_1 and rejecting heat Q_2 is given by $\eta = \frac{W_{net}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$

By the second law, it is necessary to have a temp difference $(T_1 - T_2)$ to obtain efficiency for any cycle. We know that the efficiency of all heat engines between the same temperature levels is the same, and is independent of the working substance. Therefore, for a reversible cycle, the efficiency will depend solely upon the temperature T_1 and T_2 at which heat is transferred.

$$\eta_{rev} = f(T_1, T_2)$$

$$\frac{Q_1}{Q_2} = f(T_1, T_2)$$

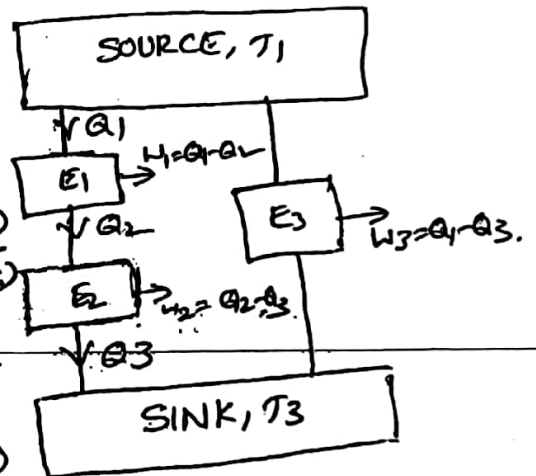
Let us consider two reversible heat engines E_1 receiving heat from the source T_1 and rejecting heat at T_2 to E_2 which in turn rejects heat to the sink at T_3 .

$$\text{Now } \frac{Q_1}{Q_2} = f(T_1, T_2) ; \frac{Q_2}{Q_3} = f(T_2, T_3)$$

E_1 and E_2 together constitute another heat engine E_3 operating between T_1 and T_3 .

$$\therefore \frac{Q_1}{Q_3} = f(T_1, T_3)$$

$$\text{Now } \frac{Q_1}{Q_2} = \frac{Q_1}{Q_3} \cdot \frac{Q_3}{Q_2} ; f(T_1, T_2) = \frac{f(T_1, T_3)}{f(T_2, T_3)}$$



The ratio $\frac{Q_1}{Q_2}$ depends only on T_1 and T_2

not on T_3 .

So the ratio can be written, $\frac{Q_1}{Q_2} = \frac{f(T_1)}{f(T_2)}$

$$\therefore \boxed{\frac{Q_1}{Q_2} = \frac{T_1}{T_2}} \text{ Thermodynamic temperature scale.}$$

Efficiency of Reversible heat engine

$$\eta_{\text{Heat Engine}} = 1 - \frac{Q_2}{Q_1}$$

$$\eta_{\text{reversible}} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

$$\boxed{\eta_{\text{max}} = \frac{T_1 - T_2}{T_1}}$$

Refrigerator

$$\text{C.O.P} = \frac{T_2}{T_1 - T_2}$$

Heat pump

$$\text{COP} = \frac{T_1}{T_1 - T_2}$$

PROB A reversible heat engine operates between -13°C and 37°C . Calculate its C.O.P as a refrigerator and a heat pump.

SOL. Given, $T_1 = T_{\text{High}} = 37^{\circ}\text{C} = 37 + 273 = 310\text{K}$
 $T_2 = T_{\text{Low}} = -13 + 273 = 260\text{K}$

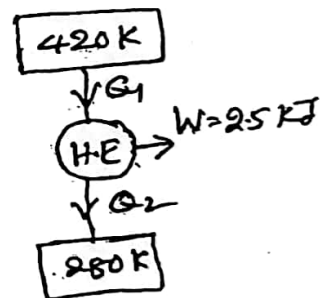
(C.O.P) Refrigerator = $\frac{T_2}{T_1 - T_2} = \frac{260}{(310 - 260)} = 5.2$

(C.O.P) Heat pump = $\frac{T_1}{T_1 - T_2} = \frac{310}{310 - 260} = 6.2$

PROB A reversible heat engine operates between two reservoirs at 420K and 280K its output from the engine is 2.5KJ . determine the efficiency of the engine and its heat interactions with heat reservoirs. subsequently the engine is reversed and made to operate as heat pump between the same reservoirs. Make calculations for the COP of heat pump and power input required when the heat transfer rate from the 280K reservoir is 5KW .

For a reversible heat engine

SOL. Given, $T_1 = 420\text{K}$
 $T_2 = 280\text{K}$
 Workout = 2.5KJ



$\eta_{\text{reversible}} = \frac{T_1 - T_2}{T_1} = \frac{420 - 280}{420} = 0.33$ (or 33%)

$\frac{W}{Q_1} = 0.33 ; Q_1 = \frac{W}{0.33} = \frac{2.5}{0.33} = 7.57\text{KJ}$

$Q_1 - Q_2 = W$
 $\therefore Q_2 = Q_1 - W = 7.57 - 2.5 = 5.07\text{KJ}$

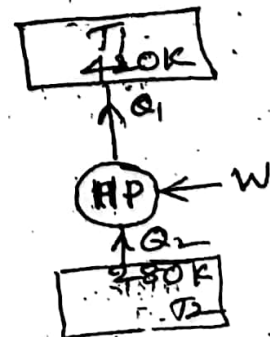
For Heat pump

Given, $T_1 = 420\text{K}; T_2 = 280\text{K}$.
 Heat removed from 280K reservoir is 5KW .

$\therefore (\text{C.O.P})_{\text{HP}} = \frac{T_2}{T_1 - T_2} = \frac{280}{420 - 280} = 2$

$\text{C.O.P} = \frac{\text{Desired effect } (Q_2)}{\text{work input}}$

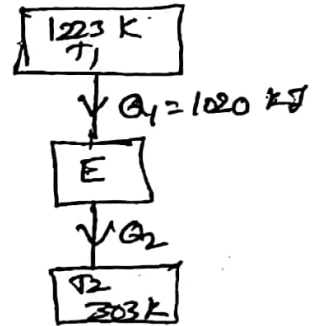
$\therefore \text{Work input} = \frac{Q_2}{\text{COP}} = \frac{5}{2} = 2.5\text{KW}$ ✓



PROB An engine working on Carnot cycle receives 1020 kJ heat from a heat reservoir at a constant temp of 950°C and rejected heat to a heat sink at a constant temp of 30°C. Calculate.

