5

Second Law of Thermodynamics and Entropy

5.1. Limitations of first law of thermodynamics and introduction to second law. 5.2. Performance of heat engines and reversed heat engines. 5.3. Reversible processes. 5.4. Statements of second law of thermodynamics—Clausius statement—Kelvin-planck statement—Equivalence of clausius statement to the kelvin—Planck statement. 5.5. Perpetual motion machine of the second kind. 5.6. Thermodynamic temperature. 5.7. Clausius inequality. 5.8. Carnot cycle. 5.9. Carnot's theorem. 5.10. Corollary of Carnot's theorem. 5.11. Efficiency of the reversible heat engine. 5.12. Entropy—Introduction—Entropy—A property of a system—Change of entropy in a reversible process. 5.13. Entropy and irreversibility. 5.14. Change in entropy of the universe. 5.15. Temperature—Entropy diagram. 5.16. Characteristics of entropy. 5.17. Entropy changes for a closed system—General case for change of entropy of a gas—Heating a gas at constant volume—Heating a gas at constant pressure—Isothermal process—Adiabatic process—Polytropic process—Approximation for heat absorbed. 5.18. Entropy changes for an open system. 5.19. The third law of thermodynamics—Highlights—Objective Type Questions—Theoretical Questions—Unsolved Examples.

5.1. LIMITATIONS OF FIRST LAW OF THERMODYNAMICS AND INTRODUCTION TO SECOND LAW

It has been observed that *energy can flow* from a system in the form of *heat* or *work*. The first law of thermodynamics sets no limit to the amount of the total energy of a system which can be caused to flow out as work. A limit is imposed, however, as a result of the principle enunciated in the second law of thermodynamics which states that heat will flow naturally from one energy reservoir to another at a lower temperature, but not in opposite direction without assistance. This is very important because a heat engine operates between two energy reservoirs at different temperatures.

Further the first law of thermodynamics *establishes equivalence between the quantity of heat used and the mechanical work but does not specify the conditions under which conversion of heat into work is possible, neither the direction in which heat transfer can take place*. This gap has been *bridged* by the second law of thermodynamics.

5.2. PERFORMANCE OF HEAT ENGINES AND REVERSED HEAT ENGINES

Refer Fig. 5.1 (*a*). A *heat engine* is used to produce the maximum work transfer from a given positive heat transfer. The measure of success is called the *thermal efficiency* of the engine and is defined by the ratio :

$$\text{Thermal efficiency, } \eta_{th} = \frac{W}{Q_1} \qquad ...(5.1)$$

where, W = Net work transfer from the engine, and

Q_1 = Heat transfer to engine.

For a *reversed heat engine* [Fig. 5.1 (*b*)] acting as a *refrigerator* when the purpose is to achieve the maximum heat transfer from the cold reservoir, the measure of success is called the *co-efficient of performance* (C.O.P.). It is defined by the ratio :

Co-efficient of performance, $(\text{C.O.P.})_{ref.} = \dfrac{Q_2}{W}$ ...(5.2)

where, Q_2 = Heat transfer *from cold reservoir*, and
W = The net work transfer to the refrigerator.

For a **reversed heat engine** [Fig. 5.1 (*b*)] acting as a *heat pump*, the measure of success is again called the *co-efficient of performance*. It is defined by the ratio :

Co-efficient of performance, $(\text{C.O.P.})_{heat\ pump} = \dfrac{Q_1}{W}$ ...(5.3)

where, Q_1 = Heat transfer *to hot reservoir*, and
W = Net work transfer to the heat pump.

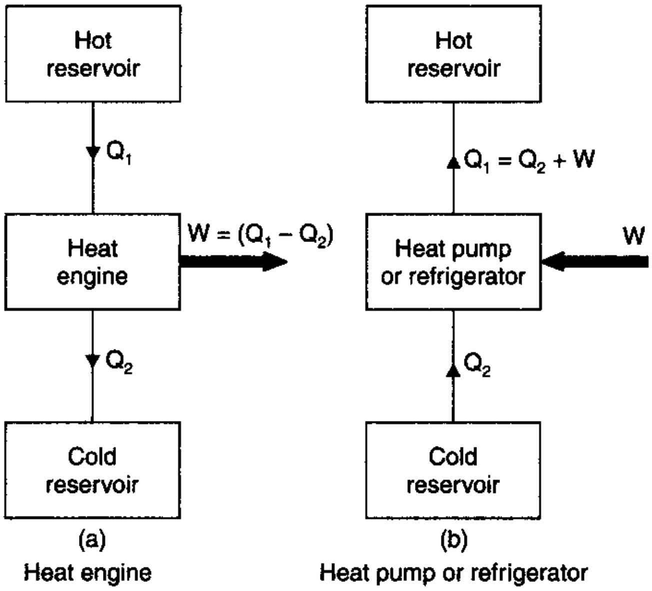


Fig. 5.1

In all the above three cases application of the first law gives the relation $Q_1 - Q_2 = W$, and this can be used to rewrite the expressions for thermal efficiency and co-efficient of performance solely in terms of the heat transfers.

$$\eta_{th} = \frac{Q_1 - Q_2}{Q_1} \quad ..(5.4)$$

$$(C.O.P.)_{ref} = \frac{Q_2}{Q_1 - Q_2} \quad ...(5.5)$$

$$(C.O.P.)_{heat\ pump} = \frac{Q_1}{Q_1 - Q_2} \quad ..(5.6)$$

It may be seen that η_{th} is *always less than unity* and $(C.O.P.)_{heat\ pump}$ is *always greater than unity*.

5.3. REVERSIBLE PROCESSES

A reversible process should fulfill the following *conditions* :

1. The process should not involve friction of any kind.
2. Heat transfer should not take place with finite temperature difference.

3. The energy transfer as heat and work during the forward process should be identically equal to energy transfer as heat and work during the reversal of the process.
4. There should be no free or unrestricted expansion.
5. There should be no mixing of the fluids.
6. The process must proceed in a series of equilibrium states.

Some examples of *ideal reversible processes* are :

(*i*) Frictionless adiabatic expansion or compression ;
(*ii*) Frictionless isothermal expansion or compression ;
(*iii*) Condensation and boiling of liquids.

Some examples of *irreversible processes are* :

(*i*) Combustion process ;
(*ii*) Mixing of two fluids ;
(*iii*) All processes involving friction ;
(*iv*) Flow of electric current through a resistance ;
(*v*) Heat flow from a higher temperature to lower temperature.

Reversible processes are preferred because the devices which produce work such as engines and turbines, reversible process of the working fluid delivers *more work* than the corresponding irreversible processes. Also in case of fans, compressors, refrigerators and pumps *less power input* is required when *reversible processes* are used in place of corresponding irreversible ones.

In thermodynamic analysis concept of reversibility, though hypothetical, is very important because a reversible process is the *most efficient process*. Only reversible processes can be truely represented on property diagrams. Thermodynamic reversibility can only be approached but can *never* be achieved. Thus the main task of the engineer is to design the system which will evolve approximate reversible processes.

5.4. STATEMENTS OF SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics has been enunciated meticulously by Clausius, Kelvin and Planck in slightly different words although both statements are basically identical. Each statement is based on an *irreversible process*. The *first considers transformation of heat between two thermal reservoirs* while the *second considers the transformation of heat into work*.

5.4.1. Clausius Statement

"It is impossible for a self acting machine working in a cyclic process unaided by any external agency, to convey heat from a body at a lower temperature to a body at a higher temperature".

In other words, heat of, itself, cannot flow from a colder to a hotter body.

5.4.2. Kelvin-Planck Statement

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

Although the Clausius and Kelvin-Planck statements appear to be different, they are really equivalent in the sense that a *violation of either statement implies violation of other.*

5.4.3. Equivalence of Clausius Statement to the Kelvin-Planck Statement

Refer Fig. 5.2. Consider a higher temperature reservoir T_1 and low temperature reservoir T_2. Fig. 5.2 shows a heat pump which requires no work and transfers an amount of Q_2 from a low temperature to a higher temperature reservoir (in violation of the Clausius statement). Let an amount of heat Q_1 (greater than Q_2) be transferred from high temperature reservoir to heat engine which devolops a net work, $W = Q_1 - Q_2$ and rejects Q_2 to the low temperature reservoir. Since there is no heat interaction with the low temperature, it can be eliminated. The combined system of the heat engine and heat pump acts then like a heat engine exchanging heat with a single reservoir, which is the violation of the Kelvin-Planck statement.

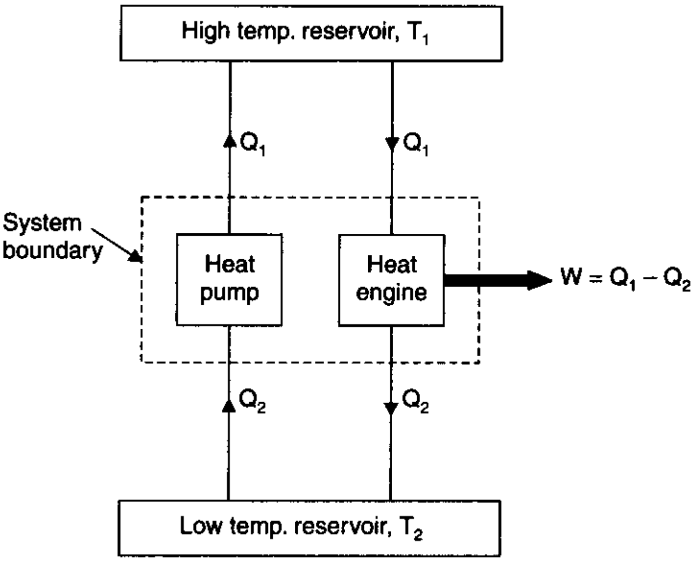


Fig. 5.2. Equivalence of Clausius statement to Kelvin-Planck statement.

5.5. PERPETUAL MOTION MACHINE OF THE SECOND KIND

— A machine which voilates the first law of thermodynamics is called the perpetual motion machine of the first kind (PMM1). Such a machine creates its own energy from nothing and *does not exist*.

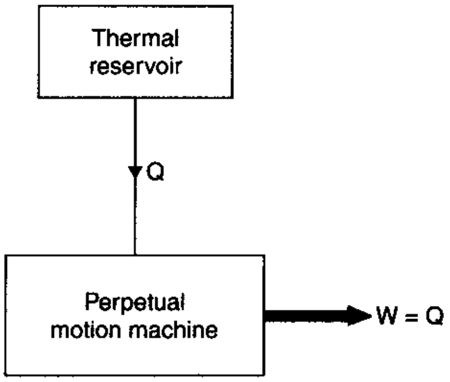


Fig. 5.3. Perpetual motion machine of second kind (PMM2).

— Without violating the first law, a machine can be imagined which would continuously absorb heat from a single thermal *reservoir and would convert this heat completely into work. The efficiency* of such a machine would be *100 per cent.* This machine is called the *perpetual motion machine of the second kind (PMM2).*

Fig. 5.3 shows the perpetual motion machine of the second kind. *A machine of this kind will evidently violates the second law of thermodynamics.*

5.6. THERMODYNAMIC TEMPERATURE

Take the case of reversible heat engine operating between two reservoirs. Its thermal efficiency is given by the eqn. (5.4),

$$\eta_{th} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

The temperature of a reservoir remains uniform and fixed irrespective of heat transfer. This means that reservoir has only one property defining its state and the heat transfer from a reservoir is some function of that property, *temperature*. Thus $Q = \phi\ (K)$, where K is the temperature of reservoir. The choice of the function is universally accepted to be such that the relation,

$$\frac{Q_1}{Q_2} = \frac{\phi(K_1)}{\phi(K_2)} \text{ becomes } \frac{Q_1}{Q_2} = \frac{T_1}{T_2} \qquad \text{...(5.7)}$$

where T_1 and T_2 are the thermodynamic temperatures of the reservoirs. Zero thermodynamic temperature (that temperature to which T_2 tends, as the heat transfer Q_2 tends to zero) has never been attained and *one form of third law of thermodynamics is the statement* :

"The temperature of a system cannot be reduced to zero in a finite number of processes."

After establishing the concept of a zero thermodynamic temperature, a reference reservoir is chosen and assigned a numerical value of temperature. Any other thermodynamic temperature may now be defined in terms of reference value and the heat transfers that would occur with reversible engine,

$$T = T_{ref.} \frac{Q}{Q_{ref.}} \qquad \text{...(5.8)}$$

The determination of thermodynamic temperature cannot be made in this way as it is not possible to build a reversible engine. Temperatures are determined by the application of thermodynamic relations to other measurements.

The SI unit of thermodynamic temperature is the kelvin (K). The relation between thermodynamic temperature and celsius scale, which is in common use is :

Thermodynamic temperature = Celsius temperature + 273.15°.

The kelvin unit of thermodynamic temperature is the fraction $\frac{1}{273.15}$ of thermodynamic temperature of 'Triple point' of water.

5.7. CLAUSIUS INEQUALITY

When a reversible engine uses more than two reservoirs the third or higher numbered reservoirs will not be equal in temperature to the original two. Consideration of expression for efficiency of the engine indicates that for maximum efficiency, all the heat transfer should take place at maximum or minimum reservoir temperatures. Any intermediate reservoir used will, therefore, lower the efficiency of the heat engine. Practical engine cycles often involve continuous changes of temperature during heat transfer. A relationship among processes in which these sort of changes occur is necessary. The ideal approach to a cycle in which temperature continually changes is to consider the system to be in communication with a large number of reservoirs in procession. Each reservoir is considered to have a temperature differing by a small amount from the previous one. In such a model it is possible to imagine that each reservoir is replaced by a reversible heat engine in communication with standard reservoirs at same temperature T_0. Fig. 5.4 shows one example to this substitution.

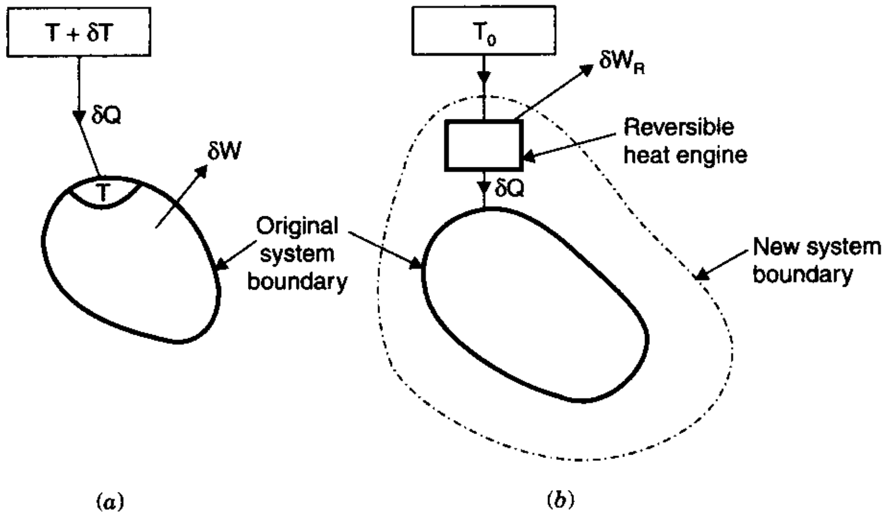


Fig. 5.4. The clausius inequality.

The system to which the heat transfer is effected is neither concerned with the source of energy it receives nor with the method of transfer, save that it must be reversible. Associated with the small heat transfer dQ to the original system is a small work transfer dW and for this system the first law gives

$$\sum_{\text{cycle}} (\delta Q - \delta W) = 0 \qquad \text{...(5.9)}$$

Now consider the engine replacing the reservoirs and apply the second law to the new system in Fig. 5.4 (*b*). If the new system is not a perpetual motion machine of second kind, no positive work transfer is possible with a single reservoir.

Therefore,
$$\sum_{\text{cycle}} (\delta W - \delta W_R) \le 0 \qquad \text{...(5.10)}$$

But by the definition of thermodynamic temperature in equation (5.8)

$$\frac{\delta W_R}{\delta Q} = \frac{\delta Q_0 - \delta Q}{\delta Q} = \frac{T_0 - T}{T} \qquad \text{...(5.11)}$$

and by combination of eqns. (5.9), (5.10) and (5.11)

$$T_0 \sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) \le 0 \text{ but } T_0 \ne 0 \text{ and therefore ;}$$

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) \le 0 \qquad \text{..(5.12)}$$

This is known as **Clausius inequality.**

Let us now consider the case of a reversible engine for which

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) \le 0 \text{ ,}$$

reverse the engine and for the reversible heat pump obtained it is possible to develop the expression,

$$-\sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) \le 0$$

The *negative sign indicates that the heat transfers have all reversed in direction when the engine was reversed.* This means that for the same machine we have two relations which are only satisfied if in the reversible case,

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) \le 0 \qquad \text{...(5.13)}$$

For a reversible case, as the number of reservoirs used tends to infinity, the limiting value of the summation will be

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) = 0$$

In words, the Clausius inequality may be expressed as follows :

"When a system performs a reversible cycle, then

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) = 0,$$

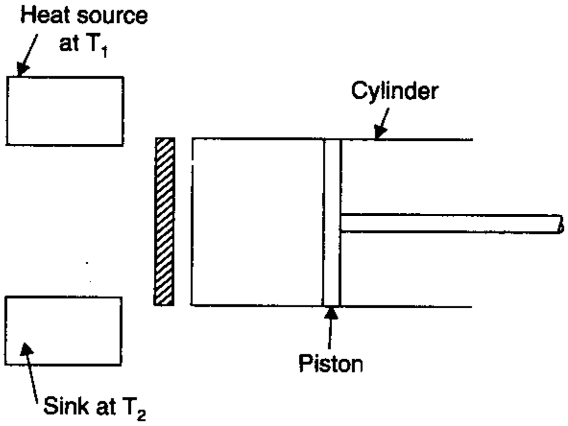
but when the cycle is not reversible

$$\sum_{\text{cycle}} \left(\frac{\delta Q}{T}\right) < 0\text{''}.$$

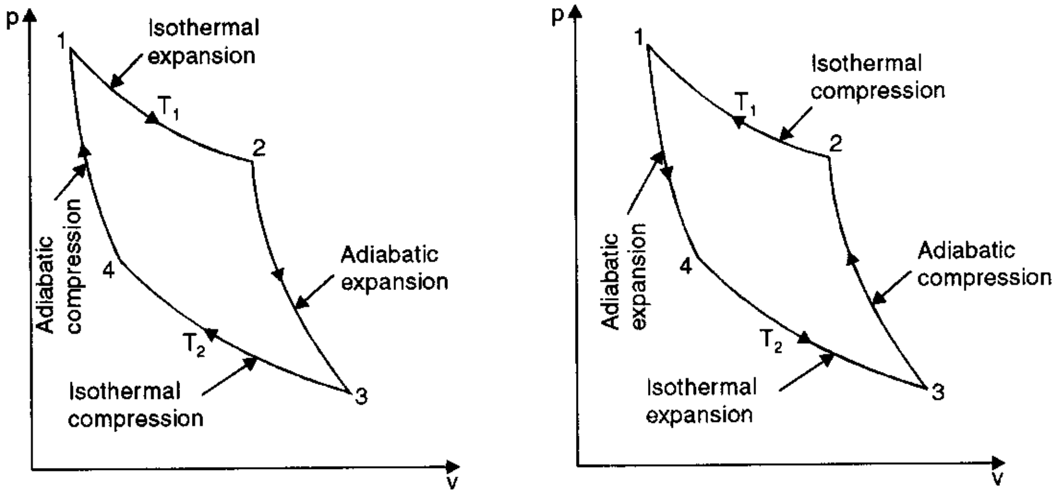
5.8. CARNOT CYCLE

The cycle was first suggested by a French engineer Sadi Carnot in 1824 which works on reversible cycle and is known as *Carnot cycle.*

Any fluid may be used to operate the Carnot cycle (Fig. 5.5) which is performed in an engine cylinder the head of which is supposed alternatively to be perfect conductor or a perfect insulator of a heat. Heat is caused to flow into the cylinder by the application of high temperature energy source to the cylinder head during expansion, and to flow from the cylinder by the application of a lower temperature energy source to the head during compression.



(*a*)



(*b*)
Carnot engine cycle

(*c*)
Carnot heat pump cycle

Fig. 5.5

The ***assumptions*** made for describing the working of the Carnot engine are as follows :

(*i*) The piston moving in a cylinder does not develop any friction during motion.

(*ii*) The walls of piston and cylinder are considered as perfect insulators of heat.

(*iii*) The cylinder head is so arranged that it can be a perfect heat conductor or perfect heat insulator.

(*iv*) The transfer of heat does not affect the temperature of source or sink.

(*v*) Working medium is a perfect gas and has constant specific heat.

(*vi*) Compression and expansion are reversible.

Following are the *four stages* of Carnot cycle :

Stage 1. (Process 1-2). Hot energy source is applied. Heat Q_1 is taken in whilst the fluid expands isothermally and reversibly at constant high temperature T_1.

Stage 2. (Process 2-3). The cylinder becomes a perfect insulator so that no heat flow takes place. The fluid expands adiabatically and reversibly whilst temperature falls from T_1 to T_2.

Stage 3. (Process 3-4). Cold energy source is applied. Heat Q_2 flows from the fluid whilst it is compressed isothermally and reversibly at constant lower temperature T_2.

Stage 4. (Process 4-1). Cylinder head becomes a perfect insulator so that no heat flow occurs. The compression is continued adiabatically and reversibly during which temperature is raised from T_2 to T_1.

The work delivered from the system during the cycle is represented by the enclosed area of the cycle. Again for a closed cycle, according to first law of the thermodynamics the work obtained is equal to the difference between the heat supplied by the source (Q_1) and the heat rejected to the sink (Q_2).

$$\therefore \qquad W = Q_1 - Q_2$$

Also, thermal efficiency, $$\eta_{th} = \frac{\text{Work done}}{\text{Heat supplied by the source}} = \frac{Q_1 - Q_2}{Q_1}$$

$$= 1 - \frac{Q_2}{Q_1} \left(= 1 - \frac{T_2}{T_1} \right) \qquad \left[\begin{array}{l} \because \quad Q_1 = m\,c_p\,T_1 \\ \quad\;\; Q_2 = m\,c_p\,T_2 \\ \text{where, } m = \text{mass of fluid.} \end{array} \right]$$

Such an engine since it consists entirely of reversible processes, can operate in the reverse direction so that it follows the cycle shown in Fig. 5.5 (*b*) and operates as a **heat pump.** Q_2 is being taken in at the lower temperature T_2 during the isothermal expansion (process 4-3) and heat Q_1 is being rejected at the upper temperature T_1 (process 2-1). Work W will be needed to drive the pump. Again, the enclosed area represents this work which is exactly equal to that flowing from it when used as engine.

The Carnot cycle *cannot be performed in practice* because of the following **reasons** :

1. It is imposible to perform a frictionless process.
2. It is impossible to transfer the heat without temperature potential.
3. Isothermal process can be achieved only if the piston moves very slowly to allow heat transfer so that the temperature remains contant. Adiabatic process can be achieved only if the piston moves as fast as possible so that the heat transfer is negligible due to very short time available. The isothermal and adiabatic processes take place during the same stroke therefore the piston has to move very slowly for part of the stroke and it has to move very fast during remaining stroke. This variation of motion of the piston during the same stroke is not possible.

5.9. CARNOT'S THEOREM

"It states that of all engines operating between a given constant temperature source and a given constant temperature sink, none has a higher efficiency than a reversible engine".

Refer Fig. 5.6.

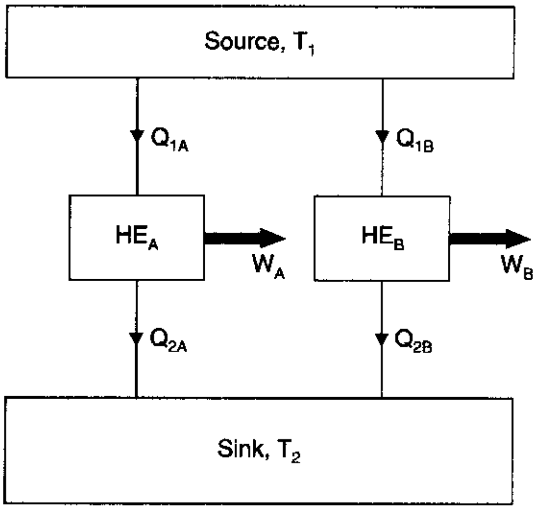


Fig. 5.6. Two cyclic heat engines HE_A and HE_B operating between the same source and sink, of which HE_B is reversible.

HE_A and HE_B are the two engines operating between the given source at temperature T_1 and the given sink at temperature T_2.

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

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

Since $$\eta_A > \eta_B$$

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

$\therefore$ $$W_A > W_B$$

Now, let HE_B be reversed. Since HE_B 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 Fig. 5.7. Since $W_A > W_B$, some part of W_A (equal to W_B) may be fed to drive the reversed heat engine $\exists H_B$. Since $Q_{1A} = Q_{1B} = Q_1$, the heat discharged by $\exists H_B$ may be supplied to HE_A. The source may, therefore, be eliminated (Fig. 5.8). The net result is that HE_A and $\exists H_B$ 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.

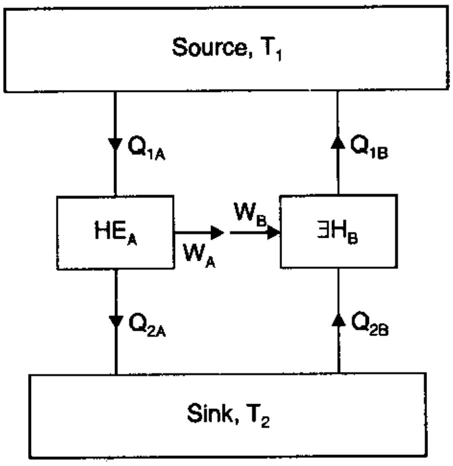


Fig. 5.7. HE_B is reversed.

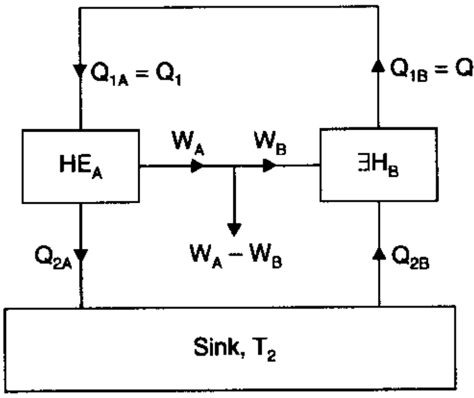


Fig. 5.8. HE_A and $\exists H_B$ together violate the Kelvin-Planck statement.

$\therefore$ $$\eta_B \geq \eta_A.$$

5.10. COROLLARY OF CARNOT'S THEOREM

"The efficiency of all reversible heat engines operating between the same temperature levels is the same".

Refer Fig. 5.6. Let both the heat engines HE_A and HE_B be *reversible*. Let us assume $\eta_A > \eta_B$. Similar to the procedure outlined in the Article 5.9, if HE_B is reversed to run say, as a heat pump using some part of the work output (W_A) of engine HE_A, we see that the combined system of heat pump HE_B and engine HE_A, becomes a *PMM2*. So η_A cannot be greater than η_B. Similary, if we assume $\eta_B > \eta_A$ and reverse the engine HE_A, we observe that η_B cannot be greater than η_A

$$\therefore \qquad \eta_A = \eta_B.$$

Since the efficiencies of all reversible engines operating between the same heat reservoirs are the same, *the efficiency of a reversible engine is independent of the nature or amount of the working substance undergoing the cycle.*

5.11. EFFICIENCY OF THE REVERSIBLE HEAT ENGINE

The efficiency of a reversible heat engine in which heat is received solely at T_1 is found to be

$$\eta_{rev.} = \eta_{max} = 1 - \left(\frac{Q_2}{Q_1}\right)_{rev.} = 1 - \frac{T_2}{T_1}$$

or

$$\eta_{rev.} = \frac{T_1 - T_2}{T_1}$$

From the above expression, it may be noted that as T_2 decreases and T_1 increases, the efficiency of the reversible cycle increases.

Since η is always less than unity, T_2 is always greater than zero and + ve.

