UNIT 8 ENTROPY - AVAILABLE AND UNAVAILABLE ENERGY

Structure

8.1 INTRODUCTION

In the previous Units, second law of thermodynamics has been introduced for systems executing thermodynamic cycles only. It has also been adequately discussed as to how the second law and its corollaries (Carnot theorems and thermodynamic temperature) can be used for several purposes such as (1) finding out the feasibility or otherwise of a cycle, (2) classification of all feasible cycles as reversible or irreversible cycles and (3) evaluation of the maximum performance of a cycle operating between given two reservoirs at different temperatures. Although these are very important, the matter does not end here. More often than not, in every day life, we come across non-cyclic processes rather than cyclic processes. It is needless to emphasise here that we must know how the second law of thermodynamics can be used to predict, preferably quantitatively, the feasibility or otherwise, the reversibility or irreversibility and performance of these non-cyclic processes. It shall be explained in detail in the course of this unit as to how the extension of the second law to non-cyclic processes is made possible with the use of 'ENTROPY', a property to be introduced for the said purpose.

Objectives

After reading this unit you must be able to

* visualise a clear picture of what $\oint \delta Q / T$ really means, its importance with regard to irreversible and reversible cycles, and how it leads to the concept of entropy,

* define and understand what entropy means,

* calculate the entropy changes in processes,

* depict the processes on coordinate system with entropy on one of the axes,

* use entropy for identifying reversible, irreversible and impossible processes, especially using the principle of increase of entropy,

* understand clearly the difference between reversible adiabatic and irreversible adiabatic processes, and

* have a clear understanding of available and unavailable energies, calculate them and show that irreversibilities increases the unavailable part of the energy.

Entropy - Available and
Unavailable Energy

8.1.1 Similarities between Energy and Entropy

It is indeed useful to recall here that first law of thermodynamics was also introduced first to systems undergoing thermodynamic cycles only. It was then extended to non - cyclic processes and in doing so a new property ENERGY was introduced. It may be said that, while the concept of ENERGY was essential to extend the first law to non-cyclic processes the concept of ENTROPY is essential to extend the second law to non-cyclic processes. The property ENTROPY is so very useful and important that in almost all subsequent chapters this property is used for several meaningful and essential purposes.

The word ENERGY is used very commonly in every day life, although may not always be with the same meaning as in science or engineering. The familiarity of the word perhaps gives a pseudo-feeling to the reader that he knows ENERGY very well. It need not necessarily be so in practice. In comparison, ENTROPY is a word that is not used in every day life. It is also difficult to see physically what entropy is.

While ENERGY was introduced it was said that its change in any process is equal to the difference between the magnitudes of the two interactions - heat and work. The mathematics required to understand this is very simple. As we see later, a higher mathematics namely integration using calculus is essential to define ENTROPY. This might further complicate matters to make the reader fear that ENTROPY is something which is very difficult to understand. In reality it is not so. It is as difficult or as easy as understanding what ENERGY is. It is because of this reason a comparison between ENERGY and ENTROPY is made here. The matter becomes clear and simple if instead of struggling to know what ENTROPY is, attention is focussed and efforts are made to understand what its use is and what it can do.

8.2 SOME IMPORTANT STATEMENTS ON $\delta Q / T$

As a preamble to defining and explaining what ENTROPY is, it is useful to make a few important statements and prove them here by using the knowledge gained so far in thermodynamics. The first statement is the Clausius' Inequality Statement.

8.2.1 Statement 1

When a system executes a cyclic process the integral around the cycle of ($\delta Q / T$) is less than or equal to zero. This statement, popularly known as the **Clausius' Inequality Statement**, can be symbolically written as

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

Let the system enclosed by the boundary S, in Fig. 8.1, undergo a cyclic process. Let, at any instant, δQ and δW be the heat and work interactions the system has with its surroundings.
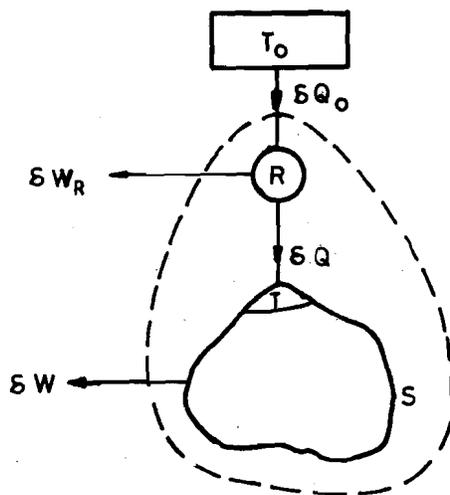

Fig. 8.1 : Diagram to prove Clausius Inequality

Let T be the temperature of part of the system at this instant. It is necessary to point out here that the directions of heat and work interactions are taken to be positive, only to get a generalised result and hence it need not be misconstrued that the system considered is already violating the second law. Although the system can exchange δQ directly with the reservoir at T_o, let it be assumed that this heat interaction occurs through a reversible heat engine R operating between T_o and the system temperature T such that, while δQ_o is the heat interaction between R and the reservoir, δQ is the heat interaction between R and the system. Under these conditions let the work output of R be δW_R. The reversible engine R is considered to be so small that it will perform a finite number of cycles in the time taken by the system S to undergo one cycle . Thus, δQ is the infinitesimal heat interaction between R and the system at temperature T in that time during which R undergoes one cycle. Conceptually R need not be a single heat engine but a multiplicity of small reversible engines, each heat engine, one at a time, having heat interactions δQ_o with the reservoir at T_o and δQ with the system at various temperatures such as $T, T + dT, T + 2dT, ...$ etc. during the time system S executes a complete cycle.