- (1) the thermal efficiency of the heat engine
- (2) Workdone.

SOL. Given, $T_1 = 950 + 273 = 1223 \text{ K}$
 $T_2 = 30 + 273 = 303 \text{ K}$
 $Q_1 = 1020 \text{ kJ}$.



(1) $\eta_{HE} = \frac{T_1 - T_2}{T_1} = \frac{1223 - 303}{1223} = 0.75 \text{ (or 75\%)}$

(2) $\text{Workdone} = \eta \times Q_1 = 0.75 \times 1020 = 765 \text{ kJ}$.

PROB A reversible heat engine operating between thermal reservoir at 900K and 300K is used to drive a reversible refrigerator for which temperature limits are 300K and 250K. The engine absorbs 1800 kJ of energy as heat from the reservoir at 900K and net output engine - refrigerator system is 360 kJ. Make calculations for the heat extracted from the refrigerator and the net heat rejected to the reservoir at 300K.

SOL. Given, $T_1 = 900 \text{ K}$
 $T_2 = 300 \text{ K}$
 $Q_1 = 1800 \text{ kJ}$

Net work output, $W = W_1 - W_2 = 360 \text{ kJ}$

For a reversible heat engine (HE)

$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{900} = 0.667 \text{ (or 66.7\%)}$

$\eta = \frac{W_1}{Q_1} = 0.667$; $W_1 = 0.667 \times Q_1$
 $= 0.667 \times 1800 = 1200.6 \text{ kJ}$

We know that, $W_{net} = W_1 - W_2 = 360 \text{ kJ}$

$\therefore W_2 = W_1 - 360 = 1200.6 - 360 = 840.6 \text{ kJ}$

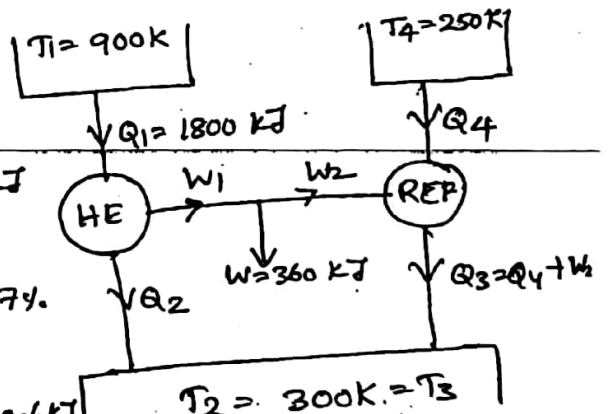
For a reversible refrigerator, $(C.O.P)_R = \frac{Q_4}{Q_3 - Q_4} = \frac{T_4}{T_3 - T_4}$
 $= \frac{250}{300 - 250} = 5$

From $(C.O.P)_R = \frac{Q_4}{W_2}$; $5 = \frac{Q_4}{840.6}$; $Q_4 = 5 \times 840.6 = 4203 \text{ kJ}$

$Q_3 = Q_4 + W_2 = 4203 + 840.6 = 5043.6 \text{ kJ}$

$Q_2 = Q_1 - W_1 = 1800 - 1200.6 = 599.4 \text{ kJ}$

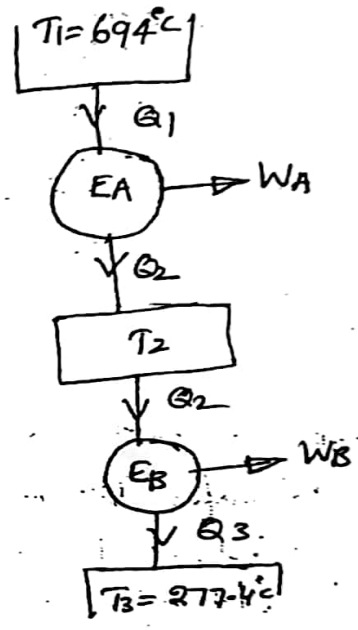
\therefore Heat rejected to 300K reservoir, $Q_3 + Q_2 = 5043.6 + 599.4 = 5643 \text{ kJ}$



PROB Two reversible heat engine A and B are arranged in series with A rejecting heat directly to B through an intermediate reservoir. Engine A receives 200 kJ of heat from a reservoir at 421°C and engine B is in thermal communication with a sink at 4.4°C. If the work output of A is twice that of B, find

- The intermediate temperature between A and B.
- Efficiency of heat engine
- Heat rejected to the cold sink.

SOL. Given,
Two heat engines are arranged in series.
 $Q_1 = 200 \text{ kJ}$
 $T_1 = 421^\circ\text{C} = 421 + 273 = 694 \text{ K}$
 $T_3 = 4.4^\circ\text{C} = 4.4 + 273 = 277.4 \text{ K}$
 $W_A = 2W_B$



For two reversible heat engines arranged in series

$$\frac{T_1}{Q_1} = \frac{T_2}{Q_2} = \frac{T_3}{Q_3}$$

$$\Rightarrow \frac{T_1}{Q_1} = \frac{T_3}{Q_3} ; Q_3 = \frac{T_3}{T_1} Q_1 = \frac{277.4}{694} \times 200 = 79.9 \text{ kJ}$$

Given that,

$$W_A = 2(W_B)$$

$$Q_1 - Q_2 = 2(Q_2 - Q_3) = 2Q_2 - 2Q_3$$

$$3Q_2 = Q_1 + 2Q_3$$

$$Q_2 = \frac{(Q_1 + 2Q_3)}{3} = \frac{(200 + 2 \times 79.9)}{3} = 119.93 \text{ kJ}$$

$$\frac{T_1}{Q_1} = \frac{T_2}{Q_2} ; T_2 = T_1 \times \frac{Q_2}{Q_1} = 694 \times \frac{119.93}{200} = 416.16 \text{ K}$$

$$\textcircled{2} \quad \eta_A = \frac{Q_1 - Q_2}{Q_1} = \frac{200 - 119.93}{200} = 0.4 \text{ (or } 40\%)$$

$$\eta_B = \frac{Q_2 - Q_3}{Q_2} = \frac{119.93 - 79.9}{119.93} = 0.33 \text{ (or } 33.7\%)$$