The C.O.P. of a refrigerator is given by

$$(\text{C.O.P.})_{ref.} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{\frac{Q_1}{Q_2} - 1}$$

For a *reversible refrigerator*, using

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

$$(\text{C.O.P.})_{rev.} = \frac{1}{\frac{T_1}{T_2} - 1}$$

$$\therefore \qquad [(\text{C.O.P.})_{ref.}]_{rev.} = \frac{T_2}{T_1 - T_2} \qquad \text{...(5.14)}$$

Similarly, for a *reversible heat pump*

$$[(\text{C.O.P.})_{heat\ pump}]_{rev.} = \frac{T_1}{T_1 - T_2} \qquad \text{...(5.15)}$$

Example 5.1. *A heat engine receives heat at the rate of 1500 kJ/min and gives an output of 8.2 kW. Determine :*

(*i*) *The thermal efficiency ;* (*ii*) *The rate of heat rejection.*

Solution. Heat received by the heat engine,

$$Q_1 = 1500 \text{ kJ/min}$$

$$= \frac{1500}{60} = 25 \text{ kJ/s}$$

Work output, $W = 8.2$ kW $= 8.2$ kJ/s.

(*i*) Thermal efficiency, $\eta_{th} = \frac{W}{Q_1}$

$$= \frac{8.2}{25} = 0.328 = 32.8\%$$

Hence, **thermal efficiency = 32.8%. (Ans.)**

(*ii*) Rate of heat rejection,

$$Q_2 = Q_1 - W = 25 - 8.2$$

$$= 16.8 \text{ kJ/s}$$

Hence, **the rate of heat rejection = 16.8 kJ/s. (Ans.)**

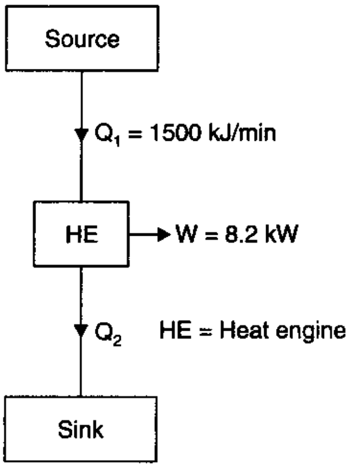


Fig. 5.9

☞**Example 5.2.** *During a process a system receives 30 kJ of heat from a reservoir and does 60 kJ of work. Is it possible to reach initial state by an adiabatic process ?*

Solution. Heat received by the system = 30 kJ

Work done = 60 kJ

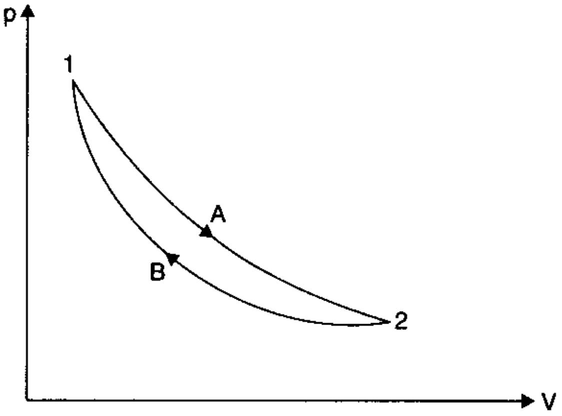


Fig. 5.10

Process 1-2 : By first law of thermodynamics,

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

$$30 = (U_2 - U_1) + 60 \qquad \therefore \qquad (U_2 - U_1) = -30 \text{ kJ.}$$

Process 2-1 : By first law of thermodynamics,

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

$$\therefore \qquad 0 = 30 + W_{2-1} \qquad \therefore \qquad W_{2-1} = -30 \text{ kJ.}$$

Thus 30 kJ work has to be done *on the system* to restore it to original state, by adiabatic process.

Example 5.3. *Find the co-efficient of performance and heat transfer rate in the condenser of a refrigerator in kJ/h which has a refrigeration capacity of 12000 kJ/h when power input is 0.75 kW.*

Solution. Refer Fig. 5.11.

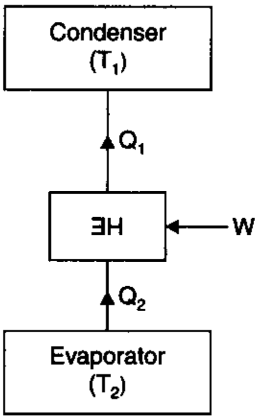


Fig. 5.11

Refrigeration capacity, Q_2 = 12000 kJ/h

Power input, W = 0.75 kW (= 0.75 × 60 × 60 kJ/h)

Co-efficient of performance, C.O.P. :

Heat transfer rate :

$$(\text{C.O.P.})_{refrigerator} = \frac{\text{Heat absorbed at lower temperature}}{\text{Work input}}$$

$$\therefore \quad \text{C.O.P.} = \frac{Q_2}{W} = \frac{12000}{0.75 \times 60 \times 60} = 4.44$$

Hence **C.O.P. = 4.44. (Ans.)**

Hence transfer rate in condenser = Q_1

According to the first law

$Q_1 = Q_2 + W = 12000 + 0.75 \times 60 \times 60 = 14700$ kJ/h

Hence, **heat transfer rate = 14700 kJ/h. (Ans.)**

Example 5.4. *A domestic food refrigerator maintains a temperature of – 12°C. The ambient air temperature is 35°C. If heat leaks into the freezer at the continuous rate of 2 kJ/s determine the least power necessary to pump this heat out continuously.*

Solution. Freezer temperature,

$$T_2 = -12 + 273 = 261 \text{ K}$$

Ambient air temperature,

$$T_1 = 35 + 273 = 308 \text{ K}$$

Rate of heat leakage into the freezer = 2 kJ/s

Least power required to pump the heat :

The refrigerator cycle removes heat from the freezer at the same rate at which heat leaks into it (Fig. 5.12).

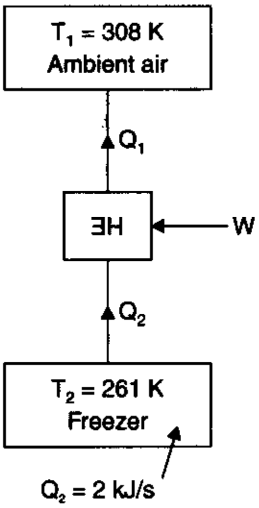


Fig. 5.12

For minimum power requirement

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

$$\therefore \quad Q_1 = \frac{Q_2}{T_2} \times T_1 = \frac{2}{261} \times 308 = 2.36 \text{ kJ/s}$$

$$\therefore \quad W = Q_1 - Q_2$$

$$= 2.36 - 2 = 0.36 \text{ kJ/s} = 0.36 \text{ kW}$$

Hence, *least power required to pump the heat continuously*

= **0.36 kW. (Ans.)**

Example 5.5. *A house requires 2 × 10^5 kJ/h for heating in winter. Heat pump is used to absorb heat from cold air outside in winter and send heat to the house. Work required to operate the heat pump is 3 × 10^4 kJ/h. Determine :*

(i) Heat abstracted from outside ;

(ii) Co-efficient of performance.

Solution. (*i*) Heat requirement of the house, Q_1 (or heat rejected)

$$= 2 \times 10^5 \text{ kJ/h}$$

Work required to operate the heat pump,

$$W = 3 \times 10^4 \text{ kJ/h}$$

Now, $$Q_1 = W + Q_2$$

where Q_2 is the heat abstracted from outside.

$\therefore$ $$2 \times 10^5 = 3 \times 10^4 + Q_2$$

Thus $$Q_2 = 2 \times 10^5 - 3 \times 10^4$$
$$= 200000 - 30000 = 170000 \text{ kJ/h}$$

Hence, **heat abstracted from outside = 170000 kJ/h. (Ans.)**

(*ii*) $$(\text{C.O.P.})_{heat\ pump} = \frac{Q_1}{Q_1 - Q_2}$$
$$= \frac{2 \times 10^5}{2 \times 10^5 - 170000} = 6.66$$

Hence, **co-efficient of performance = 6.66. (Ans.)**

Note. If the heat requirements of the house were the same but this amount of heat had to be abstracted from the house and rejected out, *i.e.*, *cooling of the house in summer*, we have

$$(\text{C.O.P.})_{refrigerator} = \frac{Q_2}{Q_1 - Q_2} = \frac{Q_2}{W}$$
$$= \frac{170000}{3 \times 10^4} = \mathbf{5.66}$$

Thus the same device has two values of C.O.P. depending upon the objective.

Example 5.6. *What is the highest possible theoretical efficiency of a heat engine operating with a hot reservoir of furnace gases at 2100°C when the cooling water available is at 15°C ?*

Solution. Temperature of furnace gases, $T_1 = 2100 + 273 = 2373$ K

Temperature of cooling water, $T_2 = 15 + 273 = 288$ K

Now, $$\eta_{max} \ (= \eta_{carnot}) = 1 - \frac{T_2}{T_1} = 1 - \frac{288}{2373} = \mathbf{0.878 \text{ or } 87.8\%.} \quad \textbf{(Ans.)}$$

Note. It should be noted that a system in practice operating between similar temperatures (*e.g.*, a steam generating plant) would have a thermal efficiency of about 30%. The discrepency is *due to irreversibility in the actual plant*, and *also because of deviations from the ideal Carnot cycle made for various practical reasons.*

Example 5.7. *A Carnot cycle operates between source and sink temperatures of 250°C and − 15°C. If the system receives 90 kJ from the source, find :*

(*i*) *Efficiency of the system ;* (*ii*) *The net work transfer ;*

(*iii*) *Heat rejected to sink.*

Solution. Temperature of source, $T_1 = 250 + 273 = 523$ K

Temperature of sink, $T_2 = -15 + 273 = 258$ K

Heat received by the system, $Q_1 = 90$ kJ

(*i*) $$\eta_{\text{carnot}} = 1 - \frac{T_2}{T_1} = 1 - \frac{258}{523} = 0.506 = \mathbf{50.6\%.} \quad \textbf{(Ans.)}$$

(*ii*) **The net work transfer,** $W = \eta_{carnot} \times Q_1$ $\left[\because \eta_{carnot} = \frac{W}{Q_1}\right]$

$= 0.506 \times 90 =$ **45.54 kJ. (Ans.)**

(*iii*) **Heat rejected to the sink,** $Q_2 = Q_1 - W$ $[\because W = Q_1 - Q_2]$

$= 90 - 45.54 =$ **44.46 kJ. (Ans.)**

Example 5.8. *An inventor claims that his engine has the following specifications :*

Temperature limits ...... *750°C and 25°C*
Power developed ...... *75 kW*
Fuel burned per hour ...... *3.9 kg*
Heating value of the fuel ...... *74500 kJ/kg*

State whether his claim is valid or not.

Solution. Temperature of source, $T_1 = 750 + 273 = 1023$ K

Temperature of sink, $T_2 = 25 + 273 = 298$ K

We know that the thermal efficiency of Carnot cycle is the maximum between the specified temperature limits.

Now, $$\eta_{carnot} = 1 - \frac{T_2}{T_1} = 1 - \frac{298}{1023} = 0.7086 \text{ or } 70.86\%$$

The actual thermal efficiency claimed,

$$\eta_{thermal} = \frac{\text{Work done}}{\text{Heat supplied}} = \frac{75 \times 1000 \times 60 \times 60}{3.9 \times 74500 \times 1000} = 0.9292 \text{ or } 92.92\%.$$

Since $\eta_{thermal} > \eta_{carnot}$, therefore claim of the inventor is **not valid** (or possible). **(Ans.)**

Example 5.9. *A cyclic heat engine operates between a source temperature of 1000°C and a sink temperature of 40°C. Find the least rate of heat rejection per kW net output of the engine ?*

Solution. Temperature of source,

$$T_1 = 1000 + 273 = 1273 \text{ K}$$

Temperature of sink,

$$T_2 = 40 + 273 = 313 \text{ K}$$

Least rate of heat rejection per kW net output :

For a reversible heat engine, the rate of heat rejection will be minimum (Fig. 5.13)

$$\eta_{max} = \eta_{rev.} = 1 - \frac{T_2}{T_1}$$

$$= 1 - \frac{313}{1273} = 0.754$$

Now $$\frac{W_{net}}{Q_1} = \eta_{max} = 0.754$$

$\therefore$ $$Q_1 = \frac{W_{net}}{0.754} = \frac{1}{0.754} = 1.326 \text{ kW}$$

Now $$Q_2 = Q_1 - W_{net} = 1.326 - 1 = 0.326 \text{ kW}$$

Hence, **the least rate of heat rejection = 0.326 kW. (Ans.)**

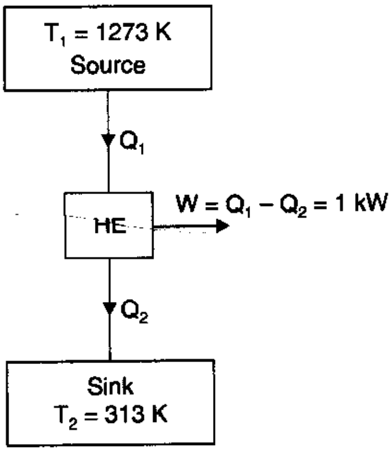


Fig. 5.13

Example 5.10. *A fish freezing plant requires 40 tons of refrigeration. The freezing temperature is – 35°C while the ambient temperature is 30°C. If the performance of the plant is 20% of the theoretical reversed Carnot cycle working within the same temperature limits, calculate the power required.*

Given : 1 ton of refrigeration = 210 kJ/min.

Solution. Cooling required = 40 tons = 40 × 210

= 8400 kJ/min

Ambient temperature, $T_1 = 30 + 273 = 303$ K

Freezing temperature, $T_2 = -35 + 273 = 238$ K

Performance of plant = 20% of the theoretical reversed Carnot cycle

$$(\text{C.O.P.})_{refrigerator} = \frac{T_2}{T_1 - T_2} = \frac{238}{303 - 238} = 3.66$$

$\therefore$ Actual C.O.P = 0.20 × 3.66 = 0.732

Now work needed to produce cooling of 40 tons is calculated as follows :

$$(\text{C.O.P.})_{actual} = \frac{\text{Cooling reqd.}}{\text{Work needed}}$$

$$0.732 = \frac{8400}{W} \quad \text{or} \quad W = \frac{8400}{0.732} \text{ kJ/min} = 191.25 \text{ kJ/s} = 191.25 \text{ kW}$$

Hence, **power required = 191.25 kW. (Ans.)**

Example 5.11. *Source 1 can supply energy at the rate of 12000 kJ/min at 320°C. A second source 2 can supply energy at the rate of 120000 kJ/min at 70°C. Which source (1 or 2) would you choose to supply energy to an ideal reversible heat engine that is to produce large amount of power if the temperature of the surroundings is 35°C ?*

Solution. Source 1 :

Rate of supply of energy = 12000 kJ/min

Temperature, $T_1 = 320 + 273 = 593$ K.

Source 2 :

Rate of supply of energy = 120000 kJ/min

Temperature, $T_1 = 70 + 273 = 343$ K

Temperature of the surroundings, $T_2 = 35°\text{C} + 273 = 308$ K

Let the Carnot engine be working in ~~the two~~ cases with the two source temperatures and the single sink ~~temperature.~~ The efficiency of the cycle will be given by :

$$\eta_1 = 1 - \frac{T_2}{T_1} = 1 - \frac{308}{593} = 0.4806 \quad \text{or} \quad 48.06\%$$

$$\eta_2 = 1 - \frac{T_2}{T_1} = 1 - \frac{308}{343} = 0.102 \quad \text{or} \quad 10.2\%$$

$\therefore$ The work delivered in the two cases is given by

$$W_1 = 12000 \times 0.4806 = 5767.2 \text{ kJ/min}$$

and $$W_2 = 120000 \times 0.102 = 12240 \text{ kJ/min.}$$

Thus, choose **source 2. (Ans.)**

Note. The source 2 is selected even though *efficiency* in this case is *lower*, because the *criterion for selection is the larger output.*

☞**Example 5.12.** *A reversible heat engine operates between two reservoirs at temperatures 700°C and 50°C. The engine drives a reversible refrigerator which operates between reservoirs at temperatures of 50°C and – 25°C. The heat transfer to the engine is 2500 kJ and the net work output of the combined engine refrigerator plant is 400 kJ.*

(i) Determine the heat transfer to the refrigerant and the net heat transfer to the reservoir at 50°C ;

(ii) Reconsider (i) given that the efficiency of the heat engine and the C.O.P. of the refrigerator are each 45 per cent of their maximum possible values.

Solution. Refer Fig. 5.14.

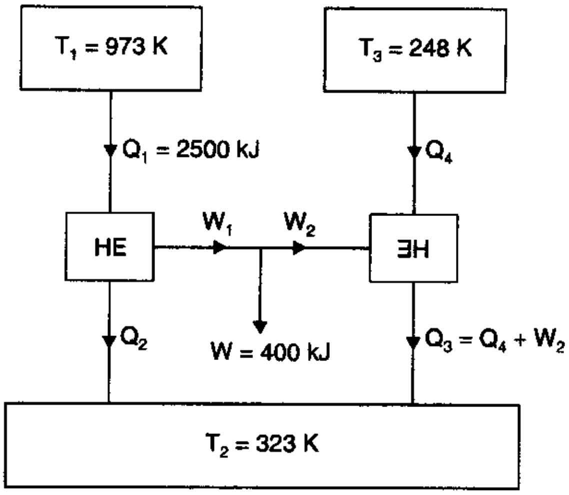


Fig. 5.14

Temperature, $T_1 = 700 + 273 = 973$ K

Temperature, $T_2 = 50 + 273 = 323$ K

Temperature, $T_3 = -25 + 273 = 248$ K

The heat transfer to the heat engine, $Q_1 = 2500$ kJ

The network output of the combined engine refrigerator plant,

$$W = W_1 - W_2 = 400 \text{ kJ}.$$

(*i*) Maximum efficiency of the heat engine cycle is given by

$$\eta_{max} = 1 - \frac{T_2}{T_1} = 1 - \frac{323}{973} = 0.668$$

Again, $$\frac{W_1}{Q_1} = 0.668$$

∴ $$W_1 = 0.668 \times 2500 = 1670 \text{ kJ}$$

$$(\text{C.O.P.})_{max} = \frac{T_3}{T_2 - T_3} = \frac{248}{323 - 248} = 3.306$$

Also, $$\text{C.O.P.} = \frac{Q_4}{W_2} = 3.306$$

Since, $W_1 - W_2 = W = 400$ kJ

$W_2 = W_1 - W = 1670 - 400 = 1270$ kJ

$\therefore$ $Q_4 = 3.306 \times 1270 = 4198.6$ kJ

$Q_3 = Q_4 + W_2 = 4198.6 + 1270 = 5468.6$ kJ

$Q_2 = Q_1 - W_1 = 2500 - 1670 = 830$ kJ.

Heat rejection to the 50°C reservoir

$= Q_2 + Q_3 = 830 + 5468.6 =$ **6298.6 kJ. (Ans.)**

(*ii*) Efficiency of actual heat engine cycle,

$\eta = 0.45\ \eta_{max} = 0.45 \times 0.668 = 0.3$

$\therefore$ $W_1 = \eta \times Q_1 = 0.3 \times 2500 = 750$ kJ

$\therefore$ $W_2 = 750 - 400 = 350$ kJ

C.O.P. of the actual refrigerator cycle,

$$\text{C.O.P.} = \frac{Q_4}{W_2} = 0.45 \times 3.306 = 1.48$$

$\therefore$ $Q_4 = 350 \times 1.48 =$ **518 kJ. (Ans.)**

$Q_3 = 518 + 350 = 868$ kJ

$Q_2 = 2500 - 750 = 1750$ kJ

Heat rejected to 50°C reservoir

$= Q_2 + Q_3 = 1750 + 868 =$ **2618 kJ. (Ans.)**

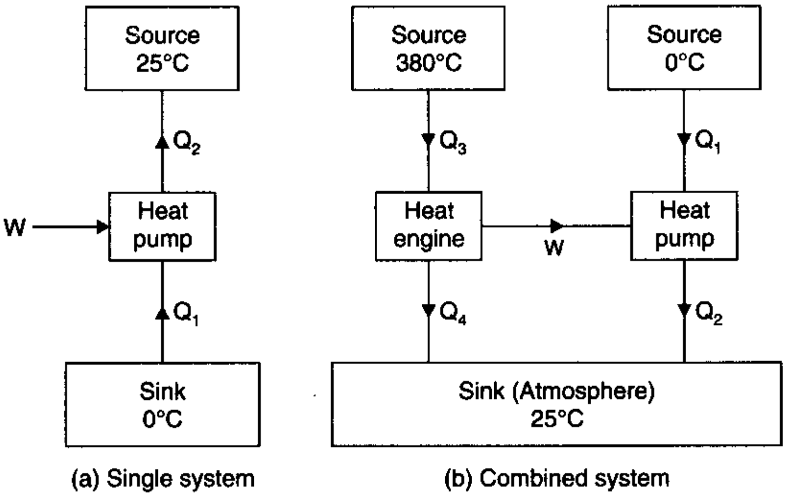
☞**Example 5.13.** (*i*) *A reversible heat pump is used to maintain a temperature of 0°C in a refrigerator when it rejects the heat to the surroundings at 25°C. If the heat removal rate from the refrigerator is 1440 kJ/min, determine the C.O.P. of the machine and work input required.*

(*ii*) *If the required input to run the pump is developed by a reversible engine which receives heat at 380°C and rejects heat to atmosphere, then determine the overall C.O.P. of the system.*

Solution. Refer Fig. 5.15 (*a*).

(*i*) Temperature, $T_1 = 25 + 273 = 298$ K

Temperature, $T_2 = 0 + 273 = 273$ K



(a) Single system (b) Combined system

Fig. 5.15

Heat removal rate from the refrigerator,

$$Q_1 = 1440 \text{ kJ/min} = 24 \text{ kJ/s}$$

Now, co-efficient of performance, for reversible heat pump,

$$\textbf{C.O.P.} = \frac{T_1}{T_1 - T_2} = \frac{298}{(298 - 273)} = \textbf{11.92. (Ans.)}$$

$$\therefore \qquad (\text{C.O.P.})_{ref.} = \frac{T_2}{T_1 - T_2} = \frac{273}{298 - 273} = 10.92$$

Now, $$10.92 = \frac{Q_1}{W} = \frac{24}{W}$$

$$\therefore \qquad W = 2.2 \text{ kW}$$

i.e., **Work input required = 2.2 kW. (Ans.)**

$$Q_2 = Q_1 + W = 24 + 2.2 = 26.2 \text{ kJ/s}$$

(*ii*) Refer Fig. 5.15 (*b*).

The overall C.O.P. is given by,

$$\text{C.O.P.} = \frac{\text{Heat removed from the refrigerator}}{\text{Heat supplied from the source}}$$

$$= \frac{Q_1}{Q_3} \qquad ...(i)$$

For the reversible engine, we can write

$$\frac{Q_3}{T_3} = \frac{Q_4}{T_4}$$

or $$\frac{Q_4 + W}{T_3} = \frac{Q_4}{T_4}$$

or $$\frac{Q_4 + 2.2}{(380 + 273)} = \frac{Q_4}{(25 + 273)}$$

or $$\frac{Q_4 + 2.2}{653} = \frac{Q_4}{298}$$

or $$298(Q_4 + 2.2) = 653\, Q_4$$

or $$Q_4(653 - 298) = 298 \times 2.2$$

or $$Q_4 = \frac{298 \times 2.2}{(653 - 298)} = 1.847 \text{ kJ/s}$$

$$\therefore \qquad Q_3 = Q_4 + W = 1.847 + 2.2 = 4.047 \text{ kJ/s}$$

Substituting this value in eqn. (*i*), we get

$$\textbf{C.O.P.} = \frac{24}{4.047} = \textbf{5.93. (Ans.)}$$

If the purpose of the system is to supply the heat to the sink at 25°C, then

$$\textbf{Overall C.O.P.} = \frac{Q_2 + Q_4}{Q_3} = \frac{26.2 + 1.847}{4.047} = \textbf{6.93. (Ans.)}$$

Example 5.14. *An ice plant working on a reversed Carnot cycle heat pump produces 15 tonnes of ice per day. The ice is formed from water at 0°C and the formed ice is maintained at 0°C. The heat is rejected to the atmosphere at 25°C. The heat pump used to run the ice plant is* *coupled to a Carnot engine which absorbs heat from a source which is maintained at 220°C by burning liquid fuel of 44500 kJ/kg calorific value and rejects the heat to the atmosphere. Determine :*

(i) Power developed by the engine ;

(ii) Fuel consumed per hour.

Take enthalpy of fusion of ice = 334.5 kJ/kg.

Solution. (*i*) Fig. 5.16 shows the arrangement of the system.

Amount of ice produced per day = 15 tonnes.

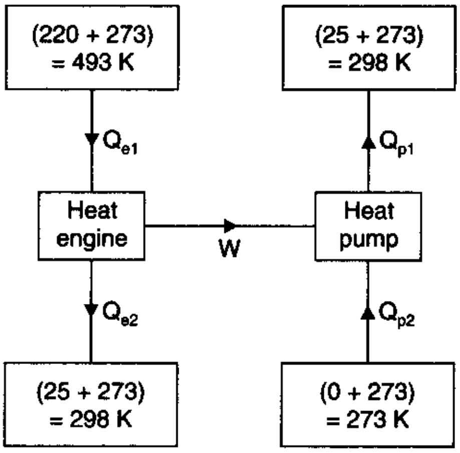


Fig. 5.16

∴ The amount of heat removed by the heat pump,

$$Q_{p_2} = \frac{15 \times 1000 \times 334.5}{24 \times 60} = 3484.4 \text{ kJ/min}$$

$$\text{C.O.P. of the heat pump} = \frac{Q_{p_2}}{W} = \frac{273}{298 - 273}$$

$$\therefore \quad W = Q_{p_2} \times \frac{298 - 273}{273} = 3484.4 \times \frac{25}{273} = 319.08 \text{ kJ/min}$$

This work must be developed by the Carnot engine,

$$W = \frac{319.08}{60} = 5.3 \text{ kJ/s} = 5.3 \text{ kW}$$

Thus **power developed by the engine = 5.3 kW. (Ans.)**

(*ii*) The efficiency of Carnot engine is given by

$$\eta_{carnot} = \frac{W}{Q_{e_1}} = 1 - \frac{298}{493} = 0.396$$

$$\therefore \quad Q_{e_1} = \frac{W}{0.396} = \frac{5.3}{0.396} = 13.38 \text{ kJ/s}$$

$$\therefore \quad Q_{e_1(per\ hour)} = 13.38 \times 60 \times 60 = 48168 \text{ kJ}$$

∴ **Quantity of fuel consumed/hour**

$$= \frac{48168}{44500} = \mathbf{1.082\ kg/h.}\ \ \textbf{(Ans.)}$$

Example 5.15. *Two Carnot engines work in series between the source and sink temperatures of 550 K and 350 K. If both engines develop equal power determine the intermediate temperature.*

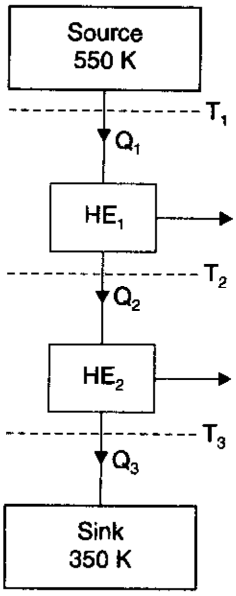


Fig. 5.17

Solution. Fig. 5.17 shows the arrangement of the system.

Temperature of the source, $T_1 = 550$ K

Temperature of the sink, $T_3 = 350$ K

Intermediate temperature, T_2 :

The efficiencies of the engines HE_1 and HE_2 are given by

$$\eta_1 = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1} = \frac{W}{Q_2 + W} \qquad ...(i)$$

$$\eta_2 = \frac{W}{Q_2} = \frac{T_2 - T_3}{T_2} = \frac{W}{Q_3 + W} \qquad ...(ii)$$

From eqn. (*i*), we get

$$W = (Q_2 + W)\left(\frac{T_1 - T_2}{T_1}\right)$$

$$\therefore \quad W\left[1 - \left(\frac{T_1 - T_2}{T_1}\right)\right] = Q_2\left(\frac{T_1 - T_2}{T_1}\right)$$

$$\therefore \quad W\left(\frac{T_2}{T_1}\right) = Q_2\left(\frac{T_1 - T_2}{T_1}\right)$$

$$\therefore \quad W = Q_2\left(\frac{T_1 - T_2}{T_2}\right) \qquad ...(iii)$$

From eqn. (*ii*), we get

$$W = Q_2\left(\frac{T_2 - T_3}{T_2}\right) \qquad ...(iv)$$

Now from eqns. (*iii*) and (*iv*), we get

$$T_1 - T_2 = T_2 - T_3$$

$$2T_2 = T_1 + T_3 = 550 + 350$$

$$\therefore \quad T_2 = 450 \text{ K}$$

Hence **intermediate temperature = 450 K. (Ans.)**

Example 5.16. *A Carnot heat engine draws heat from a reservoir at temperature T_1 and rejects heat to another reservoir at temperature T_3. The Carnot forward cycle engine drives a Carnot reversed cycle engine or Carnot refrigerator which absorbs heat from reservoir at temperature T_2 and rejects heat to a reservoir at temperature T_3. If the high temperature $T_1 = 600$ K and low temperature $T_2 = 300$ K, determine :*

(*i*) *The temperature T_3 such that heat supplied to engine Q_1 is equal to the heat absorbed by refrigerator Q_2.*

(*ii*) *The efficiency of Carnot engine and C.O.P. of Carnot refrigerator.*

Solution. Refer Fig. 5.18.

Temperature, $T_1 = 600$ K

Temperature, $T_2 = 300$ K

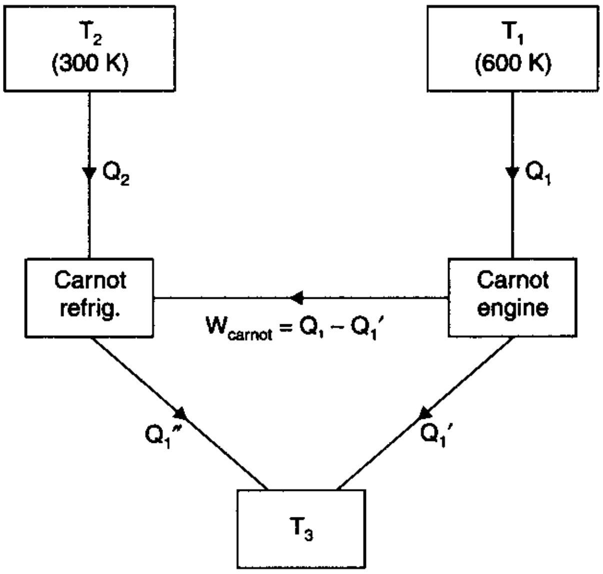


Fig. 5.18

Efficiency of Carnot engine,

$$\eta_{carnot\ engine} = \frac{Q_1 - Q_1'}{Q_1} = \frac{T_1 - T_3}{T_1}$$

$$= \frac{\text{Work of Carnot engine}}{\text{Heat supplied to the Carnot engine}} = \frac{W_{carnot}}{Q_1}$$

or $$W_{carnot} = Q_1\left(\frac{T_1 - T_3}{T_1}\right) \quad ...(i)$$

Also $$\text{C.O.P.}_{(carnot\ refrigerator)} = \frac{Q_2}{Q_1'' - Q_2} = \frac{T_2}{T_3 - T_2}$$

$$= \frac{\text{Heat absorbed}}{W_{carnot}} = \frac{Q_2}{W_{carnot}}$$

or $$W_{carnot} = Q_2\left(\frac{T_3 - T_2}{T_2}\right) \quad ...(ii)$$

(*i*) **Temperature, T_3 :**

From eqns. (*i*) and (*ii*), we get

$$Q_1\left(\frac{T_1 - T_3}{T_1}\right) = Q_2\left(\frac{T_3 - T_2}{T_2}\right)$$

∴ $$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}\left(\frac{T_1 - T_3}{T_3 - T_2}\right)$$

or $$\frac{Q_2}{Q_1} = 1 = \frac{300}{600}\left(\frac{600 - T_3}{T_3 - 300}\right)$$

or $$600 - T_3 = 2(T_3 - 300)$$

$$600 - T_3 = 2T_3 - 600 \quad \text{or} \quad T_3 = 400 \text{ K}$$

Hence, **temperature, T_3 = 400 K. (Ans.)**

(*ii*) Efficiency of Carnot engine,

$$\eta_{carnot\ engine} = \frac{T_1 - T_3}{T_1} = \frac{600 - 400}{600} = 0.3333 = \mathbf{33.33\%}. \quad \textbf{(Ans.)}$$

$$\text{C.O.P.}_{refrigerator} = \frac{T_2}{T_3 - T_2} = \frac{300}{400 - 300} = \mathbf{3}. \quad \textbf{(Ans.)}$$

Example 5.17. *A heat pump working on a reversed carnot cycle takes in energy from a reservoir maintained at 5°C and delivers it to another reservoir where temperature is 77°C. The heat pump derives power for its operation from a reversible engine operating within the higher and lower temperatures of 1077°C and 77°C. For 100 kJ/kg of energy supplied to reservoir at 77°C, estimate the energy taken from the reservoir at 1077°C.* **(U.P.S.C., 1994)**

Solution. *Given :* $T_3 = 5 + 273 = 278$ K ; $T_2 = T_4 = 77 + 273 = 350$ K ;

$T_1 = 273 + 1077 = 1350$ K ;

Energy taken from the revervoir at 1077°C, Q_1 :

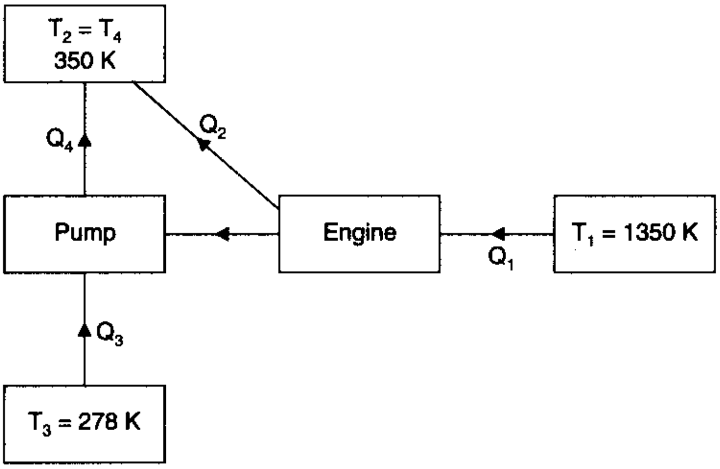


Fig. 5.19

For reversible engine, $\eta = \dfrac{Q_1 - Q_2}{Q_1} = \dfrac{T_1 - T_2}{T_1}$ ...(*i*)

or $1 - \dfrac{Q_2}{Q_1} = 1 - \dfrac{T_2}{T_1}$

∴ $\dfrac{Q_1}{Q_2} = \dfrac{T_1}{T_2}$

For reversible heat pump, C.O.P. $= \dfrac{Q_4}{Q_4 - Q_3} = \dfrac{T_4}{T_4 - T_3}$ ...(*ii*)

Since work for running the pump is being supplied by the engine

∴ $Q_1 - Q_2 = Q_4 - Q_3$

or $\dfrac{Q_1}{T_1}(T_1 - T_2) = \dfrac{Q_4}{T_4}(T_4 - T_3)$ [From (*i*) and (*ii*)]

$$\therefore \qquad \frac{Q_1}{Q_4} = \frac{T_1}{T_4}\left(\frac{T_4 - T_3}{T_1 - T_2}\right)$$

$$= \frac{1350}{350}\left(\frac{350 - 278}{1350 - 350}\right) = 0.278$$

or $$Q_4 = \frac{Q_1}{0.278} = 3.6\ Q_1$$

and $$Q_2 = \frac{T_2}{T_1} \times Q_1 = \frac{350}{1350} Q_1 = 0.259\ Q_1$$

$$\therefore \qquad Q_4 + Q_2 = (3.6 + 0.259)\ Q_1 = 100$$

$$\therefore \qquad \mathbf{Q_1} = \frac{100}{3.6 + 0.259} = \mathbf{25.9\ kJ.} \quad \textbf{(Ans.)}$$

CLAUSIUS INEQUALITY

☞**Example 5.18.** *300 kJ/s of heat is supplied at a constant fixed temperature of 290°C to a heat engine. The heat rejection takes place at 8.5°C. The following results were obtained :*

(i) 215 kJ/s are rejected.

(ii) 150 kJ/s are rejected.

(iii) 75 kJ/s are rejected.

Classify which of the result report a reversible cycle or irreversible cycle or impossible results.

Solution. Heat supplied at 290°C = 300 kJ/s

Heat rejected at 8.5°C : (*i*) 215 kJ/s, (*ii*) 150 kJ/s, (*iii*) 75 kJ/s.

Applying *Clausius inequality* to the cycle or process, we have :

(*i*) $$\sum_{\text{cycle}} \frac{\delta Q}{T} = \frac{300}{290 + 273} - \frac{215}{8.5 + 273}$$

$$= 0.5328 - 0.7637 = -\ 0.2309 < 0.$$

∴ **Cycle is irreversible. (Ans.)**

(*ii*) $$\sum_{\text{cycle}} \frac{\delta Q}{T} = \frac{300}{290 + 273} - \frac{150}{8.5 + 273}$$

$$= 0.5328 - 0.5328 = 0$$

∴ **Cycle is reversible. (Ans.)**

(*iii*) $$\sum_{\text{cycle}} \frac{\delta Q}{T} = \frac{300}{290 + 273} - \frac{75}{8.5 + 273}$$

$$= 0.5328 - 0.2664 = 0.2664 > 0.$$

This **cycle is impossible** by second law of thermodynamics, *i.e., Clausius inequality.* **(Ans.)**

Example 5.19. *A steam power plant operates between boiler temperature of 160°C and condenser temperature of 50°C. Water enters the boiler as saturated liquid and steam leaves the boiler as saturated vapour. Verify the Clausius inequality for the cycle.*

Given : Enthalpy of water entering boiler = 687 kJ/kg.

Enthalpy of steam leaving boiler = 2760 kJ/kg

Condenser pressure = 0.124×10^5 *N/m*^{2}*.*

Solution. Boiler temperature, $T_1 = 160 + 273 = 433$ K
Condenser temperature, $T_2 = 50 + 273 = 323$ K
From steam tables :

Enthalpy of water entering boiler, $h_{f_1} = 687$ kJ/kg
Enthalpy of steam leaving boiler, $h_2 = 2760$ kJ/kg
Condenser pressure = 0.124×10^5 N/m^2
Boiler pressure = 6.18×10^5 N/m^2 ......(corresponding to 160°C)
Enthalpy of vapour leaving the turbine, $h_3 = 2160$ kJ/kg
(assuming isentropic expansion)

Enthalpy of water leaving the condenser, $h_{f4} = 209$ kJ/kg

Now $Q_{boiler}, Q_1 = h_2 - h_{f1} = 2760 - 687 = 2073$ kJ/kg

and $Q_{condenser}, Q_2 = h_{f4} - h_3 = 209 - 2160 = -1951$ kJ/kg

$$\therefore \quad \sum_{\text{cycle}} \frac{\delta Q}{T} = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = \frac{2073}{433} + \left(\frac{-1951}{323}\right)$$
$$= -1.25 \text{ kJ/kg K}$$
$$< 0. \quad \ldots\ldots \textbf{ Proved.}$$

☞**Example 5.20.** *In a power plant cycle, the temperature range is 164°C to 51°C, the upper temperature being maintained in the boiler where heat is received and the lower temperature being maintained in the condenser where heat is rejected. All other processes in the steady flow cycle are adiabatic. The specific enthalpies at various points are given in Fig. 5.20.*

Verify the Clausius Inequality.

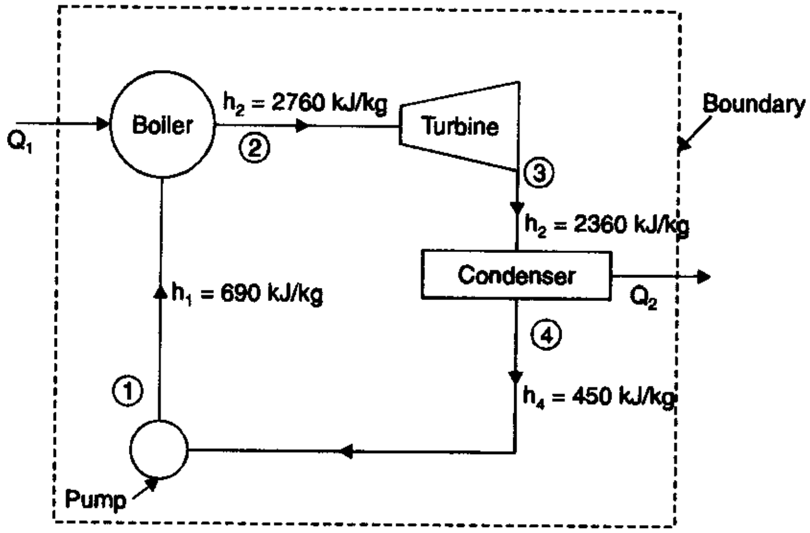


Fig. 5.20

Solution. Temperature maintained in boiler, $T_1 = 164 + 273 = 437$ K
Temperature maintained in condenser, $T_2 = 51 + 273 = 324$ K

Heat transferred in the boiler per kg of fluid,

$$Q_1 = h_2 - h_1 = 2760 - 690 = 2070 \text{ kJ/kg}$$

Heat transferred out at the condenser per kg of fluid,

$$Q_2 = h_4 - h_3 = 450 - 2360 = -\,1910 \text{ kJ/kg}$$

Since there is no transfer of heat at any other point, we have per kg

$$\sum_{\text{cycle}} \frac{\delta Q}{T} = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = \frac{2070}{437} + \left(\frac{-\,1910}{324}\right)$$

$$= 4.737 - 5.895$$

$$= -\,1.158 \text{ kJ/kg K} < 0.$$

The Clausius Inequality is proved. The steady flow cycle is obviously irreversible.

If the cycle is reversible between the same temperature limits and the heat supplied at higher temperature is same, the heat rejected can be calculated as follows :

$$\eta_{reversible} = 1 - \frac{T_2}{T_1} = 1 - \frac{324}{437} = 0.2586 \text{ or } 25.86\%$$

∴ Heat rejected per kg is given by

$$Q_2 = (1 - 0.2586) \times Q_1 = (1 - 0.2586) \times 2070 = 1534.7 \text{ kJ/kg}$$

$$\sum_{\text{cycle}} \frac{\delta Q}{T} = \frac{2070}{437} - \frac{1534.7}{324} = 4.73 - 4.73 = 0$$

i.e.,

$$\sum_{\text{cycle}} \frac{\delta Q}{T} = \frac{Q_{added}}{T_{source}} = \frac{Q_{rejected}}{T_{sink}} = 0$$

Thus **Clausius Equality sign for a reversible engine is verified.**

5.12. ENTROPY

5.12.1. Introduction

In heat engine theory, the term entropy plays a vital role and leads to important results which by other methods can be obtained much more laboriously.

It may be noted that all heat is not equally valuable for converting into work. Heat that is supplied to a substance at high temperature has a greater possibility of conversion into work than heat supplied to a substance at a lower temperature.

*"**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 small when heat is added at a high temperature and is greater when heat addition is made at a lower temperature. Thus for maximum entropy, there is minimum availability for conversion into work and for minimum entropy there is maximum availability for conversion into work."*

5.12.2. Entropy—a Property of a System

Refer Fig. 5.21. Let us consider a system undergoing a reversible process from state 1 to state 2 along path *L* and then from state 2 to the original state 1 along path *M*. Applying the Clausius theorem to this reversible cyclic process, we have

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

(where the subscript designates a reversible cycle)

Hence when the system passes through the cycle 1-L-2-M-1, we have

$$\int_{1(L)}^{2} \frac{\delta Q}{T} + \int_{2(M)}^{1} \frac{\delta Q}{T} = 0 \qquad \text{...(5.16)}$$

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

$$\int_{1(L)}^{2} \frac{\delta Q}{T} + \int_{2(N)}^{1} \frac{\delta Q}{T} = 0 \qquad \text{...(5.17)}$$

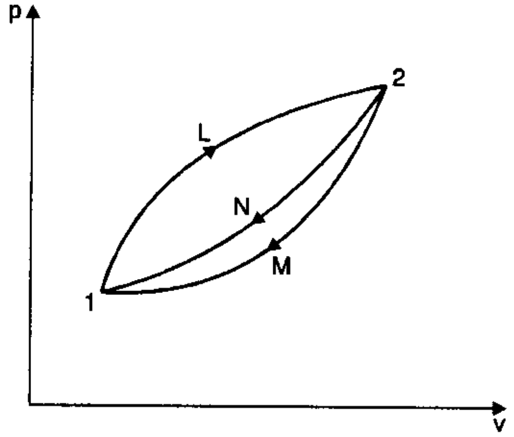


Fig. 5.21. Reversible cyclic process between two fixed end states.

Subtracting equation (5.17) from equation (5.16), we have

$$\int_{2(M)}^{1} \frac{\delta Q}{T} - \int_{2(N)}^{1} \frac{\delta Q}{T} = 0$$

or

$$\int_{1}^{2(M)} \frac{\delta Q}{T} = \int_{1}^{2(N)} \frac{\delta Q}{T}$$

As no restriction is imposed on paths L and M, 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.* This property is known as the **"entropy".**

5.12.3. Change of Entropy in a Reversible Process

Refer Fig. 5.21.

Let S_1 = Entropy at the initial state 1, and

S_2 = Entropy at the final state 2.

Then, the change in entropy of a system, as it undergoes a change from state 1 to 2, becomes

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_R \qquad \text{...(5.18)}$$

Lastly, 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 (5.18) may be written as

$$dS = \left(\frac{\delta Q}{T}\right)_R \quad ...(5.19)$$

where dS is an exact differential.

Thus, from equation (5.19), 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 (5.19) indicates that when an *inexact* differential δQ is divided by an integrating factor T during a reversible process, it becomes an *exact differential.*

The ***third law of thermodynamics*** states *"When a system is at zero absolute temperature, the entropy of system is zero".*

It is clear from the above law that the absolute value of entropy corresponding to a given state of the system could be determined by integrating $\left(\frac{\delta Q}{T}\right)_R$ between the state at absolute zero and the given state. *Zero entropy, however, means the absence of all molecular, atomic, electronic and nuclear disorders.*

As it is not practicable to get data at zero absolute temperature, the change in entropy is calculated either between two known states or by selecting some convenient point at which the entropy is given an arbitrary value of zero. For steam, the reference point at which the entropy is given an arbitrary value of zero is 0°C and for refrigerants like ammonia, Freon-12, carbon dioxide etc. the reference point is – 40°C, at which the entropy it taken as zero.

Thus, in practice we can *determine the change in entropy and not the absolute value of entropy.*

5.13. ENTROPY AND IRREVERSIBILITY

We know that change in entropy in a *reversible process* is equal to $\left(\frac{\delta Q}{T}\right)_R$ (eqn. 5.19). Let us now find the change in entropy in an *irreversible process.*

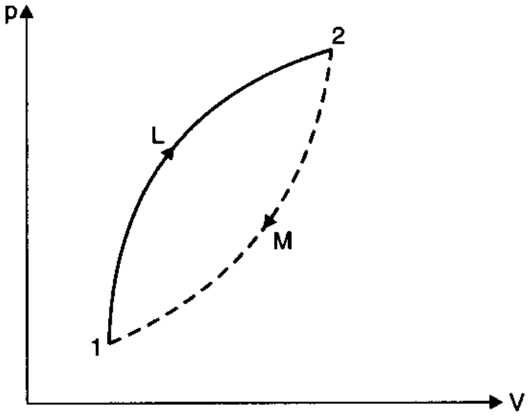


Fig. 5.22. Entropy change for an irreversible process.

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 shown in Fig. 5.22 on the thermodynamic coordinates, pressure and volume.

Since entropy is a thermodynamic property, we can write

$$\oint dS = \int_{1(L)}^{2} (dS)_R + \int_{2(M)}^{1} (dS)_I = 0 \qquad \text{...(5.20)}$$

(Subscript I represents the irreversible process).

Now for a reversible process, from eqn. (5.19), we have

$$\int_{1(L)}^{2} (dS)_R = \int_{1(L)}^{2} \left(\frac{\delta Q}{T}\right)_R \qquad \text{...(5.21)}$$

Substituting the value of $\int_{1(L)}^{2} (dS)_R$ in eqn. (5.20), we get

$$\int_{1(L)}^{2} \left(\frac{\delta Q}{T}\right)_R + \int_{2(M)}^{1} (dS)_I = 0 \qquad \text{...(5.22)}$$

Again, since in eqn. (5.20) the processes 1-L-2 and 2-M-1 together form an irreversible cycle, applying Clausius equality to this expression, we get

$$\oint \frac{\delta Q}{T} = \int_{1(L)}^{2} \left(\frac{\delta Q}{T}\right)_R + \int_{2(M)}^{1} \left(\frac{\delta Q}{T}\right)_I < 0 \qquad \text{...(5.23)}$$

Now subtracting eqn. (5.23) from eqn. (5.22), we get

$$\int_{2(M)}^{1} (dS)_I > \int_{2(M)}^{1} \left(\frac{\delta Q}{T}\right)_I$$

which for infinitesimal changes in states can be written as

$$(dS)_I > \int \left(\frac{\delta Q}{T}\right)_I \qquad \text{...(5.24)}$$

Eqn. (5.24) states that the *change in entropy in an irreversible process is greater than* $\frac{\delta Q}{T}$.

Combining eqns. (5.23) and (5.24), we can write the equation in the general form as

$$dS \geq \frac{\delta Q}{T} \qquad \text{...(5.25)}$$

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.*

Let us now consider an *isolated system.* We know that in an isolated system, matter, work or heat cannot cross the boundary of the system. Hence according to first law of thermodynamics, the internal energy of the system will remain constant.

Since for an isolated system, $\delta Q = 0$, from eqn. (5.25), we get

$$(dS)_{isolated} \geq 0 \qquad \text{...(5.26)}$$

Eqn. (5.26) states that the *entropy of an isolated system either increases or remains constant.* This is a corollary of the second law. It explains the *principle of increase in entropy.*

5.14. CHANGE IN ENTROPY OF THE UNIVERSE

We know that the entropy of an isolated system either increase or remains constant, *i.e.,*

$$(dS)_{isolated} \geq 0$$

By including any system and its surrounding within a single boundary, as shown in Fig. 5.23, an isolated system can be formed. The combination of the system and the surroundings within a single boundary is sometimes called the **Universe.** Hence, applying the principle of increase in entropy, we get

$$(dS)_{universe} \geqq 0$$

where $(dS)_{universe} = (dS)_{system} + (dS)_{surroundings}$.

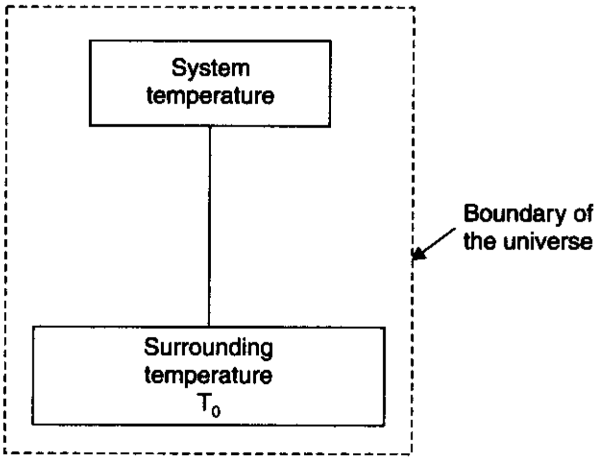


Fig. 5.23. Entropy change of universe.

In the combined closed system consider that a quantity of heat δQ is transferred from the system at temperature T to the surroundings at temperature T_0. Applying eqn. (5.24) to this process, we can write

$$(dS)_{system} > - \frac{\delta Q}{T}$$

(–ve sign indicates that heat is transferred from the system).

Similarly, since an amount of heat δQ is absorbed by the surroundings, for a reversible process, we can write

$$(dS)_{surroundings} = \frac{\delta Q}{T_0}$$

Hence, the total change in entropy for the combined system

$$(dS)_{system} + (dS)_{surroundings} \geq - \frac{\delta Q}{T} + \frac{\delta Q}{T_0}$$

or

$$(dS)_{universe} \geq dQ \left(- \frac{1}{T} + \frac{1}{T_0} \right)$$

The same result can be obtained in the case of an open system.

For both closed and open systems, we can write

$$(dS)_{universe} \geq 0 \qquad \text{...(5.27)}$$

Eqn. (5.27) states that the process involving the interaction of a system and the surroundings takes place only if the net entropy of the combined system increases or in the limit remains constant. *Since all natural processes are irreversible, the entropy is increasing continually.*

The entropy attains its maximum value when the system reaches a stable equilibrium state from a non-equilibrium state. This is the state of maximum disorder and is one of maximum thermodynamic probability.

5.15. TEMPERATURE-ENTROPY DIAGRAM

If entropy is plotted-horizontally and absolute temperature vertically the diagram so obtained is called *temperature-entropy* (*T-s*) diagram. Such a diagram is shown in Fig. 5.24. If working fluid receives a small amount of heat dQ in an elementary portion ab of an operation AB when temperature is T, and if dQ is represented by the shaded area of which T is the mean ordinate, the width of the figure must be $\frac{dQ}{T}$. This is called *'increment of entropy'* and is denoted by dS. The total heat received by the operation will be given by the area under the curve AB and $(S_B - S_A)$ will be corresponding increase of entropy.

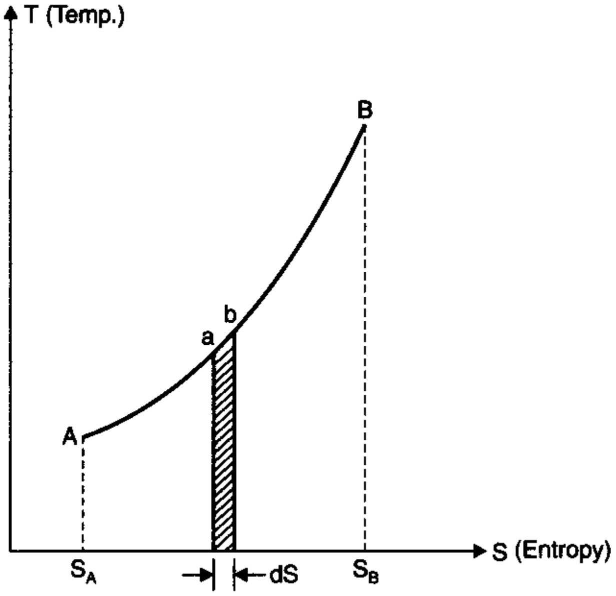


Fig. 5.24. Temperature-entropy diagram.

From above we conclude that :

$$\text{Entropy change, } \quad dS = \frac{\text{Heat change } (Q)}{\text{Absolute temperature } (T)} \ .$$

*"**Entropy** may also be defined as the thermal property of a substance which remains constant when substance is expanded or compressed adiabatically in a cylinder".*

Note. 's' stands for specific entropy whereas 'S' means total entropy (*i.e.*, $S = ms$).

5.16. CHARACTERISTICS OF ENTROPY

The characteristics of entropy in a summarised form are given below :

1. It increases when heat is supplied irrespective of the fact whether temperature changes or not.
2. It decrease when heat is removed whether temperature changes or not.

3. It remains unchanged in all adiabatic frictionless processes.

4. It increases if temperature of heat is lowered without work being done as in a throttling process.

5.17. ENTROPY CHANGES FOR A CLOSED SYSTEM

5.17.1. General Case for Change of Entropy of a Gas

Let 1 kg of gas at a pressure p_1, volume v_1, absolute temperature T_1 and entropy s_1, be heated such that its final pressure, volume, absolute temperature and entropy are p_2, v_2, T_2 and s_2 respectively. Then by law of conservation of energy,

$$dQ = du + dW$$

where, dQ = Small change of heat,

du = Small internal energy, and

dW = Small change of work done (pdv).