$\textcircled{3}$ Heat rejected to cold sink, $Q_3 = 79.9 \text{ kJ}$

PROB A reversible heat engine receives heat from a reservoir at 700°C and rejects heat to another reservoir at temp T_2 . A second heat engine receives the heat rejected by the first engine and rejects heat to a sink at 37°C. Calculate temp T_2 for

- Equal efficiency for both engines
- Equal work for both engines

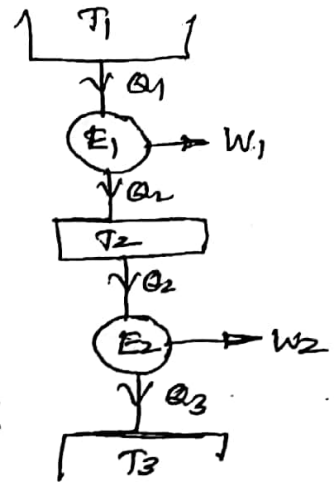
SOL. Given, $T_1 = 700^\circ\text{C} = 973\text{ K}$
 $T_3 = 37^\circ\text{C} = 310\text{ K}$

(i) For equal efficiency of both the engines

$$\eta_1 = \eta_2$$

$$1 - \frac{T_2}{T_1} = 1 - \frac{T_3}{T_2}$$

$$T_2^2 = T_1 T_3 ; T_2 = \sqrt{T_1 T_3} = \sqrt{973 \times 310} = 549.21\text{ K}$$



(ii) Equal work

$$W_1 = Q_1 - Q_2 ; W_2 = Q_2 - Q_3$$

$$W_1 = W_2 ; Q_1 - Q_2 = Q_2 - Q_3$$

$$Q_1 - 2Q_2 + Q_3 = 0$$

$$\frac{Q_1}{Q_2} - 2 + \frac{Q_3}{Q_2} = 0 ; \frac{Q_1}{Q_2} + \frac{Q_3}{Q_2} = 2$$

$$\frac{T_1}{T_2} + \frac{T_3}{T_2} = 2$$

$$\therefore T_2 = \frac{T_1 + T_3}{2} = \frac{973 + 310}{2} = 641.5\text{ K}$$

PROB. A heat engine is used to drive a heat pump. The heat transferred from the heat engine and from the heat pump are used to heat the water circulating through the radiators of a building. The efficiency of a heat engine is 27% and COP of heat pump is 4. Evaluate the ratio of heat through

SOL. $\eta_{HE} = 27\%$

$$(COP)_{HP} = 4$$

The work produced by heat engine is utilized to heat the water from the pump.

$$W_{HE} = W_{HP}$$

$$\eta_{HE} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 0.27$$

$$Q_2 = 0.73 Q_1 \quad \text{--- (1)}$$

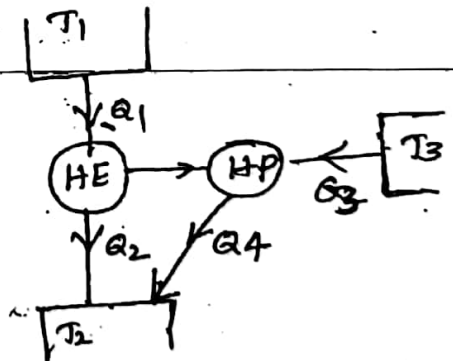
$$(C.O.P)_{HP} = \frac{Q_4}{Q_4 - Q_3} = 4 ; Q_4 = 4(Q_4 - Q_3) \quad \text{--- (2)}$$

$$W_{HE} = W_{HP}$$

$$Q_1 - Q_2 = Q_4 - Q_3 \quad \text{--- (3)}$$

Substituting equation (3) in (2), $Q_4 = 4(Q_1 - Q_2) = 4Q_1 - 4Q_2$

Ratio of heat transfer to cooling water $(Q_4 + Q_2)$
 heat transfer to the heat engine Q_1



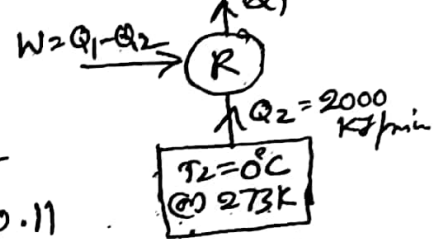
$$= \frac{Q_2 + 4Q_1 - 4Q_2}{Q_1} = \frac{4Q_1 - 3Q_2}{Q_1}$$

$$= \frac{4Q_1 - 3 \times 0.73Q_1}{Q_1} = 1.81 \checkmark$$

PROB. Determine the power required to run a refrigerator that transfers 2000 kJ/min of heat from a cooled space at 0°C to the surrounding atmosphere at 27°C. The refrigerator operates on reversed Carnot cycle.

SOL.

For a refrigeration system,



$$(C.O.P)_{Ref} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

$$= \frac{273}{300 - 273} = 10.11$$

We know, $(C.O.P) = 10.11 = \frac{Q_2}{Q_1 - Q_2} = \frac{2000}{Q_1 - 2000}$

$$\therefore (Q_1 - 2000) 10.11 = 2000$$

$$\therefore Q_1 = \frac{2000}{10.11} + 2000 = 2197.8 \text{ kJ/min}$$

power required, $W = (Q_1 - Q_2) = 2197.8 - 2000 = 197.8 \text{ kJ/min}$

PROB. An engine operating on a Carnot cycle works with its temperatures of 600K and 300K. If the engine receives 2000 kJ of heat, evaluate workdone and Thermal eff of the engine.

SOL.

For a Carnot cycle,

$$\eta_{Carnot} = \frac{\text{workdone}}{\text{Heat supplied}} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

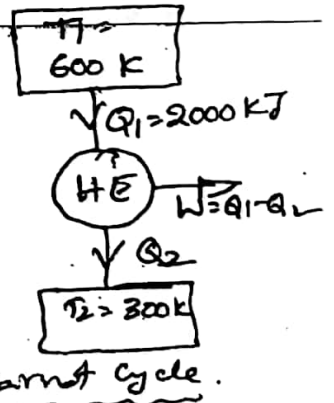
$$= 1 - \frac{T_2}{T_1} = 1 - \frac{300}{600} = 0.5 \text{ (or) } 50\%$$

\therefore We know, $\eta_{Carnot} = 0.5 = \frac{\text{workdone}}{\text{Heat supplied}}$

$$= \frac{Q_1 - Q_2}{Q_1} = \frac{2000 - Q_2}{2000}$$

$$\therefore Q_2 = 2000 - 1000 = 1000 \text{ kJ}$$

\therefore workdone, $W = Q_1 - Q_2 = 2000 - 1000 = 1000 \text{ kJ}$
 $= 1 \text{ MJ} \checkmark$



Entropy (ENTROPY)

The first law of thermodynamics was stated in terms of cycles first and it was shown that the cyclic integral of heat to the cyclic integral of work. When first law applied for thermodynamic processes the existence of a property, the internal energy.

Similarly, the second law was also first stated in terms of cycles executed by systems [heat engine cycle].

When second law applied for thermodynamic processes, leads to definition of a property called Entropy.

Entropy of a system is a measure of the degree of molecular disorder existing in the system. It is an important thermodynamic property of a working substance, which increases with the addition of heat and decreases with its removal. It is ~~not~~ difficult to define the term entropy, but it is easy to define the change of entropy of a working substance.

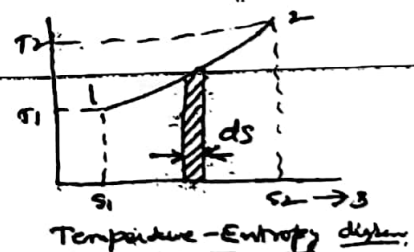
On a reversible process, over a small range of temperature, the increase (or) decrease of entropy, when multiplied by the absolute temperature gives the heat absorbed (or) rejected by the working substance.

$$\therefore \delta Q = T ds \quad \text{or} \quad \boxed{ds = \frac{\delta Q}{T}}$$

ds = Change of entropy
 T = Absolute temperature
 δQ = Heat added (or) rejected.

Relation between Heat and Entropy :-

Consider the heating of a working substance by a reversible process shown by a curve from 1 to 2 on T-S diagram.



Let a small quantity of heat (δQ) is added (or) supplied to the working substance, which increases entropy by (ds). Let the absolute temperature at this instant be T .

According to definition of entropy

$$\boxed{\delta Q = T ds}$$

total heat supplied (or) rejected, $\int \delta Q = \int T ds$.

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

The change in entropy may be regarded as a measure of the rate of the availability (or) unavailability of heat for transformation into work.

The increase in entropy is obtained from a given quantity of heat at low temperature.

Available and Unavailable Heat energy :-

Available heat energy :- is that part of the heat energy (or) heat supplied which can be converted into mechanical work.

Unavailable heat energy :- is that part of heat energy which cannot be converted into mechanical work.

The common term used for unavailable heat energy, according to second law of Thermodynamics, is the heat rejected by the system to the surroundings.

-- Total heat to energy supplied to the system

$$SQ = \text{Available heat energy} + \text{Unavailable heat energy}$$

$$= A.H.E + U.H.E = \text{Workdone} + \text{Heat rejected.}$$

The maximum possible efficiency obtainable by the engine working on a Carnot cycle is given by

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

$T_1 = \text{Maximum Absolute temperature}$
 $T_2 = \text{Lowest absolute temperature}$

$$= \frac{\text{Max. Work obtained}}{\text{Heat supplied @ absorbed}} = \frac{\delta W}{\delta Q} = 1 - \frac{T_2}{T_1}$$

$$(1) \quad \delta W = \delta Q \left[1 - \frac{T_2}{T_1} \right]$$

w. ~~Since~~ Lowest practical temp of heat rejection is the temp. of surroundings (T_0).

$$\therefore \delta W = \delta Q \left[1 - \frac{T_0}{T_1} \right] = \delta Q - \delta Q \times \frac{T_0}{T_1}$$

We also know, workdone, $\delta W = \text{Heat supplied} - \text{Unavailable heat energy}$

$$= \delta Q - U.H.E$$

$$\therefore U.H.E = T_0 \left(\frac{\delta Q}{T_1} \right) = T_0 \cdot ds$$

Expt. The unavailable heat energy (U.H.E) (or) heat rejected is the product of the lowest temperature of heat rejection and change of entropy of the system during the process of supplying heat.

Change in entropy may be regarded as a measure of Unavailable form of heat energy (or) irreversibility of the process.

Clausius inequality:-

The Clausius inequality states that whenever a closed system undergoes a cyclic process, the cyclic integral of $\frac{\delta Q}{T}$ is less than zero for an irreversible process and is equal to zero for a reversible cyclic process.

$$\oint \frac{\delta Q}{T} < 0, \text{ for an irreversible cyclic process} \quad \text{--- (1)}$$

$$\oint \frac{\delta Q}{T} = 0, \text{ for a reversible cyclic process.} \quad \text{--- (2)}$$

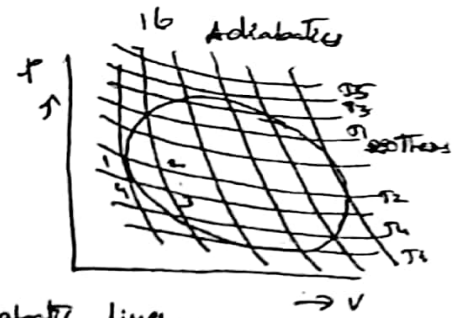
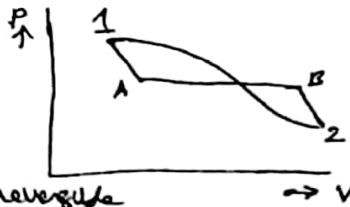
The Clausius inequality is written as $\oint \frac{\delta Q}{T} \leq 0$.