Now $$dQ = c_v dT + pdv$$

Dividing both sides by T, we get

$$\frac{dQ}{T} = \frac{c_v dT}{T} + \frac{pdv}{T}$$

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

and as $$pv = RT$$

$\therefore$ $$\frac{p}{T} = \frac{R}{v}$$

Hence $$ds = \frac{c_v dT}{T} + R\frac{dv}{v}$$

Integrating both sides, we get

$$\int_{s_1}^{s_2} ds = c_v \int_{T_1}^{T_2} \frac{dT}{T} + R\int_{v_1}^{v_2} \frac{dv}{v}$$

or $$(s_2 - s_1) = c_v \log_e \frac{T_2}{T_1} + R \log_e \frac{v_2}{v_1} \quad ...(5.28)$$

This expression can be reproduced in the following way :

According to the gas equation, we have

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$$

or $$\frac{T_2}{T_1} = \frac{p_2}{p_1} \times \frac{v_2}{v_1}$$

Substituting the value of $\frac{T_2}{T_1}$ in eqn. (5.28), we get

$$s_2 - s_1 = c_v \log_e \frac{p_2}{p_1} \times \frac{v_2}{v_1} + R \log_e \frac{v_2}{v_1}$$

$$= c_v \log_e \frac{p_2}{p_1} + c_v \log_e \frac{v_2}{v_1} + R \log_e \frac{v_2}{v_1}$$

$$= c_v \log_e \frac{p_2}{p_1} + (c_v + R) \log_e \frac{v_2}{v_1}$$

$$= c_v \log_e \frac{p_2}{p_1} + c_p \log_e \frac{v_2}{v_1}$$

$$\therefore \quad s_2 - s_1 = c_v \log_e \frac{p_2}{p_1} + c_p \log_e \frac{v_2}{v_1} \quad \text{...(5.29)}$$

Again, from gas equation,

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2} \quad \text{or} \quad \frac{v_2}{v_1} = \frac{p_1}{p_2} \times \frac{T_2}{T_1}$$

Putting the value of $\frac{v_2}{v_1}$ in eqn. (5.28), we get

$$(s_2 - s_1) = c_v \log_e \frac{T_2}{T_1} + R \log_e \frac{p_1}{p_2} \times \frac{T_2}{T_1}$$

$$= c_v \log_e \frac{T_2}{T_1} + R \log_e \frac{p_1}{p_2} + R \log_e \frac{T_2}{T_1}$$

$$= (c_v + R) \log_e \frac{T_2}{T_1} - R \log_e \frac{p_2}{p_1}$$

$$= c_p \log_e \frac{T_2}{T_1} - R \log_e \frac{p_2}{p_1}$$

$$\therefore \quad s_2 - s_1 = c_p \log_e \frac{T_2}{T_1} - R \log_e \frac{p_2}{p_1}. \quad \text{...(5.30)}$$

5.17.2. Heating a Gas at Constant Volume

Refer Fig. 5.25. 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.

Then $\quad Q = c_v(T_2 - T_1)$

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

$$dQ = c_v dT$$

Dividing both sides by T, we get

$$\frac{dQ}{T} = c_v \cdot \frac{dT}{T}$$

or

$$ds = c_v \cdot \frac{dT}{T}$$

Integrating both sides, we get

$$\int_{s_1}^{s_2} ds = c_v \int_{T_1}^{T_2} \frac{dT}{T}$$

or

$$s_2 - s_1 = c_v \log_e \frac{T_2}{T_1} \quad \text{...(5.31)}$$

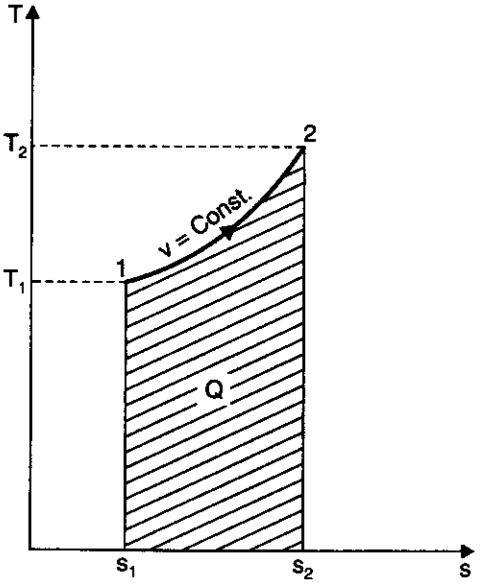


Fig. 5.25. T-s diagram : Constant volume process

5.17.3. Heating a Gas at Constant Pressure

Refer Fig. 5.26. 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.

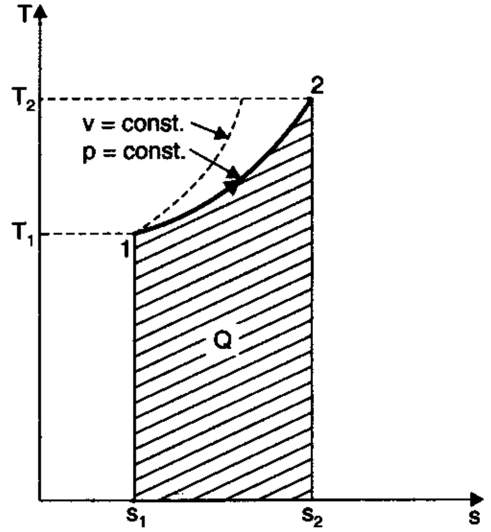


Fig. 5.26. *T-s* diagram : Constant pressure process.

Then, $Q = c_p(T_2 - T_1)$.

Differentiating to find small increase in heat, dQ of this gas when the temperature rise is dT.

$$dQ = c_p \, . \, dT$$

Dividing both sides by T, we get

$$\frac{dQ}{T} = c_p . \frac{dT}{T}$$

or

$$ds = c_p \, . \, \frac{dT}{T}$$

Integrating both sides, we get

$$\int_{s_1}^{s_2} ds = c_p \int_{T_1}^{T_2} \frac{dT}{T}$$

$$s_2 - s_1 = c_p \log_e \frac{T_2}{T_1} \qquad \text{...(5.32)}$$

5.17.4. Isothermal Process

An isothermal expansion 1-2 at constant temperature T is shown in Fig. 5.27.

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. In other words, $Q = W$.

But $$Q = \int_{s_1}^{s_2} Tds = T(s_2 - s_1)$$

and $$W = p_1 v_1 \log_e \frac{v_2}{v_1} = RT_1 \log_e \frac{v_2}{v_1} \text{ per kg of gas} \qquad [\because \; p_1 v_1 = RT_1]$$

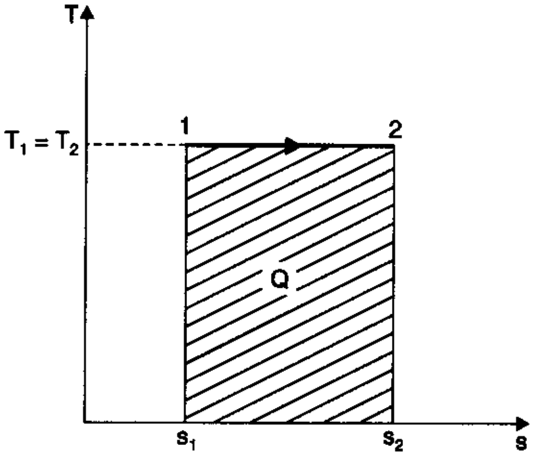


Fig. 5.27. *T-s* diagram : Isothermal process.

$$\therefore \qquad T(s_2 - s_1) = RT_1 \log_e \frac{v_2}{v_1}$$

or $$s_2 - s_1 = R \log_e \frac{v_2}{v_1}. \qquad [\because \; T_1 = T_2 = T] \qquad ...(5.33)$$

5.17.5. Adiabatic Process (Reversible)

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

$$dQ = 0$$

or $$\frac{dQ}{dT} = 0$$

or $$ds = 0 \qquad ...(5.34)$$

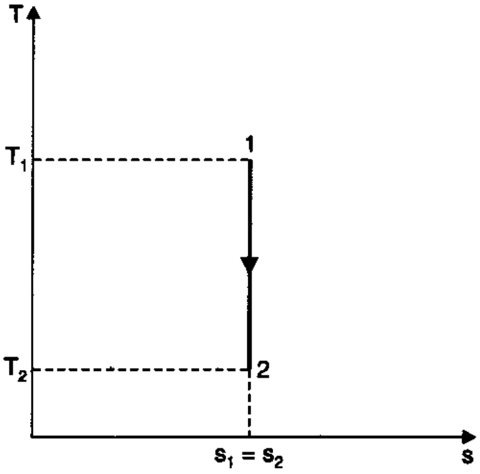


Fig. 5.28. *T-s* diagram : Adiabatic process.

This shows that there is no change in entropy and hence it is known as *isentropic process.*

Fig. 5.28 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.

5.17.6. Polytropic Process

Refer Fig. 5.29.

The expression for 'entropy change' in polytropic process (pv^n = constant) can be obtained from eqn. (5.28)

i.e.,
$$s_2 - s_1 = c_v \log_e \frac{T_2}{T_1} + R \log_e \frac{v_2}{v_1}$$

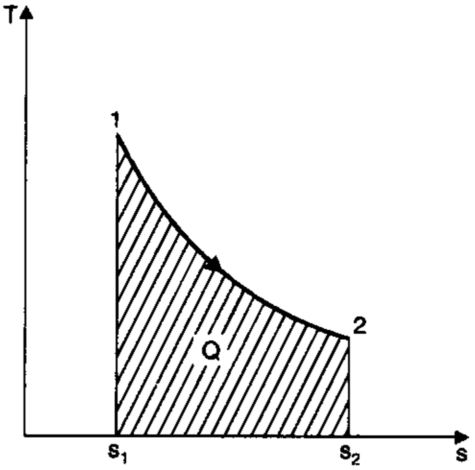


Fig. 5.29. *T-s* diagram : Polytropic process.

Also
$$p_1 v_1^n = p_2 v_2^n$$

or
$$\frac{p_1}{p_2} = \left(\frac{v_2}{v_1}\right)^n \qquad \text{...(i)}$$

Again, as
$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$$

or
$$\frac{p_1}{p_2} = \frac{v_2}{v_1} \times \frac{T_1}{T_2} \qquad \text{...(ii)}$$

From (*i*) and (*ii*), we get
$$\left(\frac{v_2}{v_1}\right)^n = \frac{v_2}{v_1} \times \frac{T_1}{T_2}$$

or
$$\left(\frac{v_2}{v_1}\right)^{n-1} = \frac{T_1}{T_2}$$

or
$$\frac{v_2}{v_1} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{n-1}}$$

Substituting the value of $\frac{v_2}{v_1}$ in eqn. (5.28), we get
$$s_2 - s_1 = c_v \log_e \frac{T_2}{T_1} + R \log_e \left(\frac{T_1}{T_2}\right)^{\frac{1}{n-1}} = c_v \log_e \frac{T_2}{T_1} + R \left(\frac{1}{n-1}\right) \log_e \frac{T_1}{T_2}$$

$$= c_v \log_e \frac{T_2}{T_1} - R\left(\frac{1}{n-1}\right)\log_e \frac{T_2}{T_1}$$

$$= c_v \log_e \frac{T_2}{T_1} - (c_p - c_v) \times \left(\frac{1}{n-1}\right)\log_e \frac{T_2}{T_1} \qquad [\because \ R = c_p - c_v]$$

$$= c_v \log_e \frac{T_2}{T_1} - (\gamma . c_v - c_v) \times \left(\frac{1}{n-1}\right)\log_e \frac{T_2}{T_1} \qquad [\because \ c_p = \gamma . c_v]$$

$$= c_v\left[1 - \left(\frac{\gamma-1}{n-1}\right)\right]\log_e \frac{T_2}{T_1} = c_v\left[\frac{(n-1)-(\gamma-1)}{(n-1)}\right]\log_e \frac{T_2}{T_1}$$

$$= c_v\left(\frac{n-1-\gamma+1)}{n-1}\right)\log_e \frac{T_2}{T_1}$$

$$= c_v . \left(\frac{n-\gamma}{n-1}\right)\log_e \frac{T_2}{T_1} \text{ per kg of gas}$$

$$\therefore \qquad s_2 - s_1 = c_v\left(\frac{n-\gamma}{n-1}\right)\log_e \frac{T_2}{T_1} \text{ per kg of gas} \qquad ...(5.35)$$

5.17.7. Approximation For Heat Absorbed

The curve *LM* shown in the Fig. 5.30 is obtained by heating 1 kg of gas from initial state *L* to final state *M*. Let temperature during heating increases from T_1 to T_2. Then heat absorbed by the gas will be given by the area (shown shaded) under curve *LM*.

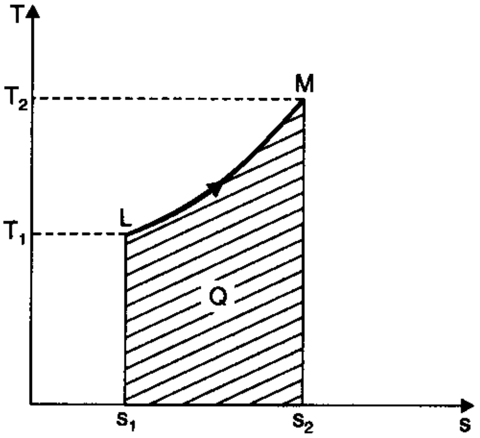


Fig. 5.30

As the curve on *T-s* diagram which represents the heating of the gas, usually has very slight curvature, it can be assumed a straight line for a small temperature range. Then,

Heat absorbed = Area under the curve *LM*

$$= (s_2 - s_1)\left(\frac{T_1 + T_2}{2}\right) \qquad ...(5.36)$$

In other words, heat absorbed *approximately* equals the product of change of entropy and mean absolute temperature.

Table 5.1. Summary of Formulae

S. No.	*Process*	*Change of entropy (per kg)*
1.	General case	(*i*) $c_v \log_e \frac{T_2}{T_1} + R \log_e \frac{v_2}{v_1}$ (in terms of T and v) (*ii*) $c_v \log_e \frac{p_2}{p_1} + c_v \log_e \frac{v_2}{v_1}$ (in terms of p and v) (*iii*) $c_p \log_e \frac{T_2}{T_1} - R \log_e \frac{p_2}{p_1}$ (in terms of T and p)
2.	Constant volume	$c_v \log_e \frac{T_2}{T_1}$
3.	Constant pressure	$c_p \log_e \frac{T_2}{T_1}$
4.	Isothermal	$R \log_e \frac{v_2}{v_1}$
5.	Adiabatic	Zero
6.	Polytropic	$c_v \left(\frac{n-\gamma}{n-1}\right) \log_e \frac{T_2}{T_1}$

5.18. ENTROPY CHANGES FOR AN OPEN SYSTEM

In an open system, as compared with closed system, there is additional change of entropy due to the mass crossing the boundaries of the system. *The net change of entropy of a system due to mass transport is equal to the difference between the product of the mass and its specific entropy at the inlet and at the outlet of the system.* Therefore, the total change of entropy of the system during a small interval is given by

$$dS \geq \frac{dQ}{T_0} + \Sigma s_i \,.\, dm_i - \Sigma s_0 \,.\, dm_0$$

where,
T_0 = Temperature of the surroundings,
s_i = Specific entropy at the inlet,
s_0 = Specific entropy at the outlet,
dm_i = Mass entering the system, and
dm_0 = Mass leaving the system.

(Subscripts i and 0 refer to inlet and outlet conditions)

The above equation in general form can be written as

$$dS \geq \frac{dQ}{T_0} + \sum s \,.\, dm \qquad \text{...(5.37)}$$

In equation (5.37) entropy flow *into* the system is considered *positive* and entropy *out-flow* is considered *negative*. The *equality sign is applicable to reversible process* in which the heat interactions and mass transport to and from the system is accomplished reversibly. The *inequality sign is applicable to irreversible processes.*

If equation (5.37) is divided by dt, then it becomes a rate equation and is written as

$$\frac{dS}{dt} \geq \frac{1}{T_0} \cdot \frac{dQ}{dt} + \sum s \cdot \frac{dm}{dt} \qquad \text{...(5.38)}$$

In a steady-state, steady flow process, the rate of change of entropy of the system $\left(\frac{dS}{dt}\right)$ becomes zero.

$$\therefore \qquad O \geq \frac{1}{T_0} \frac{dQ}{dt} + \sum s \cdot \frac{dm}{dt}$$

or

$$\frac{1}{T_0} \dot{Q} + \Sigma s \,.\, \dot{m} \leq 0 \qquad \text{...(5.39)}$$

where $\dot{Q} = \frac{dQ}{dt}$

and $\dot{m} = \frac{dm}{dt}$.

For *adiabatic steady flow process,* $\dot{Q} = 0$

$$\sum s \,.\, \dot{m} \leq 0 \qquad \text{...(5.40)}$$

If the process is *reversible adiabatic*, then

$$\sum s \,.\, \dot{m} = 0 \qquad \text{...(5.41)}$$

5.19. THE THIRD LAW OF THERMODYNAMICS

- The third law of thermodynamics is stated as follow :

  "The entropy of all perfect crystalline solids is zero at absolute zero temperature".
- The third law of thermodynamics, often referred to as *Nernst Law*, provides the basis for the calculation of absolute entropies of substances.

According to this law, if the entropy is zero at $T = 0$, the absolute entropy $s_{ab.}$ of a substance at any temperature T and pressure p is expressed by the expression.

$$s_{ab} = \int_0^{T_s = T_{f1}} c_{ps} \frac{dT}{T} + \frac{h_{sf}}{T_s} + \int_{T_s}^{T_{f2} = T_g} c_{pf} \frac{dT}{T} + \frac{h_{fg}}{T_g} \int_{T_g}^{T} c_{pg} \frac{dT}{T} \qquad \text{...(5.42)}$$

where $T_s = T_{f1} = T_{sf} = T_{sat}$ ...... for fusion,

$T_{f2} = T_g = T_{fg} = T_{sat}$ ......for vaporisation

c_{ps}, c_{pf}, c_{pg} = Constant pressure specific heats for solids, liquids and gas,

h_{sf}, h_{fg} = Latent heats of fusion and vaporisation.

Thus by putting $s = 0$ at $T = 0$, one may integrate zero kelvin and standard state of 278.15 K and 1 atm., and find the entropy difference.

- Further, it can be shown that the entropy of a crystalline substance at $T = 0$ is not a function of pressure, *viz.,*

$$\left(\frac{\partial s}{\partial p}\right)_{T=0} = 0$$

However, *at temperatures above absolute zero, the entropy is a function of pressure also.* The absolute entropy of a substance at 1 atm pressure can be calculated using eqn. (5.42) ; for pressures different from 1 atm, necessary corrections have to be applied.

ENTROPY

Exmaple 5.21. *An iron cube at a temperature of 400°C is dropped into an insulated bath containing 10 kg water at 25°C. The water finally reaches a temperature of 50°C at steady state. Given that the specific heat of water is equal to 4186 J/kg K. Find the entropy changes for the iron cube and the water. Is the process reversible ? If so why ?* **(GATE, 1996)**

Solution. *Given* : Temperature of iron cube = 400°C = 673 K
Temperature of water = 25°C = 298 K
Mass of water = 10 kg
Temperature of water and cube after equilibrium = 50°C = 323 K
Specific heat of water, c_{pw} = 4186 J/kg K

Entropy changes for the iron cube and the water :

Is the process reversible ?

Now, Heat lost by iron cube = Heat gained by water

$$m_i\, c_{pi}\,(673 - 323) = m_w\, c_{pw}\,(323 - 298)$$
$$= 10 \times 4186\,(323 - 298)$$

$$\therefore \qquad m_i\, c_{pi} = \frac{10 \times 4186\,(323 - 298)}{(623 - 323)} = 2990$$

where, m_i = Mass of iron, kg, and
c_{pi} = Specific heat of iron, J/kg K

$$\text{Entropy of iron at } 673 \text{ K} = m_i\, c_{pi} \ln\left(\frac{673}{273}\right)$$
$$= 2990 \ln\left(\frac{673}{273}\right)$$
$$= 2697.8 \text{ J/K} \qquad \text{[Taking 0°C as datum]}$$

$$\text{Entropy of water at } 298 \text{ K} = m_w\, c_{pw} \ln\left(\frac{298}{273}\right)$$
$$= 10 \times 4186 \ln\left(\frac{298}{273}\right) = 3667.8 \text{ J/K}$$

$$\text{Entropy of iron at } 323 \text{ K} = 2990 \times \ln\left(\frac{323}{273}\right) = 502.8 \text{ J/K}$$

$$\text{Entropy water at } 323 \text{ K} = 10 \times 4186 \ln\left(\frac{323}{273}\right) = 7040.04 \text{ J/K}$$

Changes in entropy of iron = 502.8 − 2697.8 = − 2195 J/K
Change in entropy of water = 7040.04 − 3667.8 = 3372.24 J/K
Net change in entropy = 3372.24 − 2195 = 1177.24 J/K

Since $\Delta S > 0$ hence the process is **irrevesible. (Ans.)**

Example 5.22. *An ideal gas is heated from temperature T_1 to T_2 by keeping its volume constant. The gas is expanded back to its initial temperature according to the law pv^n = constant. If the entropy change in the two processes are equal, find the value of n in terms of the adiabatic index γ.* **(U.P.S.C., 1997)**

Solution. Change in entropy during constant volume process

$$= m\, c_v \ln \left(\frac{T_2}{T_1}\right) \qquad ...(i)$$

Change in entropy during polytropic process (pv^n = constant)

$$= m\, c_v \left(\frac{\gamma - n}{n - 1}\right) \ln \left(\frac{T_2}{T_1}\right) \qquad ...(ii)$$

For the same entropy, equating (*i*) and (*ii*), we have

$$\frac{\gamma - n}{n - 1} = 1, \qquad \text{or} \qquad (\gamma - n) = (n - 1) \qquad \text{or} \qquad 2n = \gamma + 1$$

$$\therefore \qquad \mathbf{n} = \frac{\gamma + 1}{2}. \quad \textbf{(Ans).}$$

Example 5.23. *Air at 20°C and 1.05 bar occupies 0.025 m³. The air is heated at constant volume until the pressure is 4.5 bar, and then cooled at constant pressure back to original temperature. Calculate :*

(*i*) *The net heat flow from the air.*

(*ii*) *The net entropy change.*

Sketch the process on T-s diagram.

Solution. The processes are shown on a *T-s* diagram in Fig. 5.31.

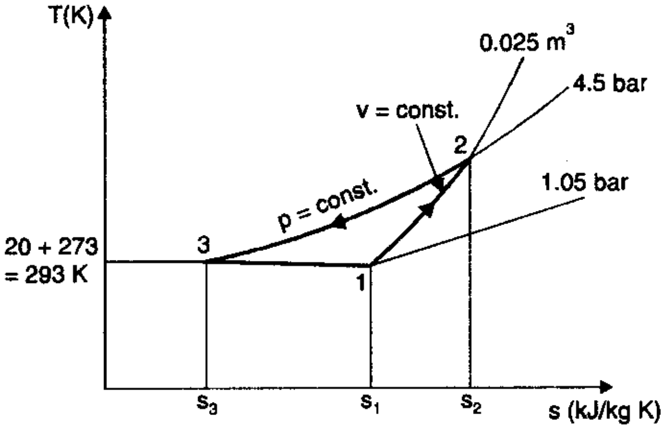


Fig. 5.31

For air :

Temperature, $T_1 = 20 + 273 = 293$ K

Volume, $V_1 = V_3 = 0.025$ m³

Pressure, $p_1 = 1.05$ bar $= 1.05 \times 10^5$ N/m²

Pressure, $p_2 = 4.5$ bar $= 4.5 \times 10^5$ N/m².

(*i*) **Net heat flow :**

For a perfect gas (corresponding to point 1 of air),

$$m = \frac{p_1 V_1}{R T_1} = \frac{1.05 \times 10^5 \times 0.025}{0.287 \times 10^3 \times 293} = 0.0312 \text{ kg}$$

For a perfect gas at *constant volume*,

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

$$\frac{1.05}{293} = \frac{4.5}{T_2} \quad \text{or} \quad T_2 = \frac{4.5 \times 293}{1.05} = 1255.7 \text{ K.}$$

At **constant volume,**

$$Q = mc_v\,(T_2 - T_1) = 0.0312 \times 0.718\,(1255.7 - 293)$$

i.e., $Q_{1-2} = 21.56$ kJ.

Also, at **constant pressure,**

$$Q = m \times c_p \times (T_3 - T_2) = 0.0312 \times 1.005\,(293 - 1255.7)$$

i.e., $Q_{2-3} = -\ 30.18$ kJ

∴ **Net heat flow** $= Q_{1-2} + Q_{2-3} = 21.56 + (-\ 30.18) = -\ 8.62$ kJ

i.e., **Heat rejected = 8.62 kJ. (Ans.)**

(*ii*) **Net entropy change :**

Referring to Fig. 5.31.

Net decrease in entropy,

$$S_1 - S_2 = (S_2 - S_3) - (S_2 - S_1)$$

At **constant pressure**, $dQ = mc_p\, dT$, hence

$$m(s_2 - s_3) = \int_{293}^{1255.7} \frac{mc_p dT}{T}$$

$$= 0.0312 \times 1.005 \times \log_e \frac{1255.7}{293}$$

i.e., $S_2 - S_3 = 0.0456$ kJ/K

At **constant volume**, $dQ = mc_v\, dT$, hence

$$m(s_2 - s_1) = \int_{293}^{1255.7} \frac{mc_v dT}{T}$$

$$= 0.0312 \times 0.718 \times \log_e \frac{1255.7}{293} = 0.0326 \text{ kJ/K}$$

i.e., $S_2 - S_1 = 0.0326$ kJ/K

$$\therefore \quad m(s_1 - s_3) = S_1 - S_3 = (S_2 - S_3) - (S_2 - S_1)$$

$$= 0.0456 - 0.0326 = 0.013 \text{ kJ/K}$$

Hence, **decrease in entropy = 0.013 kJ/K. (Ans.)**

Note that since *entropy is a property*, the decrease in entropy is given by $S_1 - S_3$, is *independent of the process undergone between states 1 and 3.*

Example 5.24. *0.04 m*^{3} *of nitrogen contained in a cylinder behind a piston is initially at 1.05 bar and 15°C. The gas is compressed isothermally and reversibly until the pressure is 4.8 bar. Calculate :*

(*i*) *The change of entropy,*

(*ii*) *The heat flow, and*

(*iii*) *The work done.*

Sketch the process on a p-v and T-s diagram.

Assume nitrogen to act as a perfect gas. Molecular weight of nitrogen = 28.

Solution. Refer Fig. 5.32.

Initial pressure, $p_1 = 1.05 \text{ bar} = 1.05 \times 10^5 \text{ N/m}^2$

Initial volume, $V_1 = 0.04 \text{ m}^3$

Temperature, $T_1 = 15 + 273 = 288 \text{ K}$

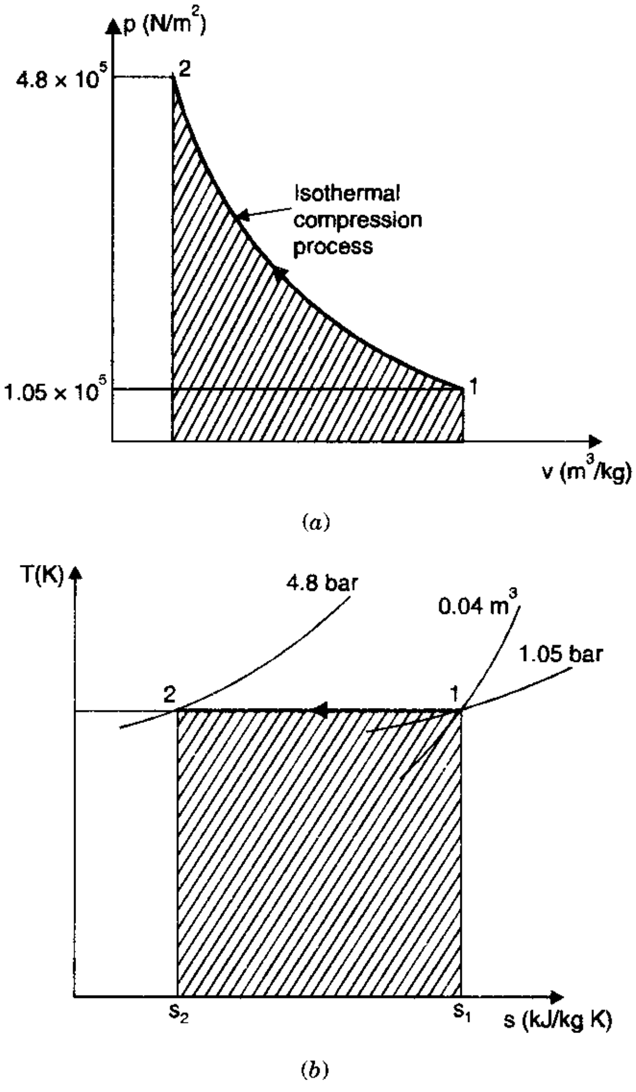
Final pressure, $p_2 = 4.8 \text{ bar} = 4.8 \times 10^5 \text{ N/m}^2$

Final temperature, $T_2 = T_1 = 288 \text{ K}$.