Units of Entropy $ds = \frac{\delta Q}{T}$ $\frac{KJ}{K}$ units.

The entropy of a substance is zero at absolute zero temperature.

Clausius Theorem

It states that a reversible line can be replaced by two reversible adiabatic lines and a reversible isothermal line



1-2 process \rightarrow reversible process, 1-A, B-2 \rightarrow two adiabatic lines, A-B \rightarrow isothermal line.

$$Q_{1-2} = W_{1-2} + U_2 - U_1$$

For process 1, 1-A, A-B and B-2, $Q_{1-A-B-2} = W_{1-A-B-2} + U_2 - U_1$

$$\text{Since } W_{1-2} = W_{1-A-B-2}$$

$$Q_{1-2} = W_{1-2} + Q_{1-A} + Q_{A-B} + Q_{B-2}$$

$Q_{1-A} = Q_{B-2} = 0$ two adiabatic processes.

$$\boxed{Q_{1-2} = Q_{A-B}}$$

From figure B, consider a smooth closed curve representing a reversible cycle.

A reversible closed cycle curve is divided into no. of small Carnot cycles.

For a small Carnot cycle, Q_1 is heat supplied at T_1 and Q_2 is heat rejected at T_2 .

Thus according to absolute temperature scale for a reversible cycle,

$$\frac{\delta Q_1}{T_1} = \frac{\delta Q_2}{T_2}$$

Consider a sign convention for heat transfer, $-ve$ is for heat rejection.

$$\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0$$

For all small Carnot cycles, $\left(\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2}\right) + \left(\frac{\delta Q_3}{T_3} + \frac{\delta Q_4}{T_4}\right) + \dots = 0$

$$\boxed{\oint \frac{\delta Q}{T} = 0} \rightarrow \text{Clausius Theorem.}$$

Principle of increase of Entropy

The Clausius inequality states that whenever a closed system undergoes a cyclic process, the cyclic integral of $\frac{\delta Q}{T}$ is less than zero for an irreversible process. For reversible process, $\frac{\delta Q}{T}$ is zero.

$$\oint \frac{\delta Q}{T} \leq 0 \quad \text{--- (1)}$$

Let us know that change in entropy, $ds = \frac{\delta Q}{T}$

Since, entropy is a thermodynamic property and the cyclic integral of a thermodynamic property is zero, therefore (1) can be written \rightarrow

$$\oint \frac{\delta Q}{T} \leq \oint ds$$

$$\frac{\delta Q}{T} \leq ds$$

$$ds \geq \frac{\delta Q}{T} \quad \text{--- (2)}$$

When the process is reversible, $ds = \frac{\delta Q}{T}$

When the process is irreversible, $ds > \frac{\delta Q}{T}$

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If we apply equation (2) to an isolated system like universe for which $\delta Q = 0$, then the equation (2) can be written as $ds > 0$

For a reversible cyclic process, $ds = 0$ (or) $s = \text{constant}$.

For a irreversible process, $ds > 0$

Since in practice all processes are irreversible, therefore the entropy of such a system like universe goes on increasing.
 \therefore This is known as principle of increase in entropy.

General Case for change of Entropy of a Gas

Let 1 kg of gas at a pressure P_1 , volume V_1 , absolute temp T_1 , & Entropy S_1 , be heated to P_2, V_2, T_2 & S_2 respectively. By Law of Conservation of energy.

$$dq = du + dw = C_v dT + P dV$$

Dividing on both sides by T , we get

$$\frac{dq}{T} = \frac{C_v dT}{T} + \frac{P dV}{T}$$

$$ds = \frac{C_v dT}{T} + \frac{R dV}{V}$$

$$\begin{aligned} \therefore P V &= R T \\ \frac{P}{T} &= \frac{R}{V} \end{aligned}$$

Integrating both sides, we get

$$\int_1^2 ds = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\therefore S_2 - S_1 = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad (P, V) \quad (1)$$

$$\begin{aligned} S_2 - S_1 &= C_v \ln \frac{P_2 V_2}{P_1 V_1} + R \ln \frac{V_2}{V_1} \quad \left[\because \frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1} \right. \\ &= C_v \ln \frac{P_2}{P_1} + C_v \ln \frac{V_2}{V_1} + R \ln \frac{V_2}{V_1} \\ &= C_v \ln \frac{P_2}{P_1} + (C_v + R) \ln \frac{V_2}{V_1} \end{aligned}$$

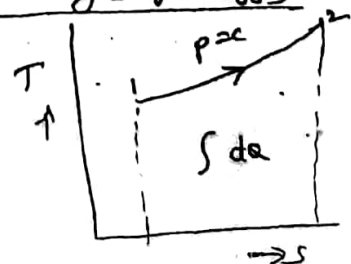
$$\therefore S_2 - S_1 = C_v \ln \frac{P_2}{P_1} + C_p \ln \frac{V_2}{V_1} \quad (P, V) \quad (2)$$

Simplifying, $S_2 - S_1 = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \quad (3)$

Entropy change in different reversible gas processes

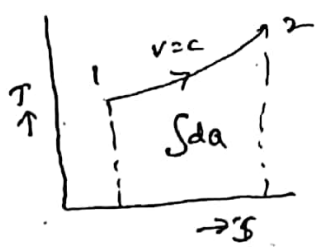
(i) Reversible Constant pressure process

$$ds = \int \frac{dq}{T} = \int \frac{m C_p dT}{T} = m C_p \ln \frac{T_2}{T_1}$$



② Reversible constant volume process

$$ds = \int \frac{dq}{T} = \int m c_v \frac{dT}{T} = m c_v \ln \frac{T_2}{T_1}$$



③ Reversible isothermal process

$$ds = \int \frac{dq}{T} = \int \frac{p dv}{T} = \int \frac{mR}{v} dv$$
$$s_2 - s_1 = mR \ln \frac{v_2}{v_1} = mR \ln \frac{p_1}{p_2}$$