The process is shown on a *p-v* and a *T-s* diagram in Figs. 5.32 (*a*) and 5.32 (*b*) respectively. The shaded area in Fig. 5.32 (*a*) represents **work input**, and the shaded area on Fig. 5.32 (*b*) represents **heat rejected.**

Characteristic gas constant,

$$R = \frac{\text{Universal gas constant, } R_0}{\text{Molecular weight, } M} = \frac{8314}{28} = 297 \text{ Nm/kg K}$$



(*a*)

(*b*)

Fig. 5.32

Now, using characteristic gas equation (to find mass 'm' of nitrogen), we have :

$$p_1V_1 = mRT_1$$

$$m = \frac{p_1V_1}{RT_1} = \frac{1.05 \times 10^5 \times 0.04}{297 \times 288} = 0.0491 \text{ kg}$$

(*i*) **The change of entropy,**

$$S_2 - S_1 = mR \log_e \frac{p_1}{p_2}$$

$$= 0.0491 \times \frac{297}{10^3} \log_e \left(\frac{1.05}{4.8}\right)$$

i.e., $S_2 - S_1 = - 0.02216$ kJ/K.

∴ **Decrease in entropy, $S_1 - S_2 = 0.02216$ kJ/K. (Ans.)**

(*ii*) **Heat rejected** = Shaded area on Fig. 5.32 (*b*)

$$= T(S_1 - S_2) = 288 \times 0.02216 = \mathbf{6.382 \text{ kJ.}} \quad \textbf{(Ans.)}$$

(*iii*) For an isothermal process for a perfect gas,

$$W = Q = 6.382 \text{ kJ}$$

Hence, **the work done on air = 6.382 kJ. (Ans.)**

Example 5.25. *1 kg of gas enclosed in an isolated box of volume v_1, temperature T_1 and pressure p_1 is allowed to expand freely till volume increases to $v_2 = 2v_1$.*

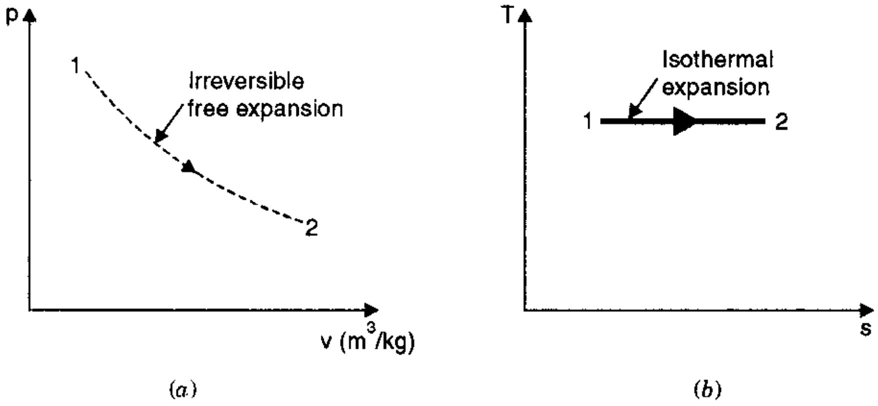
Determine the change in entropy.

Take R for gas as 287 kJ/kg K.

Solution. During the process of free expansion in an isolated box,

$$\Delta U = 0, W = 0 \text{ and } Q = \Delta U + W = 0$$

The process is represented by dotted line on p-v diagram as shown in Fig. 5.33 (*a*) where $v_2 = 2v_1$.



(*a*) (*b*)

Fig. 5.33

To calculate the entropy change, assume that the irreversible free expansion process is replaced by a reversible isothermal process as temperature in free expansion remains constant, in such a way that the volume increases to double of its original as shown in Fig. 5.33 (*b*). As the work is developed by the system and heat is given to the system at constant temperature, during isothermal reversible system then as per first law of thermodynamics :

$$\Delta U = 0,\ Q = W$$

i.e.,
$$Q = \int_{v_1}^{v_2} p\,.dv$$

$$= \int_{v_1}^{v_2} \frac{RT}{v}\,.dv \qquad \left[\because\ pv = RT \text{ and } p = \frac{RT}{v}\right]$$

$$= RT \log_e \frac{v_2}{v_1}$$

$$\therefore \quad \frac{Q}{T} = R \log_e \frac{v_2}{v_1}$$

But this is the expression for change in entropy of the system. Entropy being the property of the system, its change is same whether it is reversible or irreversible process.

∴ For the given process,

$$\Delta s = R \log_e \left(\frac{v_2}{v_1}\right)$$

$$= 287 \log_e (2) \qquad [\because\ v_2 = 2v_1 \text{ (given)}]$$

$$= 198.9 \text{ kJ/kg K}$$

Hence **change in entropy = 198.9 kJ/kg K. (Ans.)**

Example 5.26. *0.04 kg of carbon dioxide (molecular weight = 44) is compressed from 1 bar, 20°C, until the pressure is 9 bar, and the volume is then 0.003 m³. Calculate the change of entropy.*

Take c_p for carbon dioxide as 0.88 kJ/kg K, and assume carbon dioxide to be a perfect gas.

Solution. Mass of carbon dioxide, $m = 0.04$ kg

Molecular weight, $M = 44$

Initial pressure, $p_1 = 1 \text{ bar} = 1 \times 10^5 \text{ N/m}^2$

Initial temperature, $T_1 = 20 + 273 = 293$ K

Final pressure, $p_2 = 9$ bar

Final volume, $V_2 = 0.003 \text{ m}^3$

c_p for carbon dioxide $= 0.88$ kJ/kg K

Change of entropy :

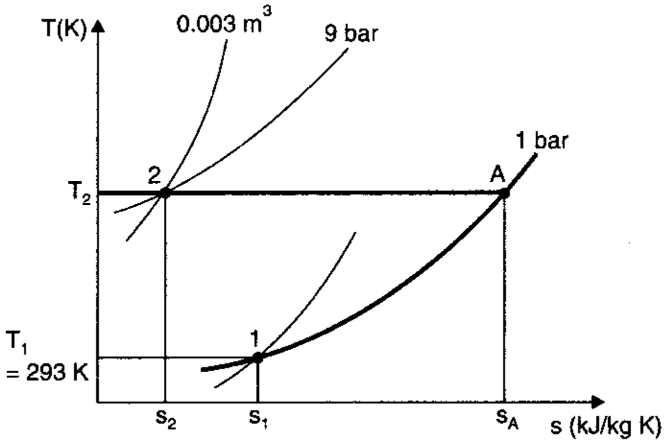


Fig. 5.34

Characteristics gas constant,

$$R = \frac{R_0}{M} = \frac{8314}{44} = 189 \text{ Nm/kg K}$$

To find T_2, using the relation,

$$p_2V_2 = mRT_2$$

$$\therefore \quad T_2 = \frac{p_2V_2}{mR} = \frac{9 \times 10^5 \times 0.003}{0.04 \times 189} = 357 \text{ K}$$

Now $$s_A - s_2 = R \log_e \frac{p_2}{p_1} = \frac{189}{10^3} \log_e \left(\frac{9}{1}\right)$$

$$= 0.4153 \text{ kJ/kg K}$$

Also at constant pressure from 1 to A

$$s_A - s_1 = c_p \log_e \frac{T_2}{T_1} = 0.88 \log_e \left(\frac{357}{293}\right)$$

$$= 0.1738 \text{ kJ/kg K}$$

Then $$(s_1 - s_2) = (s_A - s_2) - (s_A - s_1)$$

$$= 0.4153 - 0.1738 = 0.2415 \text{ kJ/kg K}$$

Hence for 0.04 kg of carbon dioxide **decrease in entropy,**

$$S_1 - S_2 = m(s_1 - s_2) = 0.04 \times 0.2415$$

$$= \mathbf{0.00966 \text{ kJ/K.}} \quad \textbf{(Ans.)}$$

Note. In short, the change of entropy can be found by using the following relation :

$$(s_2 - s_1) = c_p \log_e \frac{T_2}{T_1} - R \log_e \frac{p_2}{p_1} = 0.88 \log_e \left(\frac{357}{293}\right) - \frac{189}{10^3} \log_e \left(\frac{9}{1}\right)$$

$$= 0.1738 - 0.4153 = -0.2415 \text{ kJ/kg K}$$

$$\therefore \quad S_2 - S_1 = m(s_2 - s_1) = 0.04 \times (-0.2415)$$

$$= -0.00966 \text{ kJ/K}$$

(– ve sign means *decrease* in entropy)

or $$S_1 - S_2 = 0.00966 \text{ kJ/K.}$$

Example 5.27. *Calculate the change of entropy of 1 kg of air expanding polytropically in a cylinder behind a piston from 7 bar and 600°C to 1.05 bar. The index of expansion is 1.25.*

Solution. The process is shown on a T-s diagram in Fig. 5.35.

Initial pressure, $p_1 = 7 \text{ bar} = 7 \times 10^5 \text{ N/m}^2$

Initial temperature, $T_1 = 600 + 273 = 873 \text{ K}$

Final pressure, $p_2 = 1.05 \text{ bar} = 1.05 \times 10^5 \text{ N/m}^2$

Index of expansion, $n = 1.25$

Mass of air $= 1 \text{ kg}$

To find T_2, using the relation,

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}$$

$$\therefore \quad \frac{T_2}{873} = \left(\frac{1.05}{7}\right)^{\frac{1.25-1}{1.25}}$$

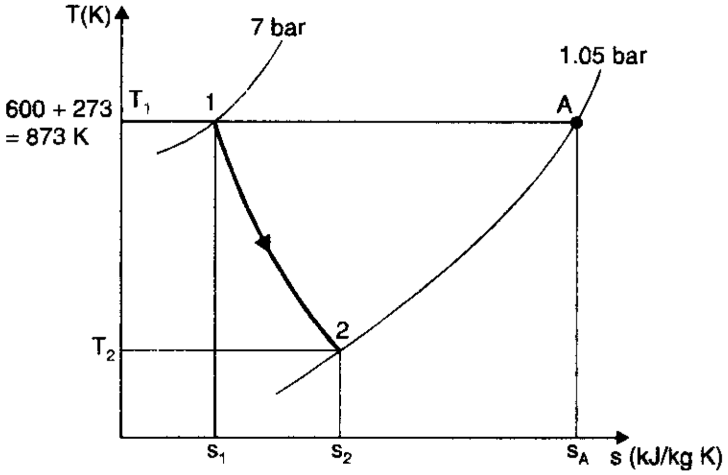


Fig. 5.35

or $$T_2 = 873 \times \left(\frac{1.05}{7}\right)^{\frac{0.25}{1.25}} = 873 \times (0.15)^{0.2} = 597.3 \text{ K}.$$

Now replace the process 1 to 2 by processes, 1 to A and A to 2.

Then at *constant temperature* from 1 to A,

$$s_A - s_1 = R \log_e \frac{v_2}{v_1} = R \log_e \frac{p_1}{p_2} = 0.287 \log_e \left(\frac{7}{1.05}\right) = 0.544 \text{ kJ/kg K}.$$

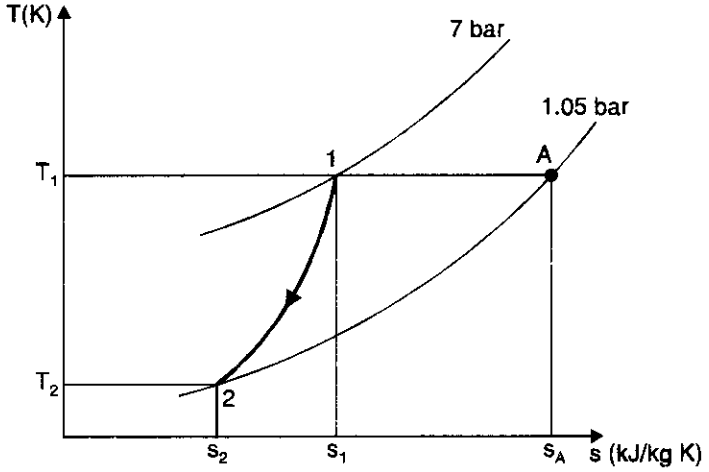


Fig. 5.36

At *constant pressure* from A to 2

$$s_A - s_2 = c_p \log_e \frac{T_1}{T_2} = 1.005 \log_e \frac{873}{597.3} = 0.3814 \text{ kJ/kg K}$$

Then $s_2 - s_1 = 0.544 - 0.3814 = 0.1626$ kJ/kg K

i.e., **Increase in entropy = 0.1626 kJ/kg K. (Ans.)**

Note that if in this problem $s_A - s_2$ happened to be greater than $s_A - s_1$, this would mean that s_1 was greater than s_2, and the process should appear as in Fig. 5.36.

Note. The change of entropy can also be found by using the following relation :

$$s_2 - s_1 = c_v \left(\frac{n-\gamma}{n-1}\right) \log_e \frac{T_2}{T_1}$$

$$= 0.718 \left(\frac{1.25 - 1.399}{1.25 - 1}\right) \log_e \left(\frac{597.3}{873}\right) \qquad \left[\because \gamma = \frac{c_p}{c_v} = \frac{1.005}{0.718} = 1.399\right]$$

$$= 0.718 \times (-0.596) \times (-0.3795) = 0.1626 \text{ kJ/kg K (increase).}$$

Example 5.28. *In an air turbine the air expands from 7 bar and 460°C to 1.012 bar and 160°C. The heat loss from the turbine can be assumed to be negligible.*

(*i*) *Show that the process is irreversible ;*

(*ii*) *Calculate the change of entropy per kg of air.*

Solution. Refer Fig. 5.37.

Initial pressure, $p_1 = 7 \text{ bar} = 7 \times 10^5 \text{ N/m}^2$

Initial temperature, $T_1 = 460 + 273 = 733 \text{ K}$

Final pressure, $p_2 = 1.012 \text{ bar} = 1.012 \times 10^5 \text{ N/m}^2$

Final temperature, $T_2 = 160 + 273 = 433 \text{ K}$

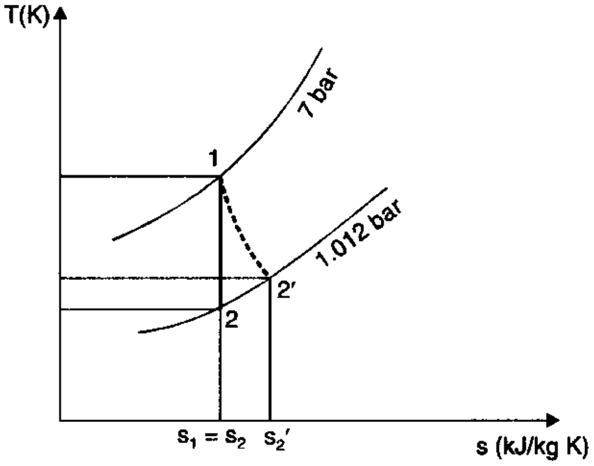


Fig. 5.37

(*i*) **To prove that the process is irreversible :**

Since the heat loss is negligible, the process is ***adiabatic.***

For a reversible adiabatic process for a perfect gas, using the following equation, we have :

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}$$

$$\frac{T_2}{733} = \left(\frac{1.012}{7}\right)^{\left(\frac{1.4-1}{1.4}\right)}$$

$$\therefore \qquad T_2 = 733 \times \left(\frac{1.012}{7}\right)^{\frac{0.4}{1.4}} = 733 \times (0.1446)^{0.286} = 421.6 \text{ K}$$

$$= 421.6 - 273 = 148.6°\text{C}.$$

But the actual temperature is 160°C at the pressure of 1.012 bar, hence the process is irreversible. **Proved.**

(*ii*) **Change of entropy per kg of air :**

The change of entropy $s_2' - s_1$, can be found by considering a reversible constant pressure process between 2 and 2′.

$$\therefore \qquad s_2' - s_2 = c_p \log_e \frac{T_2'}{T_2} = 1.005 \log_e \frac{433}{421.6} = 0.02681 \text{ kJ/kg K}$$

i.e., **Increase of entropy, $s_2' - s_1$ = 0.02681 kJ/kg K. (Ans.)**

☞**Example 5.29.** *A fluid undergoes a reversible adiabatic compression from 4 bar, 0.3 m³ to 0.08 m³ according to the law, $pv^{1.25}$ = constant.*

Determine : (*i*) *Change in enthalpy ;* (*ii*) *Change in internal energy ;*
(*iii*) *Change in entropy ;* (*iv*) *Heat transfer ;*
(*v*) *Work transfer.*

Solution. Refer Fig. 5.38.

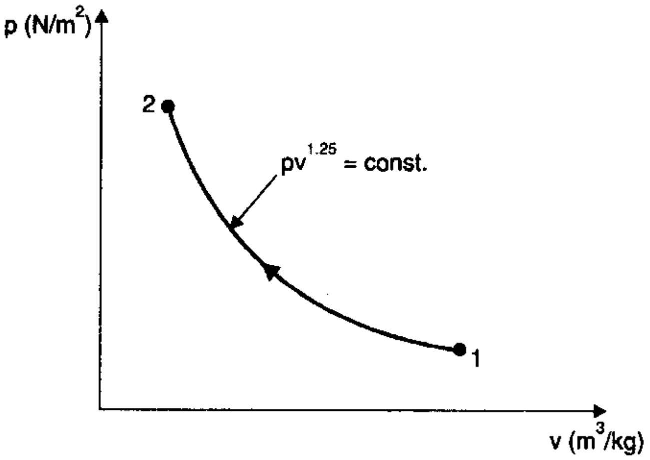


Fig. 5.38

Initial volume, $V_1 = 0.3 \text{ m}^3$
Initial pressure, $p_1 = 4 \text{ bar} = 4 \times 10^5 \text{ N/m}^2$
Final volume, $V_2 = 0.08 \text{ m}^3$
Law of compression : $pv^{1.25}$ = constant.

For reversible adiabatic process,

$$p_1 V_1^n = p_2 V_2^n$$

or

$$\frac{p_2}{p_1} = \left(\frac{V_1}{V_2}\right)^n$$

$$p_2 = p_1 \times \left(\frac{V_1}{V_2}\right)^n = 4 \times \left(\frac{0.3}{0.08}\right)^{1.25} = 20.87 \text{ bar}.$$

(*i*) **Change in enthalpy, $H_2 - H_1$:**

We know that, $$\int_{H_1}^{H_2} dH = \int_{p_1}^{p_2} V dp \qquad ...(i)$$

Also $$p_1V_1^n = pV^n$$

$$\therefore \qquad V = \left(\frac{p_1V_1^n}{p}\right)^{1/n}$$

Substituting this value of V in eqn. (*i*), we get

$$\int_{H_1}^{H_2} dH = \int_{p_1}^{p_2} \left[\left(\frac{p_1V_1^n}{p}\right)\right]^{1/n} dp$$

$$= (p_1V_1^n)^{1/n} \int_{p_1}^{p_2} p^{-1/n}\, dp$$

$$= (p_1V_1^n)^{1/n} \left[\frac{p^{-\frac{1}{n}+1}}{-\frac{1}{n}+1}\right]_{p_1}^{p_2}$$

$$= [(p_1V_1^n)]^{1/n} \left[\frac{p_2^{\left(1-\frac{1}{n}\right)} - p_1^{\left(1-\frac{1}{n}\right)}}{1-\frac{1}{n}}\right]$$

$$= (p_1V_1^n)^{1/n} \times \frac{n}{(n-1)} \left[(p_2)^{\left(1-\frac{1}{n}\right)} - (p_1)^{\left(1-\frac{1}{n}\right)}\right]$$

$$= \frac{n(p_2V_2 - p_1V_1)}{(n-1)} \qquad [\because \ p_1V_1^n = p_2V_2^n]$$

$$= \frac{1.25}{(1.25-1)\times 10^3}\ [20.87 \times 10^5 \times 0.08 - 4 \times 10^5 \times 0.3]\ \text{kJ}$$

$$= \frac{1.25}{0.25 \times 10^3} \times 10^5\ (20.87 \times 0.08 - 4 \times 0.3)\ \text{kJ} = 234.8\ \text{kJ}.$$

Hence, **change in enthalpy = 234.8 kJ. (Ans.)**

(*ii*) **Change in internal energy, $U_2 - U_1$:**

$$H_2 - H_1 = (U_2 + p_2V_2) - (U_1 + p_1V_1)$$

$$= (U_2 - U_1) + (p_2V_2 - p_1V_1)$$

$$\therefore \qquad U_2 - U_1 = (H_2 - H_1) - (p_2V_2 - p_1V_1)$$

$$= 234.8 - \left(\frac{20.87 \times 10^5 \times 0.08 - 4 \times 10^5 \times 0.3}{10^3}\right) \text{kJ}$$

$$= 234.8 - 46.96 = 187.84\ \text{kJ}.$$

Hence, **change in internal energy = 187.84 kJ. (Ans.)**

(*iii*) **Change in entropy, $S_2 - S_1 = 0$. (Ans.)**

(*iv*) **Heat transfer, $Q_{1-2} = 0$. (Ans.)**

(*v*) **Work transfer, W_{1-2} :**

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

$$\therefore \quad W_{1-2} = Q_{1-2} - (U_2 - U_1)$$

$$= 0 - 187.84 = -187.84 \text{ kJ}$$

Hence, **work done on the fluid = 187.84 kJ. (Ans.)**

☞**Example 5.30.** *An insulated cylinder of volume capacity 4 m³ contains 20 kg of nitrogen. Paddle work is done on the gas by stirring it till the pressure in the vessel gets increased from 4 bar to 8 bar. Determine :*

(*i*) *Change in internal energy,*

(*ii*) *Work done,*

(*iii*) *Heat transferred, and*

(*iv*) *Change in entropy.*

Take for nitrogen : c_p = 1.04 kJ/kg K, and c_v = 0.7432 kJ/kg K.

Solution. Pressure, $p_1 = 4 \text{ bar} = 4 \times 10^5 \text{ N/m}^2$

Pressure, $p_2 = 8 \text{ bar} = 8 \times 10^5 \text{ N/m}^2$

Volume, $V_1 = V_2 = 4 \text{ m}^3$

and it is constant for both end states.

Now,

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

or

$$\frac{T_2}{T_1} = \frac{p_2}{p_1} = \frac{8 \times 10^5}{4 \times 10^5} = 2$$

Also, $R = c_p - c_v = 1.04 - 0.7432 = 0.2968 \text{ kJ/kg K}.$

The mass of the gas in the cylinder is given by

$$m = \frac{pV}{RT} \quad \text{or} \quad mT = \frac{pV}{R}$$

$$\therefore \quad mT_1 = \frac{p_1V_1}{R} = \frac{4 \times 10^5 \times 4}{0.2968 \times 1000} = 5390.8 \text{ kg K}$$

and

$$mT_2 = \frac{p_2V_2}{R} = \frac{8 \times 10^5 \times 4}{0.2968 \times 1000} = 10781.6 \text{ kg K.}$$

(*i*) **Change in internal energy,**

$$\Delta U = (U_2 - U_1)$$

$$= mc_v (T_2 - T_1) = c_v (mT_2 - mT_1)$$

$$= 0.7432\ (10781.6 - 5390.8) = \mathbf{4006.4\ kJ.} \quad \textbf{(Ans.)}$$

(*ii*) **Work done, W :**

Energy in the form of paddle work crosses into the system, but there is no change in system boundary or *pdv* work is absent. No heat is transferred to the system. We have

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

But $Q_{1-2} = 0$

$$\therefore \quad W_{1-2} = -(U_2 - U_1) = \mathbf{-\ 4006.4\ kJ\ or\ kN\text{-}m.} \quad \textbf{(Ans.)}$$

(*iii*) **Heat transferred,** $Q_{1-2} = 0$. **(Ans.)**

(*iv*) **Change in entropy,**

$$S_2 - S_1 = mc_v \log_e \frac{T_2}{T_1}$$

For constant volume process

$$= 20 \times 0.7432 \log_e 2 = \mathbf{10.3\ kJ/K.}\quad \textbf{(Ans.)}$$

Example 5.31. *5 m^3 of air at 2 bar, 27°C is compressed up to 6 bar pressure following $pv^{1.3}$ = constant. It is subsequently expanded adiabatically to 2 bar. Considering the two processes to be reversible, determine the net work. Also plot the processes on T-S diagram.*

Solution. Refer Fig. 5.39.

Given : $V_1 = 5\ \text{m}^3$; $p_1 = 2$ bar ; $T_1 = 27 + 273 = 300$ K ; $p_2 = 6$ bar ; $p_3 = 2$ bar

Net work :

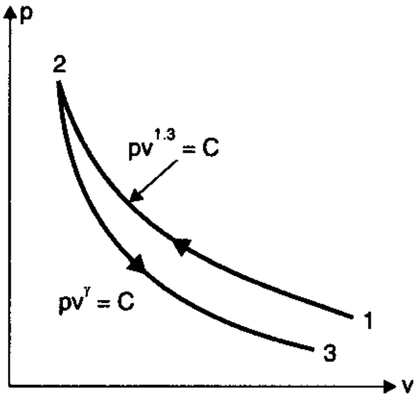


Fig. 5.39. *p-V* diagram.

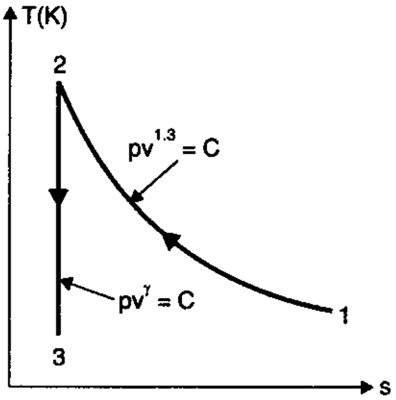


Fig. 5.40. *T-s* diagram.

Mass of air, $$m = \frac{p_1V_1}{RT_1} = \frac{2 \times 10^5 \times 5}{287 \times 300} = 11.61 \text{ kg.}$$

Considering polytropic compression process 1-2, we have

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}} \quad \text{or} \quad \frac{T_2}{300} = \left(\frac{6}{2}\right)^{\frac{1.3-1}{1.3}} \quad \text{or} \quad T_2 = 386.5 \text{ K.}$$

Considering isentropic process 2-3, we get

$$\frac{T_2}{T_3} = \left(\frac{p_2}{p_3}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{6}{2}\right)^{\frac{1.4-1}{1.4}} = 1.369 \qquad (\because\ p_3 = p_1)$$

$$\therefore \qquad T_3 = \frac{T_2}{1.369} = \frac{386.5}{1.369} = 282.3 \text{ K}$$

Now, work done during polytropic *compression* 1-2,

$$W_{1-2} = \frac{mR(T_1 - T_2)}{n-1} = \frac{11.61 \times 0.287\,(300 - 386.5)}{1.3 - 1} = -\ 960.7 \text{ kJ}$$

and, work done during *adiabatic expansion* 2-3,

$$W_{2-3} = \frac{mR(T_2 - T_3)}{\gamma - 1} = \frac{11.61 \times 0.287\,(386.5 - 282.3)}{1.4 - 1} = 868 \text{ kJ}$$

$\therefore$ Net work done = $W_{1-2} + W_{2-3} = -\ 960.7 + 868 = -\ 92.7$ kJ

Hence **net work done on the air = 92.7 kJ. (Ans.)**

The process plotted on *T-s* diagram is shown in Fig. 5.40.

Example 5.32. *A rigid cylinder containing 0.004 m³ of nitrogen at 1 bar and 300 K is heated reversibly until temperature becomes 400 K. Determine :*

(*i*) *The heat supplied.* (*ii*) *The entropy change.*

Assume nitrogen to be perfect gas (molecular mass = 28) and take $\gamma = 1.4$.

Solution. *Given :* $V_1 = 0.004$ m³ ; $p_1 = 1$ bar ; $T_1 = 300$ K ; $T_2 = 400$ K ; M for $N_2 = 28$; $\gamma = 1.4$.

(*i*) **The heat supplied :**

$$\text{Gas constant } R = \frac{R_0 \text{ (Universal gas constant)}}{M \text{ (Molecular mass)}} = \frac{8.314}{28} = 0.297 \text{ kg/kg K}$$

$$\text{Mass, } m = \frac{p_1V_1}{RT_1} = \frac{(1 \times 10^5) \times 0.004}{(0.297 \times 1000) \times 300} = 0.00449 \text{ kg}$$

$$c_v = \frac{R}{\gamma - 1} = \frac{0.297}{1.4 - 1} = 0.742 \text{ kJ/kg K}$$

$$\therefore \text{ Heat supplied} = m\, c_v(T_2 - T_1)$$

$$= 0.00449 \times 0.742(400 - 300) = \mathbf{0.333\ kJ.} \quad \textbf{(Ans.)}$$

(*ii*) **The entropy change :**

$$\text{The entropy change, } S_2 - S_1 = m\, c_v \log_e \left(\frac{T_2}{T_1}\right)$$

$$= 0.00449 \times 0.742 \times \log_e \left(\frac{400}{300}\right) = \mathbf{9.584 \times 10^{-4}\ kJ/kg\ K.} \quad \textbf{(Ans.)}$$

Example 5.33. *A piston-cylinder arrangement contains 0.05 m³ of nitrogen at 1 bar and 280 K. The piston moves inwards and the gas is compressed isothermally and reversibly until the pressure becomes 5 bar. Determine :*

(*i*) *Change in entropy.* (*ii*) *Work done.*

Assume nitrogen to be a perfect gas.

Solution. *Given :* $V_1 = 0.05$ m³ ; $p_1 = 1$ bar ; $T_1 = 280$ K ; $p_2 = 5$ bar.

(*i*) **Change in entropy, ($S_2 - S_1$) :**

$$\text{Gas constant, } R = \frac{R_0}{M} = \frac{8.314}{28} = 0.297 \text{ kJ/kg K}$$

$$\text{Mass of the gas, } m = \frac{p_1V_1}{RT_1} = \frac{(1 \times 10^5) \times 0.05}{(0.297 \times 1000) \times 280} = 0.06 \text{ kg}$$

$$\therefore \text{ Change in entropy } S_2 - S_1 = mR \log_e \left(\frac{p_1}{p_2}\right)$$

$$= 0.06 \times 0.297 \log_e \left(\frac{1}{5}\right) = \mathbf{-\ 0.0287\ kJ/K.} \quad \textbf{(Ans.)}$$

$$\text{Heat interaction, } Q = T(S_2 - S_1)$$

$$= 280 \times (-\ 0.0287) = -\ 8.036 \text{ kJ}$$

$$\therefore \text{ Work done, } W = Q = \mathbf{-\ 8.036\ kJ.} \quad \textbf{(Ans.)} \qquad (\because \text{ In its other process, } W = Q)$$

$$\left[\begin{aligned} &\textit{Alternatively} : W = p_1V_1 \log_e \left(\frac{V_2}{V_1}\right) = p_1V_1 \log_e \left(\frac{p_1}{p_2}\right) \\ &\qquad = 1 \times 10^5 \times 0.05 \times \log_e \left(\frac{1}{5}\right) \times 10^{-3} \text{ kJ} = 8.04 \text{ kJ} \end{aligned}\right]$$

Example 5.34. *1 kg of air initially at 8 bar pressure and 380 K expands polytropically ($pv^{1.2}$ = constant) until the pressure is reduced to one-fifth value. Calculate :*

(i) Final specific volume and temperature.

(ii) Change of internal energy, work done and heat interaction.

(iii) Change in entropy.

Take : $R = 0.287$ kJ/kg K and $\gamma = 1.4$.

Solution. *Given :* $m = 1$ kg ; $p_1 = 8$ bar ; $T_1 = 380$ K ; Law of expansion : $pv^{1.2}$ = constant ;

$$p_2 = \frac{p_1}{5} = \frac{8}{5} = 1.6 \text{ bar} \; ; \; R = 0.287 \text{ kJ/kg K} \; ; \; \gamma = 0.4.$$

(*i*) **Final specific volume and temperature, $\mathbf{v_2}$, $\mathbf{T_2}$:**

$$p_1 v_1 = RT_1$$

or,
$$v_1 = \frac{RT_1}{p_1} = \frac{(0.287 \times 10^3) \times 380}{8 \times 10^5} = 0.1363 \text{ m}^3\text{/kg.}$$

Also,
$$p_1 v_1^n = p_2 v_2^n \quad \text{or} \quad v_2 = v_1 \times \left(\frac{p_1}{p_2}\right)^{\frac{1}{n}}$$

$$\therefore \quad v_2 = 0.1363 \times \left(\frac{8}{1.6}\right)^{\frac{1}{1.2}} = \mathbf{0.5211 \ m^3/kg.} \quad \textbf{(Ans.)}$$

Again,
$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}} \quad \text{or} \quad \frac{T_2}{380} = \left(\frac{1}{5}\right)^{\frac{1.2-1}{1.2}}$$

$$\therefore \quad T_2 = 290.6 \text{ K}$$

$$\left[\textbf{Alternatively : } T_2 = \frac{p_2 v_2}{R} = \frac{1.6 \times 10^5 \times 0.5211}{287} = 290.6 \text{ K}\right]$$

(*ii*) **Change of internal energy, work done and heat interaction :**

Change of internal energy

$$\mathbf{u_2 - u_1} = c_v(T_2 - T_1) = \frac{R}{\gamma - 1}(T_2 - T_1)$$

$$= \frac{0.287}{1.4 - 1}(290.6 - 380) = \mathbf{-\ 64.14 \ kJ/kg} \textit{ (Decrease).} \quad \textbf{(Ans.)}$$

Work done,
$$\mathbf{W_{1\text{-}2}} = \frac{p_1 v_1 - p_2 v_2}{n - 1} = \frac{R(T_1 - T_2)}{n - 1}$$

$$= \frac{0.287(380 - 290.6)}{1.2 - 1} = \mathbf{128.29 \ kJ/kg} \textit{ (Work done by air).} \quad \textbf{(Ans.)}$$

Heat interaction, $Q_{1-2} = (u_2 - u_1) + W = -\ 64.14 + 128.29 =$ **64.15 kJ/kg** (*Heat received*). **(Ans.)**

$$\left[\textit{Alternatively} : Q = \frac{\gamma - n}{\gamma - 1} \times W = \frac{1.4 - 1.2}{1.4 - 1} \times 128.29 = 64.15 \text{ kJ/kg}\right]$$

(*iii*) **Change in entropy, $(\mathbf{s_2 - s_1})$:**

$$s_2 - s_1 = c_v \log_e \frac{T_2}{T_1} + R \log_e \frac{v_2}{v_1}$$

$$= \frac{0.287}{1.4-1} \times \log_e \left(\frac{290.6}{380}\right) + 0.287 \log_e \left(\frac{0.5211}{0.1363}\right)$$

$$= -0.192 + 0.385 = \mathbf{0.193\ kJ/kg\ K}$$ *(increase)*. **(Ans.)**

Example 5.35. (*a*) *Show that approximate change of entropy during a polytropic process equals the quantity of heat transferred divided by the mean absolute temperature.*

(*b*) *One kg of air at 290 K is compressed in a cylinder according to the polytropic law* $pv^{1.3}$ = *constant. If the compression ratio is 16, calculate the entropy change of air during the compression process stating whether it is an increase or decrease.*

What would be the percentage error if the entropy change is calculated by dividing the quantity of heat exchanged by the mean absolute temperature during the process ?

Take $\gamma = 1.4$ *and* $c_v = 0.718$ *kJ/kg K.*

Solution. (*a*) In Fig. 5.41 curve 1-2 represents the polytropic process ($pv^n = c$) from state point 1 to state point 2. The area under the process curve 1-2 on *T-S* diagram represents the heat transferred during the process. The slope of the curve 1-2 is usually *small* and can be considered to be a straight line (shotted dotted).

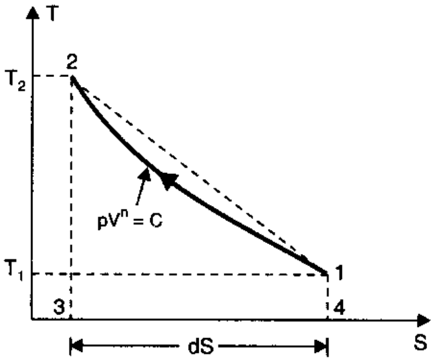


Fig. 5.41

Heat transferred = Area of trapezium 1-2-3-4

= Base × mean ordinate

$$= dS \times \left(\frac{T_1 + T_2}{2}\right)$$

= Entropy change × mean absolute temperature during the process

or, Entropy change $= \dfrac{\text{Heat transferred}}{\text{Mean absolute temperature}}$

(*b*) *Given :* $m = 1$ kg ; $T_1 = 290$ K ; $pv^{1.3}$ = constant ; $r = 16$; $\gamma = 1.4$; $c_v = 0.718$ kJ/kg K

For a polytropic process : $\dfrac{T_2}{T_1} = \left(\dfrac{v_1}{v_2}\right)^{n-1}$

or, $T_2 = 290 \times (16)^{1.3-1} = 666.2$ K

Now, $s_2 - s_1 = c_v \left(\dfrac{n-\gamma}{n-1}\right) \log_e \left(\dfrac{T_2}{T_1}\right)$ ... per kg

$$= 0.718 \left(\frac{1.3-1.4}{1.3-1}\right) \log_e \left(\frac{666.2}{290}\right) = \mathbf{-0.199\ kJ/kg\ K.}$$ **(Ans.)**

The –ve sign indicates *decrease* in entropy.

Heat transferred during the process is given by,

$$Q = \frac{\gamma - n}{\gamma - 1} \times W = \frac{\gamma - n}{\gamma - 1} \times \frac{R(T_1 - T_2)}{n-1} = c_v \left(\frac{\gamma - n}{\gamma - 1}\right)(T_1 - T_2) \text{ ...per kg}$$

$$= 0.718 \left(\frac{1.4 - 1.3}{1.3 - 1}\right)(290 - 666.2) = -90.04 \text{ kJ/kg} \qquad \left(\because c_v = \frac{R}{\gamma - 1}\right)$$

Mean absolute temperature, $T_{\text{mean}} = \frac{T_1 + T_2}{2} = \frac{290 + 666.2}{2} = 478.1$ K

Approximate change of entropy $= \frac{Q}{T_{\text{mean}}} = \frac{-90.04}{478.1} = -0.188$ kJ/kg K

$\therefore$ % age error $= \frac{0.199 - 0.188}{0.199} \times 100 =$ **5.53%. (Ans.)**

- The approximate value of entropy change is lower, because in the relation $Q = T_{av} \times dS$ actual value of heat transferred is substituted instead of approximate value (*i.e.*, Area under the straight line) which is higher.

Example 5.36. *1.2 m^3 of air is heated reversibly at constant pressure from 300 K to 600 K, and is then cooled reversibly at constant volume back to initial temperature. If the initial pressure is 1 bar, calculate :*

(i) The net heat flow.

(ii) The overall change in entropy.

Represent the processes on T-S plot.

Take c_p = 1.005 kJ/kg K and R = 0.287 kJ/kg K

Solution. *Given :* $V_1 = 1.2$ m^3 ; $p_1 = p_2$; $T_1 = 300$ K ; $T_2 = 600$ K ; $p_1 = 1$ bar ;
$c_p = 1.005$ kJ/kg K ; $R = 0.287$ kJ/kg K

Fig. 5.42 shows the *T-S* plot of the processes.

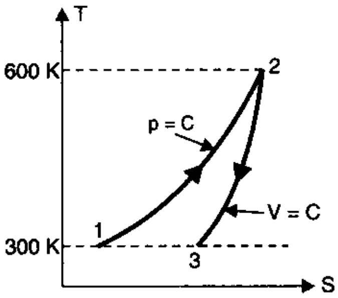


Fig. 5.42

(*i*) **The net heat flow, Q :**

Mass of air, $m = \frac{p_1V_1}{RT_1} = \frac{1 \times 10^5 \times 1.2}{(0.287 \times 1000) \times 300} = 1.394$ kg

$$\begin{aligned} Q &= Q_{1-2} + Q_{2-3} \\ &= mc_p(T_2 - T_1) + mc_v(T_3 - T_2) \\ &= mc_p(T_2 - T_1) + mc_v(T_1 - T_2) \quad ...(\because T_1 = T_3) \\ &= m(T_2 - T_1)(c_p - c_v) = m(T_2 - T_1) \times R \\ &= 1.394(600 - 300) \times 0.287 = \mathbf{120\ kJ.}\ \mathbf{(Ans.)} \end{aligned}$$

(*ii*) **The overall change in entropy :**

Entropy change during *constant pressure process 1-2*,

$$S_2 - S_1 = mc_p \log_e \left(\frac{T_2}{T_1}\right)$$

$$= 1.394 \times 1.005 \log_e \left(\frac{600}{300}\right) = 0.9711 \text{ kJ/K}$$

Entropy change during *constant volume process 2-3* ;

$$S_3 - S_2 = mc_v \log_e \left(\frac{T_3}{T_2}\right) = m(c_p - R) \log_e \left(\frac{T_1}{T_2}\right)$$

$$= 1.394 \times (1.005 - 0.287) \log_e \left(\frac{300}{600}\right) = -0.6938 \text{ kJ/K}$$

∴ Overall change of entropy

$$= (S_2 - S_1) + (S_3 - S_2)$$
$$= 0.9771 + (-0.6938) = \mathbf{0.2833\ kJ/K.}\quad \textbf{(Ans.)}$$

Example 5.37. *A closed system contains air at a pressure 1 bar, temperature 300 K and volume 0.018 m³. This system undergoes a thermodynamic cycle consisting of the following three processes in series : (i) Constant volume heat addition till pressure becomes 5 bar, (ii) Constant pressure cooling, and (iii) Isothermal heating to initial state.*

Represent the cycle on T-S and p-V plots and evaluate the change in entropy for each process.

Take c_p = 0.718 kJ/kg K and R = 0.287 kJ/kg K.

Solution. *Given :* p_1 = 1 bar ; T_1 = 300 K ; V_1 = 0.018 m³ ; p_2 = 5 bar ;
c_v = 0.718 kJ/kg K ; R = 0.287 kJ/kg K.

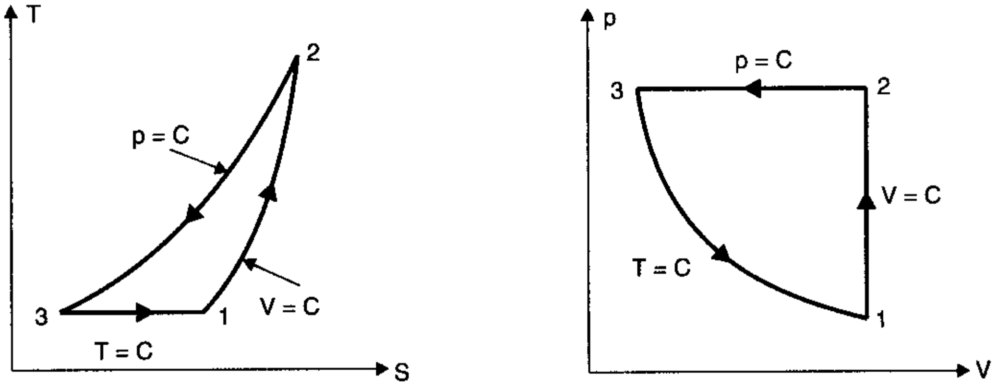


Fig. 5.43. *T-S* and *p-V* diagrams.

$$\text{Mass of air, } m = \frac{p_1V_1}{RT_1} = \frac{(1\times10^5)\times0.018}{(0.287\times1000)\times300} = 0.0209 \text{ kg}$$

Refer to Fig. 5.43.

- *Constant volume process 1-2 :*

$$\frac{p_1}{T_1} = \frac{p_2}{T_2} \quad \text{or} \quad T_2 = T_1 \times \frac{p_2}{p_1} = 300 \times \frac{5}{1} = 1500 \text{ K}$$

$$\therefore \text{ Change in entropy, } \mathbf{S_2 - S_1} = mc_v \log_e \left(\frac{T_2}{T_1}\right)$$

$$= 0.0209 \times 0.718 \times \log_e \left(\frac{1500}{300}\right) = \mathbf{0.0241\ kJ/K.}\quad \textbf{(Ans.)}$$

- *Constant pressure process 2-3 :*

$$T_3 = T_1 = 300 \text{ K}$$

Now, change in entropy,

$$\mathbf{S_3 - S_2} = mc_p \log_e \left(\frac{T_3}{T_2}\right) = m(c_v + R) \log_e \left(\frac{T_3}{T_2}\right)$$

$$= 0.0209 \times (0.718 + 0.287) \times \log_e \left(\frac{300}{1500}\right)$$

$$= -\ \mathbf{0.0338\ kJ/K.}\ \ \textbf{(Ans.)}$$

- *Constant temperature (isothermal) process 3-1* :

$$p_3 = p_2 = 5 \text{ bar}$$

Change in entropy,

$$\mathbf{S_1 - S_3} = mR \log_e \left(\frac{p_3}{p_1}\right)$$

$$= 0.0209 \times 0.287 \times \log_e \left(\frac{5}{1}\right) = \mathbf{0.00965\ kJ/K.}\ \ \textbf{(Ans.)}$$

Example 5.38. *Derive expressions for entropy change with variable specific heat.*

Solution. Let us assume that the specific heats of a gas vary with temperature according to the linear relations :

$$c_p = a + kT, \quad \text{and} \quad c_v = b + kT$$

where, a, b and k = Constants, and T = Temperature, K.

For *unit mass* of gas, $Q = T\,ds = du + pdv$

$$= c_v dT + pdv$$

or,

$$ds = c_v \frac{dT}{T} + \frac{pdv}{T} = c_v \frac{dT}{T} + R\frac{dv}{v} \qquad (\because \ pv = RT)$$

Now,

$$R = c_p - c_v = (a + kT) - (b + kT) = a - b$$

$\therefore$

$$ds = (b + kT)\frac{dT}{T} + (a - b)\frac{dv}{v}$$

This is the differential form of entropy change.

Integrating both sides between limits 1 and 2, we get

$$s_2 - s_1 = b \log_e \left(\frac{T_2}{T_1}\right) + k(T_2 - T_1) + (a - b)\log_e \left(\frac{v_2}{v_1}\right) \qquad ...(1)$$

For the entropy change the following expressions can be obtained by suitable manipulations to *eqn. (1)* :

1. *Expression for entropy change in terms of* **temperature** *only* :

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{n-1}$$

or,

$$\log_e \frac{T_2}{T_1} = (n-1)\log_e \left(\frac{v_1}{v_2}\right) = -(n-1)\log_e\left(\frac{v_2}{v_1}\right)$$

$\therefore$

$$s_2 - s_1 = b\log_e\left(\frac{T_2}{T_1}\right) + k(T_2 - T_1) - \left(\frac{a-b}{n-1}\right)\log_e\left(\frac{T_2}{T_1}\right) \qquad ...[\text{From eqn. (1)}]$$

or,

$$\mathbf{s_2 - s_1} = \left(b - \frac{a-b}{n-1}\right)\log_e\left(\frac{T_2}{T_1}\right) + k(T_2 - T_1) \qquad ...(i)$$

2. *Expression for entropy change in terms of* **pressure, volume and temperature.**

From eqn. (1), we have

$$s_2 - s_1 = b \log_e \left(\frac{T_2}{T_1}\right) + k(T_2 - T_1) + a \log_e \left(\frac{v_2}{v_1}\right) - b \log_e \left(\frac{v_2}{v_1}\right)$$

$$= a \log_e \left(\frac{v_2}{v_1}\right) + b \log_e \left(\frac{T_2}{T_1} \times \frac{v_1}{v_2}\right) + k(T_2 - T_1)$$

or,
$$\mathbf{s_2 - s_1} = a \log_e \left(\frac{v_2}{v_1}\right) + b \log_e \left(\frac{p_2}{p_1}\right) + k(T_2 - T_1) \qquad ...(ii)$$

3. *Expression for entropy change in terms of* **pressure and temperature only.**

Again, from eqn. (1), we have

$$s_2 - s_1 = b \log_e \left(\frac{T_2}{T_1}\right) + k\,(T_2 - T_1) + a \log_e \left(\frac{v_2}{v_1}\right) - b \log_e \left(\frac{v_2}{v_1}\right)$$

$$= a \log_e \left(\frac{T_2}{T_1} \times \frac{p_1}{p_2}\right) + b \log_e \left(\frac{T_2}{T_1} \times \frac{v_1}{v_2}\right) + k\,(T_2 - T_1)$$

$$= a \log_e \left(\frac{T_2}{T_1}\right) - a \log_e \left(\frac{p_2}{p_1}\right) + b \log_e \left(\frac{p_2}{p_1}\right) + k(T_2 - T_1)$$

or,
$$\mathbf{s_2 - s_1} = a \log_e \left(\frac{T_2}{T_1}\right) + (b - a) \log_e \left(\frac{p_2}{p_1}\right) + k(T_2 - T_1) \qquad ...(iii)$$

- Derivation of the formula $T^b v^{a-b} e^{kT}$ = constant for the *adiabatic expansion of gas* :

We know that, $ds = (a - b)\dfrac{dv}{v} + (b + kT)\dfrac{dT}{T}$

$$\left.\begin{aligned} s_2 - s_1 &= a \log_e v - b \log_e v + b \log_e T + kT \\ &= a \log_e v + b \log_e \left(\frac{T}{v}\right) + kT \\ &= a \log_e v + b \log_e \left(\frac{p}{R}\right) + kT \\ &= a \log_e v + \log_e \left(\frac{p}{a - b}\right)^b + kT \end{aligned}\right\} = 0 \text{ for adiabatic expansion}$$

This gives :
$$v^a p^b e^{kT} = \text{constant}$$
$$p v^{a-b} e^{kT} = \text{constant}$$
$$T^b v^{a-b} e^{kT} = \text{constant}$$

The above expressions can be obtained by taking kT on right-side and taking the antilog of the resulting expressions.

Example 5.39. *Determine the entropy change of 4 kg of a perfect gas whose temperature varies from 127°C to 227°C during a constant volume process. The specific heat varies linearly with absolute temperature and is represented by the relation :*

$$c_v = (0.48 + 0.0096\ T)\ \text{kJ/kg K.}$$

Solution. *Given :* $m = 4$ kg ; $T_1 = 127 + 273 = 400$ K ; $T_2 = 227 + 273 = 500$ K ;

$$c_v = (0.48 + 0.0096\ T)\ \text{kJ/kg K.}$$

Entropy variation for a constant volume process is given by :

$$dS = mc_v \frac{dT}{T}, \quad \text{or,} \quad dS = 4 \times (0.48 + 0.0096T) \frac{dT}{T}$$

Integrating both sides, we get,

$$S_2 - S_1 = 4 \times 0.48 \int_{T_1}^{T_2} dT + 4 \times 0.0096 \int_{T_1}^{T_2} dT$$

$$= 1.92 \log_e \left(\frac{T_2}{T_1}\right) + 0.0384\ (T_2 - T_1)$$

$$= 1.92 \log_e \left(\frac{500}{400}\right) + 0.0384(500 - 400) = 4.268 \text{ kJ/K}$$

i.e., $\mathbf{S_2 - S_1 = 4.268}$ **kJ. (Ans.)**

Example 5.40. *The specific heats of a gas vary linearly with absolute temperature according to the following relations :*

c_p = (0.85 + 0.00025 T) kg/kg K, and

c_v = (0.56 + 0.00025 T) kJ/kg K

If the entropy of the gas at 1 bar pressure and 273 K is zero, find the entropy of the gas at 25 bar and 750 K temperature.

Solution. *Given :* $c_p = (0.85 + 0.00025\ T)$ kJ/kg K ; $c_v = (0.56 + 0.00025\ T)$ kJ/kg K ;

$p_1 = 1$ bar ; $T_1 = 273$ K ; $p_2 = 25$ bar ; $T_2 = 750$ K.

We know that, $$ds = c_v \frac{dT}{T} + \frac{p}{T} dv = c_v \frac{dT}{T} + R \frac{dv}{v}$$

Integrating both sides, we get,

$$s_2 - s_1 = \int c_v \frac{dT}{T} + R \log_e \left(\frac{v_2}{v_1}\right)$$

$$= \int c_v \frac{dT}{T} + (c_p - c_v) \log_e \left(\frac{p_1}{p_2} \times \frac{T_2}{T_1}\right)$$

$$= \int \left(\frac{0.56}{T} + 0.00025\right) dT + 0.29 \log_e \left(\frac{1}{25} \times \frac{750}{273}\right)$$

$$= \left[0.56 \log_e \left(\frac{T_2}{T_1}\right) + 0.00025\ (T_2 - T_1)\right] - 0.6404$$

$$= 0.56 \log_e \left(\frac{750}{273}\right) + 0.00025(750 - 273) - 0.6404 = 0.0448 \text{ kJ/kg K}$$

i.e., $\mathbf{s_2 - s_1 = 0.0448}$ **kJ/kg K. (Ans.)**

Example 5.41. *An insulated vessel of 0.5 m^3 capacity is divided by a rigid conducting diaphragm into two chambers A and B, each having a capacity of 0.25 m^3. Chamber A contains air at 1.4 bar pressure and 290 K temperature and the corresponding parameters for air in chamber B are 4.2 bar and 440 K. Calculate :*

(i) Final equilibrium temperature,

(ii) Final pressure on each side of the diaphragm, and

(iii) Entropy change of system.

For air take c_v = 0.715 kJ/kg K and R = 0.287 kJ/kg K.

Solution. *Given :* $V_A = 0.25\ \text{m}^3$; $p_{Ai} = 1.4$ bar ; $T_{Ai} = 290$ K ; $V_B = 0.25\ \text{m}^3$; $p_{Bi} = 4.2$ bar ; $T_{Bi} = 440$ K ; $c_v = 0.715$ kJ/kg K.

(*i*) **Final equilibrium temperature, T_f :**

Mass of air, $$m_A = \frac{p_{Ai}V_A}{RT_{Ai}} = \frac{(1.4 \times 10^5) \times 0.25}{(0.287 \times 1000) \times 290} = 0.4205 \text{ kg}$$

$$m_B = \frac{p_{Bi}V_B}{RT_{Bi}} = \frac{(4.2 \times 10^5) \times 0.25}{(0.287 \times 1000) \times 440} = 0.8315 \text{ kg}$$

Let T_f be the final equilibrium temperature (K). Since the diaphragm is conducting,

Heat gained by air in chamber A = Heat lost by air in chamber B

$$m_A\, c_v\, (T_f - 290) = m_B\, c_v (440 - T_f)$$

or, $$0.4205 \times (T_f - 290) = 0.8315(440 - T_f)$$

or, $$0.4205\, T_f - 121.94 = 365.86 - 0.8315\, T_f$$

$\therefore$ $$T_f = \mathbf{389.6\ K.}\ \textbf{(Ans.)}$$

(*ii*) **Final pressure on each side of the diaphragm : p_{Af} ; p_{Bf}**

$$p_{Af} = \frac{1.4 \times 389.6}{290} = \mathbf{1.88\ bar.}\ \textbf{(Ans.)}$$

$$p_{Bf} = \frac{4.2 \times 389.6}{440} = \mathbf{3.72\ bar.}\ \textbf{(Ans.)}$$

(*iii*) **Entropy change of the system :**

$$\text{Entropy change for chamber } A = m_A\, c_v \log_e \left(\frac{T_f}{T_{Ai}}\right)$$

$$= 0.4205 \times 0.715 \times \log_e \left(\frac{389.6}{290}\right) = 0.0888 \text{ kJ/K}$$

$$\text{Entropy change for chamber } B = m_B\, c_v \log_e \left(\frac{T_f}{T_{Bi}}\right)$$

$$= 0.8315 \times 0.715 \times \log_e \left(\frac{389.6}{440}\right) = -\,0.0723 \text{ kJ/K}$$

$\therefore$ Net change of entropy = 0.0888 + (– 0.0723) = **0.0165 kJ/K. (Ans.)**

Example 5.42. *A certain gas has a specific heat at constant volume of 1.25 kJ/kg K. When it is expanded reversibly and adiabatically from a specific volume of 0.0624 m³/kg and a temperature of 530 K to a specific volume of 0.186 m³/kg its temperature falls by 165 K. When it is expanded into an evacuated space from the same initial condition to the same final specific volume its temperature falls only by 25 K.*

Find the change in entropy in each of the adiabatic processes.