④ Reversible adiabatic process

$$ds = \int \frac{dq}{T} = 0$$

⑤ Reversible polytropic process

$$ds = \int \frac{dq}{T} = \frac{\gamma - \eta}{\gamma - 1} \int \frac{dw}{T} = \frac{\gamma - \eta}{\gamma - 1} mR \ln \frac{v_2}{v_1} = \frac{\gamma - \eta}{\gamma - 1} m c_v \ln \frac{T_2}{T_1}$$
$$(s_2 - s_1) = \frac{\gamma - \eta}{\gamma - 1} \int \frac{p dv}{T} = \frac{\gamma - \eta}{\gamma - 1} mR \int \frac{dv}{v} = \frac{\gamma - \eta}{\gamma - 1} mR \ln \frac{v_2}{v_1}$$

Third Law of Thermodynamics:

Entropy is a measure of the uncertainty of molecular position in matter in either phase. This uncertainty of molecular position in matter is a function of temperature and it decreases as temperature decreases. It is due to different energy levels of molecules in the matter. The molecules of a substance become motionless at absolute zero temperature, thus having zero entropy.

The entropy of a pure substance at absolute zero temperature is zero. This statement is known as Third Law of Thermodynamics.

$$\text{If } S=0 \text{ as } T \rightarrow 0$$

This law is useful in calculating the absolute entropy of a substance. This is also useful in calculating thermodynamic properties such as heat, temperature and is also useful in analysing chemical and phase equilibrium. This law is significant in explaining the behaviour of solids at low temperature.

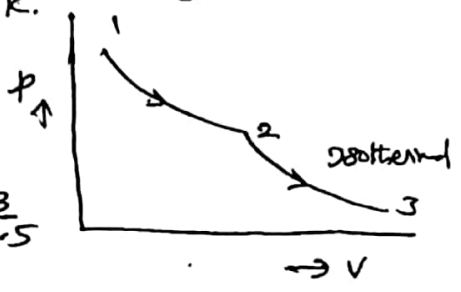
PROB: The volume of 1 kg of air increases from 0.5 m³ to 1.3 m³ while its pressure decreases from 1 MPa to 250 kPa. Then 420 kJ of heat were added to it isothermally. Calculate the total entropy change for the system for the combined process. Assume for air $C_p = 1.005 \text{ kJ/kgK}$, $C_v = C_p - R = 0.718 \text{ kJ/kgK}$, $R = 0.287 \text{ kJ/kgK}$.

SOL: Process 1-2 (general process)

$$S_2 - S_1 = m C_v \ln \frac{P_2}{P_1} + m C_p \ln \frac{V_2}{V_1}$$

$$= 1 \times 0.718 \ln \frac{250 \times 10^3}{1 \times 10^6} + 1 \times 1.005 \ln \frac{1.3}{0.5}$$

$$= -0.035 \text{ kJ/K}$$



Process 2-3 Isothermal process

To find $\frac{V_3}{V_2}$, we know $Q_{2-3} = P_2 V_2 \ln \frac{V_3}{V_2}$

$$+ (420) \times 10^3 = 250 \times 10^3 \times 1.3 \ln \frac{V_3}{V_2}$$

$$\therefore \frac{V_3}{V_2} = 3.64$$

$$\therefore S_3 - S_2 = m R \ln \frac{V_3}{V_2} = 1 \times 0.287 \ln 3.64$$

$$= 0.37 \text{ kJ/K}$$

$$\therefore \text{Total entropy change} = (S_3 - S_1) = (S_2 - S_1) + (S_3 - S_2)$$

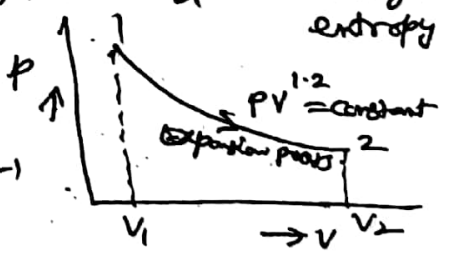
$$= -0.035 + 0.37 = 0.335 \text{ kJ/K}$$

PROB: A closed system consists of 1 kg of air which is initially at 1.5 bar and 67°C. The volume doubles as the system undergoes a process according to the law $PV^{1.2} = C$. Find work done, heat transfer and change in entropy.

SOL: $m = 1 \text{ kg}$, $P_1 = 1.5 \text{ bar}$, $T_1 = 67 + 273 = 340 \text{ K}$
 $V_2 = 2V_1$; $\frac{V_2}{V_1} = 2$

polytropic relation, $\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$; $T_2 = \frac{T_1}{\left(\frac{V_2}{V_1}\right)^{\gamma-1}}$

$$T_2 = \frac{340}{(2)^{1.2-1}} = 295 \text{ K}$$



(i) Work done $= \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} = \frac{m R (T_1 - T_2)}{\gamma - 1} = 1 \times \frac{0.287 [340 - 295]}{1.2 - 1}$

$$= 64.5 \text{ kJ}$$

(ii) Heat Transfer $Q = \frac{\gamma - \gamma}{\gamma - 1} \times \text{Work done} = \frac{1.4 - 1.2}{1.4 - 1} \times 64.5 = 32.25 \text{ kJ}$

(iii) Change of entropy, $(S_2 - S_1) = \frac{\gamma - \gamma}{\gamma - 1} \times m R \ln \frac{V_2}{V_1}$

$$= \frac{1.4 - 1.2}{1.4 - 1} \times 1 \times 0.287 \ln(2) = 0.099 \text{ kJ/K}$$

PROB. A thermal energy source at 800 K loses 2000 kJ of heat to a sink at (a) 500 K and (b) 750 K. Determine which heat transfer is more irreversible.

SOL $T_{source} = 800 \text{ K}$; $Q_{source} = 2000 \text{ kJ}$, $T_{sink} = 750 \text{ K}$.