Solution. Refer Fig. 5.44.

Specific heat of gas at constant volume, $c_v = 1.25$ kJ/kg K

Initial specific volume, $v_1 = 0.0624\ \text{m}^3/\text{kg}$

Initial temperature, $T_1 = 530$ K

Final specific volume, $v_2 = 0.186\ \text{m}^3/\text{kg}$

Temperature fall when expanded reversibly and adiabatically = 165 K
Temperature fall when expanded into an evacuated space = 25 K

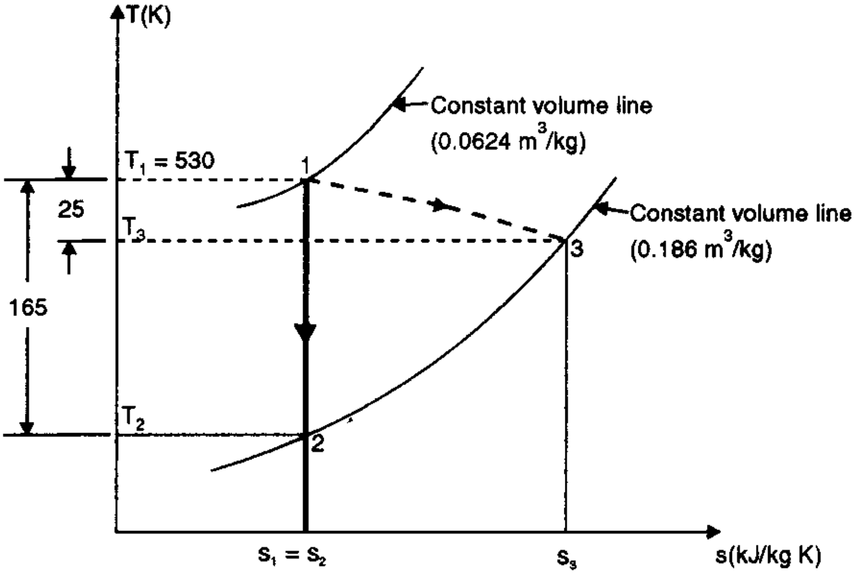


Fig. 5.44

Change in entropy :

Path 1-2 : *Reversible adiabatic process.*

Change in entropy, $(s_2 - s_1) = 0$.

Path 1-3 : *Adiabatic process such that* $v_3 = 0.186\ m^3/kg\ (= v_2)$

(States 2 and 3 lie on the same constant volume line on *T-s* diagram)

and $T_1 - T_3 = 25$ K.

Change in entropy during this adiabatic process $= s_3 - s_1$.

To calculate $(s_3 - s_1)$ a reversible path has to be selected joining 3 and 1.

This is achieved by selecting the reversible adiabatic path 1-2 and the reversible constant volume process 2-3.

$$s_3 - s_1 = (s_3 - s_2) + (s_2 - s_1)$$

$$= (s_3 - s_2) + 0 = (s_3 - s_2)$$

$$= c_v \log_e \frac{T_3}{T_2} = 1.25 \log_e \left(\frac{530 - 25}{530 - 165}\right)$$

$$= 1.25 \log_e \left(\frac{505}{365}\right) = \mathbf{0.4058\ kJ/kg\ K.}\quad \textbf{(Ans.)}$$

Example 5.43. *A heat pump operates between two identical bodies which are at temperature* T_1 *and cools one of the bodies to a temperature* T_2 $(T_2 < T_1)$. *Prove that for this operation the minimum work required by the heat pump is given by*

$$W = c_p \left(\frac{T_1^2}{T_2^2} + T_2 - 2T_1\right)$$

where c_p *is the specific heat which is same for both the bodies.*

Solution. The arrangement is shown in Fig. 5.45.

For the minimum work absorbed by the heat pump, the heat pump must be reversed Carnot cycle engine and the required condition is

$$\oint \left(\frac{dQ}{T}\right) = 0$$

For infinitely small changes, we can write

$$c_p \frac{dT_1}{T_1} + c_p \frac{dT_2}{T_2} = 0$$

If T_1' is the final temperature of the high level reservoir, then the above equation can be written as

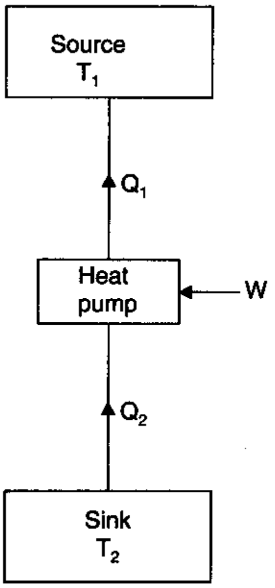


Fig. 5.45

$$c_p \int_{T_1}^{T_1'} \left(\frac{dT_1}{T_1}\right) + c_p \int_{T_1}^{T_2} \left(\frac{dT_2}{T_2}\right) = 0$$

$$\therefore \quad \log_e \left(\frac{T_1'}{T_1}\right) + \log_e \left(\frac{T_2}{T_1}\right) = 0 = \log_e (1)$$

$$\therefore \quad \log_e \left(\frac{T_1' T_2}{T_1^2}\right) = \log_e (1)$$

$$\therefore \quad T_1' = \frac{T_1^2}{T_2}$$

Now the work given to the heat pump

= Heat rejected at higher level temperature
– heat picked up at lower level temperature

$$\therefore \quad W = c_p \int_{T_1}^{T_1'} (dT) - c_p \int_{T_2}^{T_1} (dT)$$

$$= c_p [(T_1' - T_1) - (T_1 - T_2)] = c_p (T_1' + T_2 - 2T_1)$$

Now substituting the value of T_1' in the above equation in terms of T_1 and T_2

$$W = c_p \left[\frac{T_1^2}{T_2} + T_2 - 2T_1\right]. \quad \textbf{Proved.}$$

☞**Example 5.44.** *The connections of a reversible engine to three sources at 500 K, 400 K and 300 K are shown in Fig. 5.46. It draws 1500 kJ/min of energy from the source at 800 K and develops 200 kJ/min of work.*

(*i*) *Determine the heat interactions with the other two sources of heat.*

(*ii*) *Evaluate the entropy change due to each heat interaction with the engine.*

(*iii*) *Total entropy change during the cycle.*

Solution. Refer Fig. 5.46.

Temperature of source 1 = 500 K

Temperature of source 2 = 400 K

Temperature of source 3 = 300 K

Heat energy drawn from source 1, Q_1 = 1500 kJ/min

Work developed, W = 200 kJ/min.

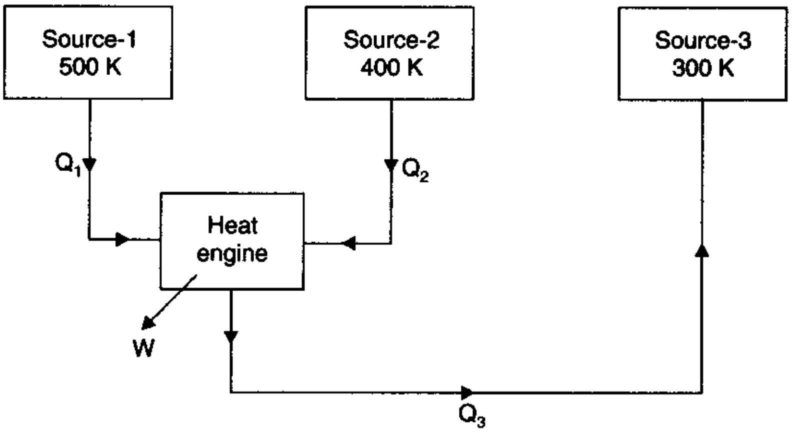


Fig. 5.46

(*i*) The direction of heat flow from source 1 is known as given in the problem. Assume that the quantities of heats Q_2 and Q_3 are taken from heat sources and their directions are arbitrarily chosen.

For the cyclic operation of the engine

$$\oint\left(\frac{dQ}{T}\right) = 0$$

$$\therefore \quad \frac{Q_1}{T_1} + \frac{Q_2}{T_2} - \frac{Q_3}{T_3} = 0$$

and $$Q_1 + Q_2 - Q_3 = W$$

$$\therefore \quad \frac{1500}{500} + \frac{Q_2}{400} - \frac{Q_3}{300} = 0 \qquad ...(i)$$

and $$1500 + Q_2 - Q_3 = 200 \qquad ...(ii)$$

Solving eqns. (*i*) and (*ii*), we get

$$Q_2 = -\ 1600 \text{ kJ/min and } Q_3 = -\ 300 \text{ kJ/min.}$$

The above values indicate that the direction of Q_2 and Q_3 are reversed. Since Q_2 should be +v and Q_3 also must be +ve but both are –ve therefore, their assumed directions should be reversed. The arrangement is shown in Fig. 5.47.

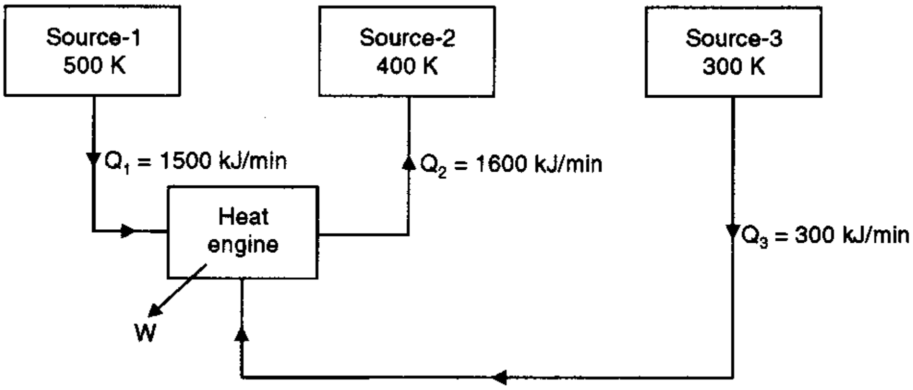


Fig. 5.47

(*ii*) *Entropy change of source 1* $= \frac{-Q_1}{T_1} = \frac{-1500}{500} = -$ **3 kJ/K. (Ans.)**

Entropy change of sink 2 $= \frac{Q_2}{T_2} = \frac{1600}{400} =$ **4 kJ/K. (Ans.)**

Entropy change of source 3 $= \frac{-Q_3}{T_3} = \frac{-300}{300} = -$ **1 kJ/K. (Ans.)**

(*iii*) Net change of the entropy $= -3 + 4 - 1 = 0$

As *the cycle is completed, the net change in entropy must be zero because entropy is a property.*

It may be observed from the new arrangement that the engine takes heat from source 1 and source 3 and rejects to source 2, only *i.e.*, the equipment does both *a heat engine and a heat pump function.*

Example 5.45. *The heat capacity of a system at constant volume is given by* $C_v = ZT^2$ *where* $Z = 0.045$ *J/K*^{3}

A system is originally at 250 K, and a thermal reservoir at 125 K is available. Determine the maximum amount of work that can be recovered as the system is cooled down to the temperature of the reservoir.

Solution. Refer Fig. 5.48.

Initial temperature of the system, $T_1 = 250$ K

Temperature of the reservoir, $T_2 = 125$ K

Heat capacity of the system at constant volume is

$$C_v = ZT^2 = 0.045\ T^2$$

[The product of mass and specific heat (*mc*) is called the *heat capacity* of the substance. The capital letter C, C_p or C_v is used for heat capacity]

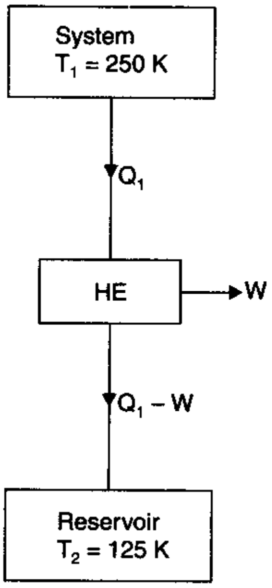


Fig. 5.48

Heat removed from the system

$$Q_1 = \int_{T_1}^{T_2} C_v\,dT = \int_{250}^{125} 0.045\ T^2\,dT$$

$$= 0.045\left[\frac{T^3}{3}\right]_{250}^{125} = \frac{0.045}{3}(125^3 - 250^3)$$

$$= -205.08 \times 10^3 \text{ J}$$

$$(\Delta S)_{system} = \int_{250}^{125} C_v \frac{dT}{T} = \int_{250}^{125} 0.045\,T^2\,\frac{dT}{T}$$

$$= 0.045\int_{250}^{125} T\,dT = 0.045\left[\frac{T^2}{2}\right]_{250}^{125}$$

$$= \frac{0.045}{2}(125^2 - 250^2) = -1054.7 \text{ J/K}$$

$$(\Delta S)_{\text{reservoir}} = \frac{Q_1 - W}{T_{\text{reservoir}}} = \frac{205.08 \times 10^3 - W}{125} \text{ J/K}$$

$$(\Delta S)_{\text{working fluid in } HE} = 0$$

$$\therefore \quad (\Delta S)_{\text{universe}} = (\Delta S)_{\text{system}} + (\Delta S)_{\text{reservoir}} = -1054.7 + \frac{205.08 \times 10^3 - W}{125}$$

Since $(\Delta S)_{\text{universe}} \geq 0$

$$\therefore \quad -1054.7 + \frac{205.08 \times 10^3 - W}{125} \geq 0$$

or $$-1054.7 + 1640.64 - \frac{W}{125} \geq 0 \quad \text{or} \quad 585.94 - \frac{W}{125} \geq 0$$

or $$585.94 \geq \frac{W}{125} \quad \text{or} \quad \frac{W}{125} \leq 585.94$$

i.e., $W_{(\text{max.})} = 585.94 \times 125 =$ **73.24 kJ. (Ans.)**

Example 5.46. *In an insulated duct air is flowing steadily. The pressure and temperature measurements of the air at two stations A and B are given below :*

Station	*Pressure*	*Temperature*
A	*140 kPa*	*60°C*
B	*110 kPa*	*15°C*

Establish the direction of the flow of the air in the duct.

For air assume that :

$$c_p = 1.005 \text{ kJ/kg K}$$

$$h = c_p T \text{ and } \frac{v}{T} = \frac{0.287}{p}$$

where p, v and T are pressure (in kPa), volume (in m³/kg) and temperature (in K) respectively.

Solution. From property relation,

$$Tds = dh - vdp$$

$$ds = \frac{dh}{T} - \frac{vdp}{T}$$

For two states at A and B the entropy changes of the system is given by

$$\int_{s_A}^{s_B} ds = \int_{T_A}^{T_B} \frac{c_p dT}{T} - \int_{p_A}^{p_B} 0.287 \frac{dp}{p}$$

$$\therefore \quad s_B - s_A = 1.005 \log_e \frac{T_B}{T_A} - 0.287 \log_e \frac{110}{140}$$

$$= 1.005 \log_e \left(\frac{15 + 273}{60 + 273}\right) - 0.287 \log_e \frac{110}{140}$$

$$= -0.1459 + 0.0692 = -0.0767 \text{ kJ/kg K}$$

$$(\Delta s)_{\text{system}} = -0.0767 \text{ kJ/kg K}$$

Since the duct is insulated, $(\Delta s)_{\text{surroundings}} = 0$

$$\therefore \quad (\Delta s)_{\text{universe}} = -0.0767 \text{ kJ/kg K.}$$

This is impossible.

So, **the flow is from B to A. (Ans.)**

Example 5.47. *3 kg of water at 80°C is mixed with 4 kg of water at 15°C in an isolated system. Calculate the change of entropy due to mixing process.*

Solution. Fig. 5.49 shows the isolated system before mixing. When barrier is removed, the water from two compartments mix each other. Let t_m is the final equilibrium temperature after mixing.

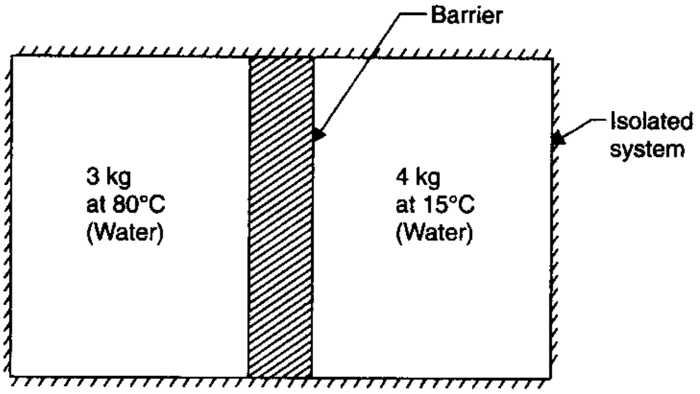


Fig. 5.49

Applying first law of thermodynamics to the isolated system :

Total energy before mixing = Total energy after mixing

$$\therefore \quad 3c_{pw}(80-0)+4c_{pw}(15-0)=7\,c_{pw}\,(t_m-0)$$

[c_{pw} = Specific heat of water at constant pressure]

or $$240c_{pw}+60c_{pw}=7c_{pw}\,t_m$$

or $$240+60=7\,t_m$$

$$\therefore \quad t_m=\frac{300}{7}=42.85°\text{C}$$

Initial entropy of the system,

$$=3c_{pw}\log_e\left(\frac{80+273}{273}\right)+4c_{pw}\log_e\left(\frac{15+273}{273}\right)$$

$$=0.7709c_{pw}+0.2139\,c_{pw}=0.9848\,c_{pw}$$

Final entropy of the system

$$=(3+4)\,c_{pw}\log_e\left(\frac{42.85+273}{273}\right)=1.0205\,c_{pw}$$

Net change in entropy,

$$\begin{aligned}\Delta S &= \text{Final entropy} - \text{Initial entropy}\\ &= 1.0205c_{pw}-0.9848\,c_{pw}=0.0357\,c_{pw}\\ &= 0.0357\times 4.187\ \text{kJ/K} \qquad [\because\ c_{pw}=4.187\ \text{kJ/kg K}]\\ &= 0.1495\ \text{kJ/K}\end{aligned}$$

Hence, **net change in entropy = 0.1495 kJ/K. (Ans.)**

Example 5.48. *A mass 'm' of fluid at temperature* T_1 *is mixed with an equal mass of the same fluid at* T_2. *Prove that the resultant change of entropy of the universe is* $2\,mc\,\dfrac{(T_1+T_2)/2}{\sqrt{T_1T_2}}$ *and also prove that it is always positive.*

Solution. Mean temperature of the mixture = $\left(\frac{T_1 + T_2}{2}\right)$.

Thus change in entropy is given by

$$\Delta S = mc \int_{T_1}^{(T_1+T_2)/2} \frac{dT}{T} - mc \int_{(T_1+T_2)/2}^{T_2} \frac{dT}{T}$$

$$= mc \log_e \left(\frac{T_1 + T_2}{2T_1}\right) - mc \log_e \left(\frac{2T_2}{T_1 + T_2}\right)$$

$$= mc \log_e \left(\frac{T_1 + T_2}{2T_1}\right) + mc \log_e \left(\frac{T_1 + T_2}{2T_2}\right) = mc \log_e \frac{(T_1 + T_2)^2}{4T_1 T_2}$$

$$= mc \log_e \left[\frac{T_1 + T_2}{2\sqrt{T_1 T_2}}\right]^2 = 2\ mc \log_e \left[\frac{T_1 + T_2}{2\sqrt{T_1 T_2}}\right]$$

$$= 2\ mc \log_e \left[\frac{(T_1 + T_2)/2}{\sqrt{T_1 T_2}}\right]$$

i.e., **Resultant change of entropy of universe**

$$= \mathbf{2\ mc\ log_e} \left[\frac{(\mathbf{T_1 + T_2})/\mathbf{2}}{\sqrt{\mathbf{T_1 T_2}}}\right] \quad \textbf{...Proved}$$

The arithmetic mean $\frac{T_1 + T_2}{2}$ is greater than geometric mean $\sqrt{T_1 T_2}$.

Therefore, $\log_e \frac{(T_1 + T_2)/2}{\sqrt{T_1 T_2}}$ is + ve.

Thus, **the entropy of the universe increases.**

☞**Example 5.49.** (*a*) *One kg of water at 0°C is brought into contact with a heat reservoir at 90°C. When the water has reached 90°C, find :*

(*i*) *Entropy change of water ;*

(*ii*) *Entropy change of the heat reservoir ;*

(*iii*) *Entropy change of the universe.*

(*b*) *If water is heated from 0°C to 90°C by first bringing it in contact with a reservoir at 40°C and then with a reservoir at 90°C, what will the entropy change of the universe be ?*

(*c*) *Explain how water might be heated from 0°C to 90°C with almost no change in the entropy of the universe.*

Solution. Mass of water, $m = 1$ kg

Temperature of water, $T_1 = 0 + 273 = 273$ K

Temperature of the heat reservoir, $T_2 = 90 + 273 = 363$ K.

(*a*) Refer Fig. 5.50. Water is being heated through a finite temperature difference. The entropy of water would increase and that of the reservoir would decrease so that net entropy change of the water (system) and the reservoir together would be positive definite. *Water is being heated, irreversibly,* and to find the entropy change of water, we have to assume a reversible path between the end states, which are at equilibrium.

(*i*) *Entropy of water,*

$$(\Delta\, s)_{water} = \int_{T_1}^{T_2} \frac{mcdT}{T} = mc \log_e \frac{T_2}{T_1}$$

(*c* = Specific heat of water)

$$= 1 \times 4.187 \times \log_e \frac{363}{273}$$

$$= \mathbf{1.193\ kJ/kg\ K.}\quad \textbf{(Ans.)}$$

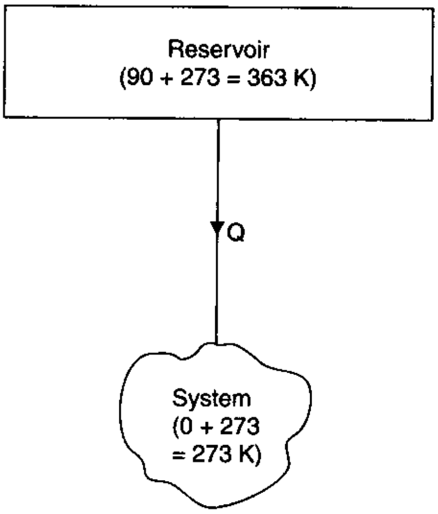


Fig. 5.50

(*ii*) The temperature of the reservoir remains *constant* irrespective of the amount of the heat withdrawn.

Amount of heat absorbed by the system from the reservoir,

$$Q = 1 \times 4.187 \times (363 - 273) = 376.8 \text{ kJ}$$

∴ *Entropy change of the reservoir,*

$$(\Delta\, s)_{reservoir} = -\frac{Q}{T} = -\frac{376.8}{363}$$

$$= -\ \mathbf{1.038\ kJ/K.}\quad \textbf{(Ans.)}$$

(–ve sign indicates decrease in entropy).

(*iii*) *Entropy change of the universe,*

$$(\Delta\, s)_{universe} = (\Delta\, s)_{water\ (or\ system)} + (\Delta\, s)_{reservoir}$$

$$= 1.193 + (-\ 1.038) = \mathbf{0.155\ kJ/K.}\quad \textbf{(Ans.)}$$

(*b*) The heating of water is being carried out in two stages, first from 0°C (273 K) to 40°C (*i.e.*, 313 K) by bringing in contact with a reservoir at 40°C (313 K), and then from 40°C (313 K) to 90°C (363 K) by bringing in contact with a second reservoir at 90°C (363 K).

$$(\Delta\, s)_{water} = \int_{273}^{313} mc \frac{dT}{T} + \int_{313}^{363} mc \frac{dT}{T} = 1 \times 4.187 \left(\log_e \frac{313}{273} + \log_e \frac{363}{313}\right)$$

$$= 4.187\ (0.1367 + 0.1482) = 1.1928 \text{ kJ/K.}$$

$$(\Delta s)_{res.\ I} = -\ \frac{1 \times 4.187 \times (313 - 273)}{313} = -\ 0.535 \text{ kJ/K} \qquad \Delta S = -\frac{Q}{T}$$

$$(\Delta s)_{res.\ II} = -\ \frac{1 \times 4.187 \times (363 - 313)}{363} = -\ 0.576 \text{ kJ/K} \qquad \Delta S = -\frac{Q}{T}$$

$$\therefore \quad (\Delta\, s)_{univ.} = (\Delta\, s)_{water} + (\Delta\, s)_{res.\ I} + (\Delta\, s)_{res.\ II}$$

$$= 1.1928 + (-\ 0.535) + (-\ 0.576) = 0.0818 \text{ kJ/K.}$$

i.e., **Entropy change of universe = 0.0818 kJ/K. (Ans.)**

(*c*) The entropy change of universe would be *less and less*, if the water is heated in *more and more stages*, by bringing the water in contact successively with *more and more heat reservoirs*, each succeeding reservoir being at a *higher temperature* than the preceding one. When water is heated in infinite steps, by bringing in contact with an infinite number of reservoirs in succession, so that at any instant the temperature difference between the water and the reservoir in contact is infinitesimally small, then the entropy change of the universe would be *zero* and the water would be *reversibly* heated.

Example 5.50. *1 kg of ice at – 5°C is exposed to the atmosphere which is at 25°C. The ice melts and comes into thermal equilibrium.*

(*i*) *Determine the entropy increase of the universe.*

(ii) What is the minimum amount of work necessary to convert the water back into ice at – 5°C ?

Take : c_p *of ice = 2.093 kJ/kg°C*

Latent heat of fusion of ice = 333.33 kJ/kg.

Solution. Mass of ice, m = 1 kg

Temperature of ice = – 5°C (= – 5 + 273 = 268 K)

Temperature of atmosphere = 25°C (= 25 + 273 = 298 K)

Heat absorbed by ice from the atmosphere (Fig. 5.51)

= Heat absorbed in solid phase + latent heat + heat absorbed in liquid phase

$= 1 \times 2.093 \times [0 - (-5)] + 1 \times 333.33 + 1 \times 4.187 \times (25 - 0)$

$= 10.46 + 333.33 + 104.67 = 448.46$ kJ.

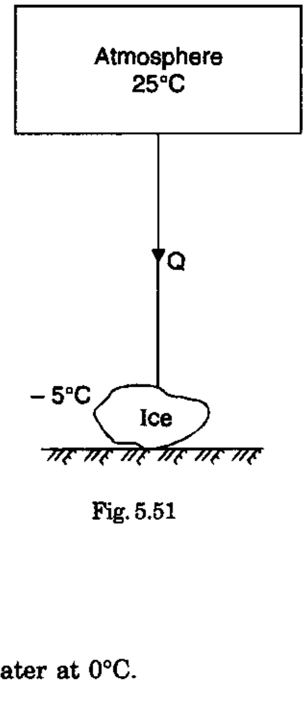


Fig. 5.51

(*i*) **Entropy increase of the universe,** $(\Delta s)_{universe}$:

Entropy change of the atmosphere,

$$(\Delta s)_{atm.} = -\frac{Q}{T} = -\frac{448.46}{298} = -1.5049 \text{ kJ/K}$$

Entropy change of system (ice) as it gets heated from – 5°C to 0°C,

$$(\Delta s_I)_{system} = \int_{268}^{273} mc_p \frac{dT}{T} = 1 \times 2.093 \log_e \frac{273}{268} = 0.0386 \text{ kJ/K}$$

Entropy change of the system as ice melts at 0°C to become water at 0°C.

$$(\Delta s_{II})_{system} = \frac{333.33}{273} = 1.2209 \text{ kJ/K}$$

Entropy change of water as it gets heated from 0°C to 25°C

$$(\Delta s_{III})_{system} = \int_{273}^{298} mc_p \frac{dT}{T} = 1 \times 4.187 \log_e \left(\frac{298}{273}\right) = 0.3668 \text{ kJ/K}$$

Total entropy change of ice as it melts into water

$$(\Delta s)_{total} = \Delta s_I + \Delta s_{II} + \Delta s_{III}$$
$$= 0.0386 + 1.2209 + 0.3668 = 1.6263 \text{ kJ/K}$$

Then temperature-entropy diagram for the system as ice at – 5°C converts to water at 25°C is shown in Fig. 5.52.

∴ **Entropy increase of the universe,**

$$(\Delta s)_{univ.} = (\Delta s)_{system} + (\Delta s)_{atm.}$$
$$= 1.6263 + (-1.5049) = \mathbf{0.1214 \text{ kJ/K}}. \quad \textbf{(Ans.)}$$

(*ii*) **Minimum amount of work necessary to convert the water back into ice at – 5°C,** $\mathbf{W_{min.}}$ **:**

To convert 1 kg of water at 25°C to ice at – 5°C, 448.46 kJ of heat have to be removed from it, and the system has to be brought from state 4 to state 1 (Fig. 5.52). A refrigerator cycle, as shown in Fig. 5.53, is assumed to accomplish this. The entropy change of the system would be the same, *i.e.*, $s_4 - s_1$, with the only difference that its sign will be negative, because heat is removed from the system (Fig. 5.52).

$$(\Delta s)_{system} = s_1 - s_4 \ (negative)$$

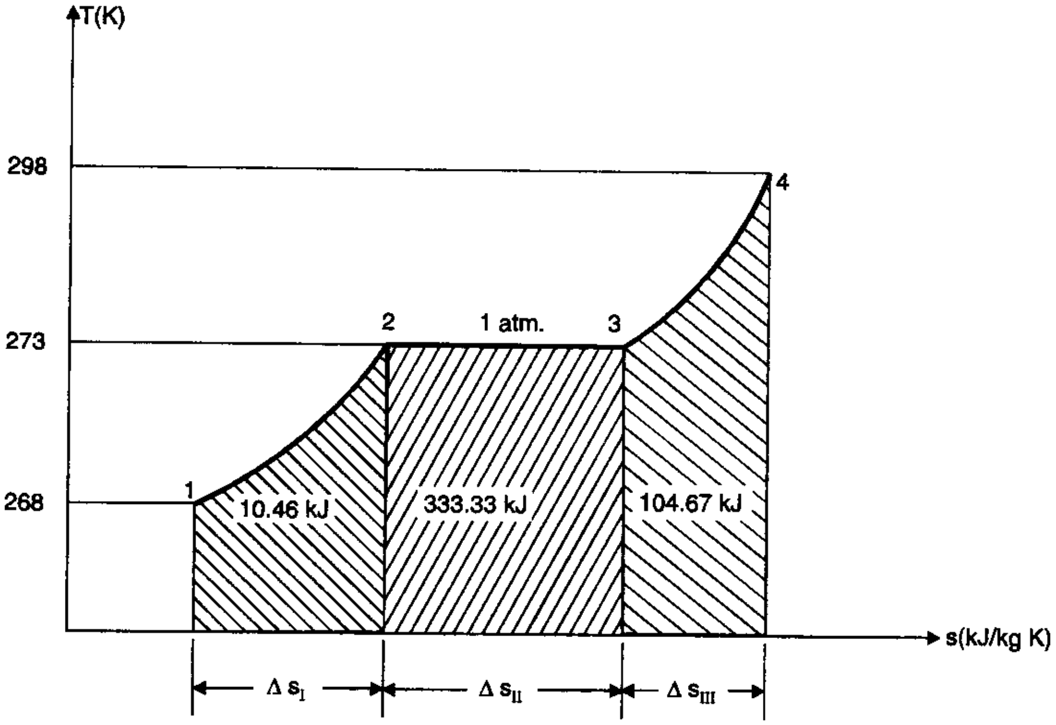


Fig. 5.52

The entropy change of the working fluid in the refrigerator would be zero, since it is operating in a cycle, *i.e.*,

$$(\Delta s)_{refrigerator} = 0.$$

The entropy change of the atmosphere (*positive*),

$$(\Delta s)_{atm.} = \frac{Q+W}{T}$$

∴ Entropy change of the universe

$$(\Delta s)_{univ.} = (\Delta s)_{system} + (\Delta s)_{refrigerator} + (\Delta s)_{atm.}$$

$$= (s_1 - s_4) + 0 + \frac{Q+W}{T} = (s_1 - s_4) + \frac{Q+W}{T}$$

By the principle of increase of entropy

$$(\Delta s)_{univ.\ or\ isolated\ system} \geq 0$$

$$\therefore \quad \left[(s_1 - s_4) + \frac{Q+W}{T}\right] \geq 0$$

$$\therefore \quad \frac{Q+W}{T} \geq (s_4 - s_1)$$

$$W \geq T(s_4 - s_1) - Q$$

$$W_{(min)} = T(s_4 - s_1) - Q$$

Here $Q = 448.46$ kJ

$T = 298$ K

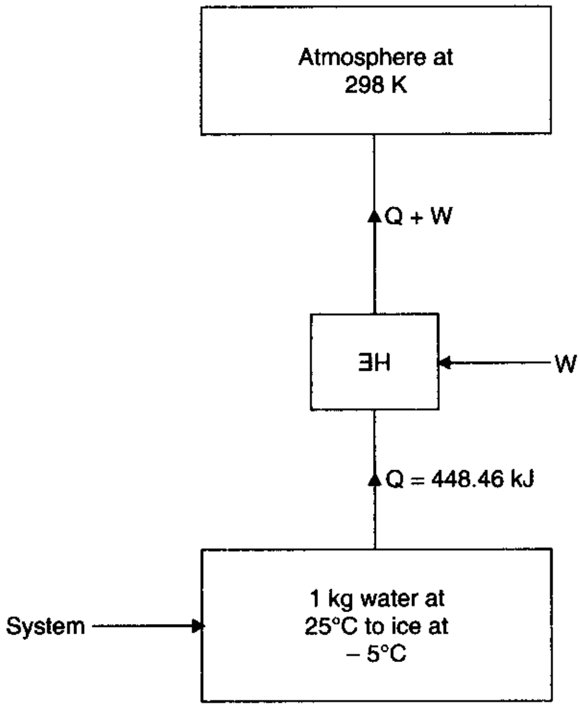


Fig. 5.53

$$s_4 - s_1 = 1.6263 \text{ kJ/K}$$

$$\therefore \quad \mathbf{W}_{(min)} = 298 \times 1.6263 - 448.46 = \mathbf{36.17 \text{ kJ}}. \quad \textbf{(Ans.)}$$

HIGHLIGHTS

1. **Clausius statement :**

   "It is impossible for a self-acting machine working in a cyclic process, unaided by any external agency, to convey heat from a body at a lower temperature to a body at a higher temperature."

   Kelvin-Planck statement :

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

   Although above statements of second law of thermodynamic appear to be different, they are really equivalent in the sense that violation of either statement implies violation of other.

2. **Perpetual motion machine of second kind** (*PMM*2) is that imaginary machine which would continuously absorb heat from a single thermal reservoir and convert this heat completely into work. The efficiency of such a machine would be 100%.

3. Clausius inequality is given by,

$$\sum_{\text{Cycle}} \left(\frac{\delta Q}{T}\right) \le 0$$

   "When a system performs a reversible cycle, then

$$\sum_{\text{Cycle}} \left(\frac{\delta Q}{T}\right) = 0,$$

but when the cycle is not reversible

$$\sum_{\text{Cycle}} \left(\frac{\delta Q}{T}\right) < 0.\text{"}$$

4. **'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 small when heat is added at a high temperature and is greater when heat addition is made at lower temperature. Thus for maximum entropy, there is a minimum availability for conversion into work and for minimum entropy there is maximum availability for conversion into work.

5. **Entropy changes for a closed system (per kg) :**

   (*i*) *General case* :

   (*a*) $c_v \log_e \frac{T_2}{T_1} + R \log_e \frac{v_2}{v_1}$ (in terms of T and v)

   (*b*) $c_v \log_e \frac{p_2}{p_1} + c_p \log_e \frac{v_2}{v_1}$ (in terms of p and v)

   (*c*) $c_p \log_e \frac{T_2}{T_1} - R \log_e \frac{p_2}{p_1}$ (in terms of T and p)

   (*ii*) *Constant volume* : $c_v \log_e \frac{T_2}{T_1}$

   (*iii*) *Constant pressure* : $c_p \log_e \frac{T_2}{T_1}$

   (*iv*) *Isothermal* : $R \log_e \frac{v_2}{v_1}$

   (*v*) *Adiabatic* : zero

   (*vi*) *Polytropic* : $c_v \left(\frac{n-\gamma}{n-1}\right) \log_e \frac{T_2}{T_1}$.

6. **Entropy change for an open system**

$$dS \geq \frac{dQ}{T_0} + \Sigma s_i \,.\, dm_i - \Sigma s_0 \,.\, dm_0$$

where, T_0 = Temperature of the surroundings.

Subscripts i and 0 refer to inlet and outlet conditions.

OBJECTIVE TYPE QUESTIONS

Choose the Correct Answer :

1. Second law of thermodynamics defines
   (*a*) heat (*b*) work (*c*) enthalpy
   (*d*) entropy (*e*) internal energy.
2. For a reversible adiabatic process, the change in entropy is
   (*a*) zero (*b*) minimum (*c*) maximum
   (*d*) infinite (*e*) unity.
3. For any reversible process, the change in entropy of the system and surroundings is
   (*a*) zero (*b*) unity (*c*) negative
   (*d*) positive (*e*) infinite.
4. For any irreversible process the net entropy change is
   (*a*) zero (*b*) positive (*c*) negative
   (*d*) infinite (*e*) unity.

5. The processes of a Carnot cycle are
   (*a*) two adiabatic and two constant volume
   (*b*) one constant volume and one constant pressure and two isentropics
   (*c*) two adiabatics and two isothermals (*d*) two constant volumes and two isothermals
   (*e*) two isothermals and two isentropics.
6. Isentropic flow is
   (*a*) irreversible adiabatic flow (*b*) ideal fluid flow (*c*) perfect gas flow
   (*d*) frictionless reversible flow (*e*) reversible adiabatic flow.
7. In a Carnot engine, when the working substance gives heat to the sink
   (*a*) the temperature of the sink increases
   (*b*) the temperature of the sink remains the same
   (*c*) the temperature of the source decreases
   (*d*) the temperatures of both the sink and the source decrease
   (*e*) changes depend on the operating conditions.
8. If the temperature of the source is increased, the efficiency of the Carnot engine
   (*a*) decreases (*b*) increases
   (*c*) does not change (*d*) will be equal to the efficiency of a practical engine
   (*e*) depends on other factors.
9. The efficiency of an ideal Carnot engine depends on
   (*a*) working substance (*b*) on the temperature of the source only
   (*c*) on the temperature of the sink only
   (*d*) on the temperatures of both the source and the sink
   (*e*) on the construction of engine.
10. The efficiency of a Carnot engine using an ideal gas as the working substance is
    (*a*) $\frac{T_1 - T_2}{T_1}$ (*b*) $\frac{T_1}{T_1 - T_2}$ (*c*) $\frac{T_1 T_2}{T_1 - T_2}$
    (*d*) $\frac{T_1 - T_2}{T_1 T_2}$ (*e*) $\frac{T_2(T_1 - T_2)}{T_1(T_1 + T_2)}$.
11. In a reversible cycle, the entropy of the system
    (*a*) increases (*b*) decreases
    (*c*) does not change (*d*) first increases and then decreases
    (*e*) depends on the properties of working substance.
12. A frictionless heat engine can be 100% efficient only if its exhaust temperature is
    (*a*) equal to its input temperature (*b*) less than its input temperature
    (*c*) 0°C (*d*) 0°K (*e*) – 100°C.
13. Kelvin-Planck's law deals with
    (*a*) conservation of energy (*b*) conservation of heat (*c*) conservation of mass
    (*d*) conversion of heat into work (*e*) conversion of work into heat.
14. Which of the following statements is *correct* according to Clausius statement of second law of thermodynamics ?
    (*a*) It is impossible to transfer heat from a body at a lower temperature to a body at a higher temperature
    (*b*) It is impossible to transfer heat from a body at a lower temperature to a body at a higher temperature, without the aid of an external source.
    (*c*) It is possible to transfer heat from a body at a lower temperature to a body at a higher temperature by using refrigeration cycle
    (*d*) None of the above.

15. According to Kelvin-Planck's statement of second law of thermodynamics

(*a*) It is impossible to construct an engine working on a cyclic process, whose sole purpose is to convert heat energy into work

(*b*) It is possible to construct an engine working on a cyclic process, whose sole purpose is to convert the heat energy into work

(*c*) It is impossible to construct a device which while working in a cyclic process produces no effect other than the transfer of heat from a colder body to a hotter body

(*d*) When two dissimilar metals are heated at one end and cooled at the other, the e.m.f. developed is proportional to the difference of their temperatures at the two end.

(*e*) None of the above.

16. The property of a working substance which increases or decreases as the heat is supplied or removed in a reversible manner is known as

(*a*) enthalpy (*b*) internal energy

(*c*) entropy (*d*) external energy.

17. The entropy may be expressed as a function of

(*a*) pressure and temperature (*b*) temperature and volume

(*c*) heat and work (*d*) all of the above

(*e*) none of the above.

18. The change of entropy, when heat is absorbed by the gas is

(*a*) positive (*b*) negative (*c*) positive or negative.

19. Which of the following statements is *correct* ?

(*a*) The increase in entropy is obtained from a given quantity of heat at a low temperature

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

(*c*) The entropy represents the maximum amount of work obtainable per degree drop in temperature

(*d*) All of the above.

20. The condition for the reversibility of a cycle is

(*a*) the pressure and temperature of working substance must not differ, appreciably from those of the surroundings at any stage in the process

(*b*) all the processes taking place in the cycle of operation, must be extremely slow

(*c*) the working parts of the engine must be friction free

(*d*) there should be no loss of energy during the cycle of operation

(*e*) all of the above.

21. In an irreversible process there is a

(*a*) loss of heat (*b*) no loss of work

(*c*) gain of heat (*d*) no gain of heat.

22. The main cause for the irreversibility is

(*a*) mechanical and fluid friction (*b*) unrestricted expansion

(*c*) heat transfer with a finite temperature difference

(*d*) all of the above.

23. The efficiency of the Carnot cycle may be increased by

(*a*) increasing the highest temperature (*b*) decreasing the highest temperature

(*c*) increasing the lowest temperature (*d*) decreasing the lowest temperature

(*e*) keeping the lowest temperature constant.

24. Which of the following is the *correct* statement ?

(*a*) All the reversible engines have the same efficiency

(*b*) All the reversible and irreversible engines have the same efficiency

(*c*) Irreversible engines have maximum efficiency

(*d*) All engines are designed as reversible in order to obtain maximum efficiency.

Answers

1.	(*d*)	**2.**	(*a*)	**3.**	(*a*)	**4.**	(*b*)	**5.**	(*e*)	**6.**	(*e*)	**7.**	(*b*)
8.	(*b*)	**9.**	(*d*)	**10.**	(*a*)	**11.**	(*c*)	**12.**	(*d*)	**13.**	(*d*)	**14.**	(*b*)
15.	(*e*)	**16.**	(*c*)	**17.**	(*a*)	**18.**	(*a*)	**19.**	(*d*)	**20.**	(*e*)	**21.**	(*a*)
22.	(*d*)	**23.**	(*d*)	**24.**	(*a*).								

THEORETICAL QUESTIONS

1. State the limitations of first law of thermodynamics.
2. What is the difference between a heat engine and a reversed heat engine ?
3. Enumerate the conditions which must be fulfilled by a reversible process. Give some examples of ideal reversible processes.
4. What is an irreversible process ? Give some examples of irreversible processes.
5. Give the following statements of second law of thermodynamics.
   (*i*) Clausius statement
   (*ii*) Kelvin-Planck statement.
6. Define heat engine, refrigerator and heat pump.
7. What is the perpetual motion machine of the second kind ?
8. What do you mean by 'Thermodynamic temperature' ?
9. What do you mean by 'Clausius inequality' ?
10. Describe the working of a Carnot cycle.
11. Derive an expression for the efficiency of the reversible heat engine.
12. What do you mean by the term 'Entropy' ?
13. What are the characteristics of entropy ?
14. Prove that entropy is a property of a system.
15. Derive an expression for the change in entropy of the universe.
16. What is a temperature-entropy diagram ?
17. Derive expressions for entropy changes for a closed system in the following cases :
   (*i*) General case for change of entropy of a gas
   (*ii*) Heating a gas at constant volume
   (*iii*) Heating a gas at constant pressure
   (*iv*) Polytropic process.
18. Give an expression for entropy changes for an open system.

UNSOLVED EXAMPLES

Heat Engines and Reversible Heat Engines

1. A cyclic heat engine operates between a source temperature of 800°C and a sink temperature of 30°C. What is the least rate of heat rejection per kW net output of the engine ? [**Ans.** 0.392 kW]

2. A domestic food freezer maintains a temperature of – 15°C. The ambient air temperature is 30°C. If heat leaks into the freezer at the continuous rate of 1.75 kJ/s what is the least power necessary to pump this heat out continuously. [**Ans.** 0.31 kW]
3. A reversible heat engine operates between two reservoirs at temperatures of 600°C and 40°C. The engine drives a reversible refrigerator which operates between reservoirs at temperatures of 40°C and – 20°C. The heat transfer to the heat engine is 2000 kJ and the net work output for the combined engine refrigerator is 360 kJ. (*i*) Calculate the heat transfer to the refrigerant and the net heat transfer to the reservoir at 40°C. (*ii*) Reconsider (*i*) given that the efficiency of the heat engine and the C.O.P. of the refrigerator are each 40 per cent of their maximum possible values.

   [**Ans.** Heat rejection to 40°C reservoir (*i*) 5539 kJ ; (*ii*) 1899.6 kJ]
4. A heat engine is supplied heat at the rate of 1700 kJ/min and gives an output of 9 kW. Determine the thermal efficiency and the rate of heat rejection. [**Ans.** 31.76% ; 9.333 kJ/s]
5. What is the highest possible theoretical efficiency of a heat engine operating with a hot reservoir of furnace gases at 2000°C when the cooling water available is at 10°C ? [**Ans.** 87.54%]
6. A Carnot cycle operates between source and sink temperatures of 260°C and – 17.8°C. If the system receives 100 kJ from the source, find (*i*) efficiency of the system, (*ii*) the net work transfer, (*iii*) heat rejected to the sink. [**Ans.** 52.2% ; 52.2 kJ ; 47.8 kJ]
7. Source *A* can supply energy at a rate of 11000 kJ/min at 320°C. A second source *B* can supply energy at a rate of 110000 kJ/min at 68°C. Which source *A* or *B*, would you choose to supply energy to an ideal reversible engine that is to produce large amount of power if the temperature of the surroundings is 40°C ? [**Ans.** Source *B*]
8. A fish freezing plant requires 50 tons of refrigeration. The freezing temperature is – 40°C while the ambient temperature is 35°C. If the performance of the plant is 15% of the theoretical reversed Carnot cycle working within the same temperature limits, calculate the power required. [**Ans.** 375 kW]

   Take 1 ton = 210 kJ/ min.

Clausius Inequality

9. A heat engine is supplied with 278 kJ/s of heat at a constant fixed temperature of 283°C and the heat rejection takes place at 5°C. The following results were reported : (*i*) 208 kJ/s are rejected, (*ii*) 139 kJ/s are rejected, (*ii*) 70 kJ/s are rejected.

   Classify which of the results report a reversible cycle or irreversible cycle or impossible results.

   [**Ans.** (*i*) Irreversible (*ii*) Reversible (*iii*) Impossible]

Entropy

10. Air at 15°C and 1.05 bar occupies 0.02 m^3. The air is heated at constant volume until the pressure is 4.2 bar, and then cooled at constant pressure back to the original temperature. Calculate the net heat flow to or from the air and the net entropy change.

    Sketch the process on a *T-s* diagram.

    [**Ans.** Heat rejected = 6.3 kJ, decrease in entropy of air = 0.0101 kJ/K]
11. 0.03 m^3 of nitrogen contained in a cylinder behind a piston is initially at 1.05 bar and 15°C. The gas is compressed isothermally and reversibly until the pressure is 4.2 bar. Calculate the change of entropy, the heat flow, and the work done, and sketch the process on a *p-v* and *T-s* diagrams. Assume nitrogen to act as a perfect gas. Molecular weight of nitrogen = 28.

    [**Ans.** 0.01516 kJ/K (decrease) ; 4.37 kJ (heat rejected) ; 4.37 kJ]
12. Calculate the change of entropy of 1 kg of air expanding polytropically in a cylinder behind a piston from 6.3 bar and 550°C to 1.05 bar. The index of expansion is 1.3. [**Ans.** 0.1 kJ/kg K (increase)]
13. 0.05 kg of carbon dioxide (molecular weight = 44) is compressed from 1 bar, 15°C, until the pressure is 8.3 bar, and the volume is then 0.004 m^3. Calculate the change of entropy. Take c_p for carbon dioxide as 0.88 kJ/kg K, and assume carbon dioxide to be a perfect gas. [**Ans.** 0.0113 kJ/K (decrease)]

14. In an air turbine the air expands from 6.8 bar and 430°C to 1.013 bar and 150°C. The heat loss from the turbine can be assumed to be negligible. Show that the process is irreversible, and calculate the change of entropy per kg of air. **[Ans.** 0.0355 kJ/kg K (increase)]

15. (*i*) One kg of water at 273 K is brought into contact with a heat reservoir at 373 K. When the water has reached 373 K, find the entropy change of the water of the heat reservoir, and of the universe.

    (*ii*) If water is heated from 273 K to 373 K by first bringing it in contact with a reservoir at 323 K and then with reservoir at 373 K, what will the entropy change of the universe be ?

    [Ans. (*i*) 0.183 kJ/K ; (*ii*) 0.098 kJ/K]

16. One kg of ice at – 5°C is exposed to the atmosphere which is at 20°C. The ice melts and comes into thermal equilibrium with the atmosphere.

    (*i*) Determine the entropy increase of the universe.

    (*ii*) What is the minimum amount of work necessary to convert the water back into ice at – 5°C ? c_p of ice is 2.093 kJ/kg °C and the latent heat of fusion of ice is 333.3 kJ/kg.

    [Ans. (*i*) 0.0949 kJ/K (increase) (*ii*) 28.5 kJ]

17. A system has a heat capacity at constant volume $C_v = AT^2$, where $A = 0.042$ J/K³. The system is originally at 200 K and a thermal reservoir at 100 K is available. What is the maximum amount of work that can be recovered as the system is cooled down to the temperature of the reservoir ? **[Ans.** 35 kJ]

18. A fluid undergoes a reversible adiabatic compression from 0.5 MPa, 0.2 m³ to 0.05 m³ according to the law, $pv^{1.3}$ = constant. Determine the change in enthalpy, internal energy and entropy, and the heat transfer and work transfer during the process. **[Ans.** 223.3 kJ ; 171.77 kJ, ; zero ; zero ; – 171.77 kJ]

19. A rigid cylinder containing 0.006 m³ of nitrogen (molecular weight 28) at 1.04 bar, 15°C, is heated reversibly until the temperature is 90°C. Calculate the change of entropy and the heat supplied. Sketch the process on *T-s* diagram. Take the isentropic index, γ, for nitrogen as 1.4, and assume that nitrogen is a perfect gas.

    [Ans. 0.00125 kJ/K ; 0.407 kJ]

20. 1 m³ of air is heated reversibly at constant pressure from 15°C to 300°C, and is then cooled reversibly at constant volume back to the initial temperature. The initial pressure is 1.03 bar. Calculate the net heat flow and overall change of entropy, and sketch the process on a *T-s* diagram. **[Ans.** 101.5 kJ ; 0.246 kJ/K]

21. 1 kg of air is allowed to expand reversibly in a cylinder behind a piston in such a way that the temperature remains constant at 260°C while the volume is doubled. The piston is then moved in, and heat is rejected by the air reversibly at constant pressure until the volume is the same as it was initially. Calculate the net heat flow and the overall change of entropy. Sketch the processes on a *T-s* diagram.

    [Ans. – 161.9 kJ/kg ; – 0.497 kJ/kg K]

22. 1 kg of air at 1.013 bar, 17°C, is compressed according to a law $pv^{1.3}$ = constant, until the pressure is 5 bar. Calculate the change of entropy and sketch the process on a *T-s* diagram, indicating the area, which represents the heat flow. **[Ans.** – 0.0885 kJ/kg K]

23. 0.06 m³ of ethane (molecular weight 30), at 6.9 bar and 60°C, is allowed to expand isentropically in a cylinder behind a piston to a pressure of 1.05 bar and a temperature of 107°C. Calculate γ, *R*, c_p, c_v for ethane, and calculate the work done during the expansion. Assume ethane to be a perfect gas.

    The same mass of ethane at 1.05 bar, 107°C, is compressed to 6.9 bar according to a law $pv^{1.4}$ = constant. Calculate the final temperature of the ethane and the heat flow to or from the cylinder walls during the compression. Calculate also the change of entropy during the compression, and sketch both processes on *p-v* and *T-s* diagrams.

    [Ans. 1.219 ; 0.277 kJ/kg K ; 1.542 kJ/kg K ; 1.265 kJ/kg K ; 54.2 kJ ; 378°C ; 43.4 kJ ; 0.0867 kJ/K]

24. In a reversible process the rate of heat transfer to the system per unit temperature rise is given by $\frac{dQ}{dT}$ = 0.5 kJ/°C. Find the change in entropy of the system if its temperature rises from 500 K to 800 K.

    [Ans. 0.235 kJ/kg°C]

25. In a reversible cycle 100 kJ of heat is received at 500 K ; then an adiabatic expansion occurs to 400 K, at which temperature 50 kJ of heat is received, then a further adiabatic expansion to 300 K at which temperature 100 kJ of heat is rejected :

(*i*) Find the change in entropy which occurs as the system is restored to its initial state in the remainder of the cycle.

(*ii*) If during the remainder of the cycle heat is transferred only at 400 K, how much heat is transferred and in what direction ? [**Ans.** 0.008 kJ/K ; + 3.2 kJ]

26. 1 kg of air is compressed according to the law $pv^{1.25}$ = constant from 1.03 bar and 15°C to 16.45 bar. Calculate the change in entropy. [**Ans.** 0.255 kJ/kg K]

27. A quantity of gas (mean molecular weight 36.2) is compressed according to the law pv^n = constant, the initial pressure and volume being 1.03 bar and 0.98 m^3 respectively. The temperature at the start of compression is 17°C and at the end it is 115°C. The amount of heat rejected during compression is 3.78 kJ, $c_p = 0.92$. Calculate :

(*i*) Value of n, (*ii*) Final pressure, (*iii*) Change in entropy.

[**Ans.** (*i*) 1.33 ; (*ii*) 1.107 bar ; (*iii*) 0.228 kJ/kg K]

6

Availability and Irreversibility

6.1. AVAILABLE AND UNAVAILABLE ENERGY

There are many forms in which an energy can exist. But even under ideal conditions all these forms cannot be converted completely into work. This indicates that energy has two parts :

— *Available part.*

— *Unavailable part.*

'***Available energy***' is the *maximum portion of energy which could be converted into useful work by ideal processes which reduce the system to a dead state* (a state in equilibrium with the earth and its atmosphere). Because there can be only one value for maximum work which the system alone could do while descending to its dead state, it follows immediately that *'Available energy' is a property.*

A system which has a pressure difference from that of surroundings, work can be obtained from an expansion process, and if the system has a different temperature, heat can be transferred to a cycle and work can be obtained. But when the temperature and pressure becomes equal to that of the earth, transfer of energy ceases, and although the system contains internal energy, this energy is ***unavailable.***

Summarily available energy denote, the latent capability of energy to do work, and in this sense it can be applied to energy in the system or in the surroundings.

The theoretical maximum amount of work which can be obtained from a system at any state p_1 *and* T_1 *when operating with a reservoir at the constant pressure and temperature* p_0 *and* T_0 *is called* '**availability**'.

6.2. AVAILABLE ENERGY REFERRED TO A CYCLE

The ***available energy (A.E.)*** or the available part of the energy supplied is the maximum work output obtainable from a certain heat input in a cyclic heat engine (Fig. 6.1). The minimum energy that has to be rejected to the sink by the second law is called the ***unavailable energy (U.E.),*** or the unavailable part of the energy supplied.

$$\therefore \quad Q_1 = \text{A.E.} + \text{U.E.}$$

or

$$W_{max} = \text{A.E.} = Q_1 - \text{U.E.}$$