The entropy change for each reservoir can be determined as $\Delta S = \frac{Q}{T}$

$$\Delta S_{source} = \frac{Q_{source}}{T_{source}} = \frac{-2000}{800} = -2.5 \text{ kJ/K}$$

$$\Delta S_{sink} = \frac{Q_{sink}}{T_{sink}} = \frac{+2000}{500} = 4 \text{ kJ/K}$$

$$\therefore \Delta S_{total} = \Delta S_{source} + \Delta S_{sink} = -2.5 + 4 = 1.5 \text{ kJ/K}$$

(b) When heat is transferred to a sink at 750 K.

$$\Delta S_{source} = -2.5 \text{ kJ/K}$$

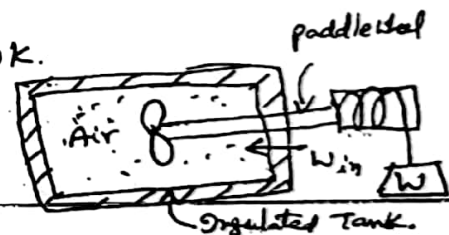
$$\Delta S_{sink} = \frac{2000}{750} = 2.7 \text{ kJ/K}$$

$$\therefore \Delta S_{total} = -2.5 + 2.7 = +0.2 \text{ kJ/K}$$

PROB. 1.5 kgs of air at 1 bar, 300 K is contained in a rigid insulated tank. During the process, 18 kJ of work is done on the gas through a paddle-wheel mechanism. Determine the final temp, final pressure of air in the tank and change in entropy. Assume specific heats of air to be constant.

SOL $C_p = 1.005 \text{ kJ/kg K}$; $C_v = 0.716 \text{ kJ/kg K}$.

For an insulated tank, heat transfer is zero. Paddle-wheel work is added to a system.



From a first law for a process,

$$Q = W_{paddle} + \Delta U; 0 = -18 \text{ kJ} + \Delta U$$

$$\therefore \Delta U = 18 \text{ kJ} = m C_v (T_2 - T_1)$$

$$18 = 1.5 \times 0.716 [T_2 - 300]; T_2 = 316.76 \text{ K} \text{ (or) } 43.76^\circ \text{C}$$

From constant volume process, $\frac{P_1}{T_1} = \frac{P_2}{T_2}; P_2 = P_1 \times \frac{T_2}{T_1} = 1 \times \frac{316.76}{300} = 1.0558 \text{ bar}$

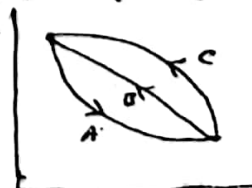
Change of entropy, $\Delta S = m C_v \ln \frac{T_2}{T_1} = 1.5 \times 0.716 \ln \frac{316.76}{300} = 0.0584 \text{ kJ/K}$

Entropy is a point (or) property function:-

The mathematical quantity $\int \frac{\delta Q}{T}$ is the property of a reversible line and is known as a point function. Consider a system taken from initial state 1 to final state 2 by a reversible path A. Subsequently, the system may be brought back to initial state by the following reversible paths B (or) C. The paths A & B together constitute a reversible cycle and so A & C.

For a reversible cycle, $\int_1^2 \frac{\delta Q}{T} \text{ via A} + \int_2^1 \frac{\delta Q}{T} \text{ via B} = 0$; $\int_1^2 \frac{\delta Q}{T} + \int_2^1 \frac{\delta Q}{T} = 0$

$\therefore \int_1^2 \frac{\delta Q}{T} \text{ via B} = \int_1^2 \frac{\delta Q}{T} \text{ via C}$; So, paths B & C, $\int \frac{\delta Q}{T}$ is same and is independent of path followed and depends only on end states 1 & 2. So, Entropy is a point function.



Entropy is a point function

GENERAL THERMODYNAMIC RELATIONS

The thermodynamic properties [pressure, volume and temperature] are directly measurable while the other properties [internal energy, enthalpy and entropy, U, H, S] are evaluated in terms of these measurable properties.

Thus, it is very important to develop the thermodynamic relations for properties which cannot be measured directly in terms of the combination of properties which can be measured directly (or) evaluated experimentally. There are other two important properties also which are known as Helmholtz function (F) and Gibbs function (G).

Helmholtz function (F):- is a property of a system and is given by subtracting the product of absolute temperature (T) and entropy (S) from the internal energy (U). Mathematically,

$$\text{Helmholtz function, } F = U - TS.$$

Since $(U - TS)$ is made up entirely of properties, therefore, Helmholtz function is also a property.

Gibbs Function (G):- The Gibbs function (also known as thermodynamic potential) is also a property of a system and is

denoted by G .

Mathematically, Gibbs function $G = (H - TS)$.

Exact differential. Suppose, Z is a function of two independent properties x and y .

$$Z = f(x, y)$$

According to condition of exact differentials,

$$dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy = M dx + N dy.$$

According to calculus,

$$\boxed{\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y}$$

* MAXWELL'S Equations

① Internal energy, $dU = \delta Q - \delta W$
 $= T ds - P dv$ [$\because \delta Q = T ds$ & $\delta W = P dv$]

The above equation is in the form,
 $dZ = M dx + N dy$

∴ Exact differential form, $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$ — (1)

(2) Enthalpy $dH = dU + d(pV)$
 $= dU + p dV + v dp$ [∵ $dU = T ds - p dv$]
 $= (T ds - p dv) + p dv + v dp =$
 $\therefore dH = T ds + v dp.$

in exact differential form, $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ — (2)

(3) Helmholtz function (F) $F = U - TS$
 $dF = dU - d(TS) = dU - T ds - S dT$
 $= (T ds - p dv) - T ds - S dT =$
 $= -p dv - S dT$

in exact differential form, $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$ — (3)

(4) Gibbs function (G) $G = H - TS$
 $dG = dH - d(TS) = dH - T ds - S dT$
 $= T ds + v dp - T ds - S dT =$
 $= v dp - S dT$

in exact differential form, $\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T$ — (4)

These 4 equations are known as Maxwell's equations.

Isothermal coefficient of compressibility (K)

It is the ratio of rate of change of volume w.r. to its original volume to that of change in pressure at a given temperature.

$K = -\left(\frac{dV}{V}\right)_T = -\frac{1}{V} \left(\frac{dV}{dP}\right)_T$ —ve sign due to increase in pressure decreases volume.

Adiabatic compressibility (K_S): It is the ratio of rate of change of volume w.r. to its original volume to that of change in pressure under adiabatic conditions.

$K_S = -\left(\frac{dV}{V}\right)_S = -\frac{1}{V} \left(\frac{dV}{dP}\right)_{S=const.}$

Coefficient of volume expansion (β): It is the ratio of change of volume w.r. to original volume to that of change in temperature at const. pressure.

$\beta = \frac{1}{V} \left(\frac{dV}{dT}\right)_P$

* Tds equations :-

Since entropy may be expressed as a function of any other two properties e.g. temperature T and specific volume v. Then,

$$s = f(T, v)$$
$$ds = \left(\frac{\partial s}{\partial T}\right)_v \cdot dT + \left(\frac{\partial s}{\partial v}\right)_T \cdot dv \quad \text{--- (1)}$$

By multiplying with T, we get, $Tds = T \left(\frac{\partial s}{\partial T}\right)_v \cdot dT + T \left(\frac{\partial s}{\partial v}\right)_T \cdot dv$

But for a reversible constant volume change,
 $dq = c_v \cdot (dT)_v = T(ds)_v$

$$c_v = T \cdot \left(\frac{\partial s}{\partial T}\right)_v$$

$H = U - TS - pdv$
Helmholtz equation,

But $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$ From Maxwell's

$Tds = c_v \cdot dT + T \left(\frac{\partial p}{\partial T}\right)_v \cdot dv$

This is 1st Tds equation.

Similarly,

$$s = f(T, p)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_p \cdot dT + \left(\frac{\partial s}{\partial p}\right)_T \cdot dp$$

By multiplying with T, $Tds = T \left(\frac{\partial s}{\partial T}\right)_p \cdot dT + T \left(\frac{\partial s}{\partial p}\right)_T \cdot dp$

For a constant pressure change,

$$dq = c_p (dT)_p = T(ds)_p$$

$$\therefore c_p = T \cdot \left(\frac{\partial s}{\partial T}\right)_p$$

\therefore But, $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$, from Gibbs' equation.
 $G = H - TS$
 $= -sdT + vdp$

$Tds = c_p dT - T \left(\frac{\partial v}{\partial T}\right)_p \cdot dp$

 \rightarrow 2nd Tds equation.

Joule Thomson Co-efficient :- The change in temperature with drop in pressure at constant enthalpy is termed as Joule-Thomson Co-efficient. $\mu = \left(\frac{dT}{dp}\right)_h$. It varies with both temperature and pressure of the gas.

* The magnitude of the Joule Thomson Coefficient is a measure of the imperfection of a gas (or) its deviation from perfect gas behaviour. When $\mu = 0$, temperature remains constant (Throttling).

PROB. Derive the equation $\left(\frac{\partial v}{\partial T}\right)_s \bigg/ \left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{\gamma - 1}$.

SOL.

For Thermodynamic properties, p, v, T , the cyclic relation is

given by $\left(\frac{\partial p}{\partial v}\right)_T \cdot \left(\frac{\partial v}{\partial T}\right)_p \cdot \left(\frac{\partial T}{\partial p}\right)_v = -1$ $\left[\because \left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial z}\right)_x \cdot \left(\frac{\partial z}{\partial x}\right)_y = -1 \right]$ — (1)

Similarly for s, v, T $\left(\frac{\partial s}{\partial v}\right)_T \cdot \left(\frac{\partial v}{\partial T}\right)_s \cdot \left(\frac{\partial T}{\partial s}\right)_v = -1$ — (2)

From the equation (1), $\left(\frac{\partial v}{\partial T}\right)_p = -\frac{1}{\left(\frac{\partial p}{\partial v}\right)_T \cdot \left(\frac{\partial T}{\partial p}\right)_v}$ — (3)

From the equation (2), $\left(\frac{\partial v}{\partial T}\right)_s = -\frac{1}{\left(\frac{\partial s}{\partial v}\right)_T \cdot \left(\frac{\partial T}{\partial s}\right)_v}$ — (4)

By,

Equation (4) / Equation (3), we get $\frac{\left(\frac{\partial v}{\partial T}\right)_s}{\left(\frac{\partial v}{\partial T}\right)_p} = \frac{\left(\frac{\partial p}{\partial v}\right)_T \cdot \left(\frac{\partial T}{\partial p}\right)_v}{\left(\frac{\partial s}{\partial v}\right)_T \cdot \left(\frac{\partial T}{\partial s}\right)_v}$

* Since, from $df = -sdt - pdv$

$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$

$= \frac{\left(\frac{\partial s}{\partial T}\right)_v}{\left(\frac{\partial p}{\partial T}\right)_v} \times \left(\frac{\partial v}{\partial p}\right)_T$

But for, $\left(\frac{\partial s}{\partial T}\right)_v = \frac{C_v}{T}$, $\left(\frac{\partial p}{\partial T}\right)_v = \frac{p}{K}$, $\left(\frac{\partial v}{\partial p}\right)_T = -\gamma K$.

$\therefore \frac{\left(\frac{\partial v}{\partial T}\right)_s}{\left(\frac{\partial v}{\partial T}\right)_p} = \frac{\frac{C_v}{T}}{\left(\frac{p}{K}\right) \times (-\gamma K)} = \frac{C_v}{-T \cdot \frac{p}{K} \cdot \gamma}$

$= \frac{C_v}{C_p - C_v}$ $[\because -T \cdot \frac{p}{K} \cdot \gamma = C_p - C_v]$

$\therefore \frac{1}{\frac{C_p}{C_v} - \frac{C_v}{C_v}} = \frac{1}{\gamma - 1}$ proved