Applying first law to the system S,

$$\oint \delta Q = \oint \delta W \tag{i}$$

Consider now the system inside the boundary shown by the broken lines. This system is also undergoing a cycle (engine R undergoing a finite number of cycles in the time during which system S undergoes one cycle) having heat interaction with only the reservoir at T_o. In accordance with the Kelvin-Plank statement of the second law of thermodynamics the work output from this system cannot be positive and hence,

$$\oint (\delta W_R + \delta W) \leq 0 \tag{ii}$$

Between equations (i) and (ii),

$$\oint (\delta W_R + \delta Q) \leq 0 \tag{iii}$$

Applying first law to engine R,

$$\delta Q_o - \delta Q = \delta W_R \tag{iv}$$

As R is a reversible engine, by the definition of thermodynamic temperature scale,

$$\frac{\delta Q_o}{T_o} = \frac{\delta Q}{T} \quad \text{or} \quad \delta Q_o = \delta Q \left(\frac{T_o}{T}\right) \tag{v}$$

Between equations (iv) and (v),

$$\delta Q \left(\frac{T_o}{T}\right) - \delta Q = \delta W_R \tag{vi}$$

Substituting for δW_R from equation (vi) in equation (iii)

$$\oint \left[\left\{ \delta Q \left(\frac{T_0}{T}\right) - \delta Q \right\} + \delta Q \right] \leq 0 \quad \text{or}$$

$$\oint \delta Q \left(\frac{T_0}{T}\right) \leq 0 \tag{vii}$$

In equation (vii), T_o is a positive number and therefore,

$$\oint \left(\frac{\delta Q}{T}\right) \leq 0 \tag{8.1}$$

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8.2.2 Statement 2

When a system undergoes an internally reversible cycle the integral around the cycle of $\left(\frac{\delta Q}{T}\right)$ is always equal to zero. This may be symbolically written as

$$\oint \left(\frac{\delta Q_R}{T}\right) = 0. \tag{8.2}$$

As shown in figure 8.2, let 1-A-2-B-1 be a reversible cycle undergone by a system. From Clausius inequality,

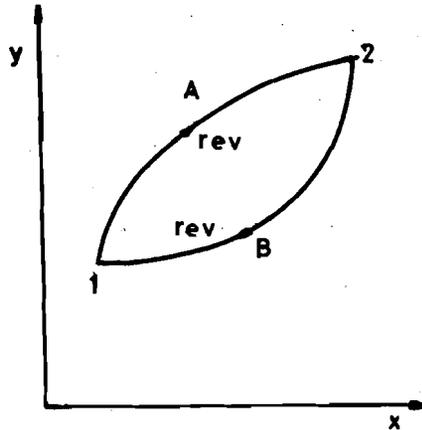$$\oint \left(\frac{\delta Q_R}{T}\right) \leq 0$$

Fig. 8.2 : Diagram to show $\oint (\delta Q_R / T) = 0$

$$\tag{i}$$

Suppose the system now undergoes the cycle 1-B-2-A-1, in the direction opposite to that of the cycle 1-A-2-B-1. Applying Clausius inequality to this cycle,

$$\oint \left(\frac{\delta Q_R'}{T}\right) \leq 0 \tag{ii}$$

In equation (i), δQ_R represents the heat interaction while the system undergoes the cycle in clockwise direction, and in equation (ii), $\delta Q_R'$ represents the heat interaction while the system undergoes the cycle in anti-clockwise direction. Both cycles are reversible and one is the reversed cycle of the other. By the concept of reversible cycles the magnitudes of δQ_R and $\delta Q_R'$ have to be necessarily the same but their directions are opposite and hence,

$$\delta Q_R' = - \delta Q_R \tag{iii}$$

Substituting for $\delta Q_R'$ from equation (iii) in equation (ii),

$$\oint \left(- \frac{\delta Q_R}{T}\right) \leq 0 \text{ or} \oint \left(\frac{\delta Q_R}{T}\right) \geq 0 \tag{iv}$$

For equations (i) and (iv) to be simultaneously true the only possibility is that

$$\oint \left(\frac{\delta Q_R}{T}\right) = 0 \tag{8.2}$$

8.2.3 Statement 3

When a system undergoes a change of state, the value of integral $\delta Q_R / T$ is independent of the path between the given two states. In other words, suppose a system can change from state 1 to state 2 through several reversible processes A, B, C ...etc. The value of $\int_1^2 \frac{\delta Q_R}{T}$ between states 1 and 2 is the same for each reversible path.

As shown in figure 8.3, consider a system that changes state from 1 to 2 as the system is subjected to a reversible process A. Assume now there exists a reversible process Z which can restore the system back to its initial state.

1-A-2-Z-1 is a reversible cycle executed by the system. Hence equation (8.2) is valid for this cycle.

$$\text{i.e. } \oint \left(\frac{\delta Q_R}{T} \right) = 0$$

This cyclic integral can now be replaced by two linear integrals, one each for the processes A and Z.
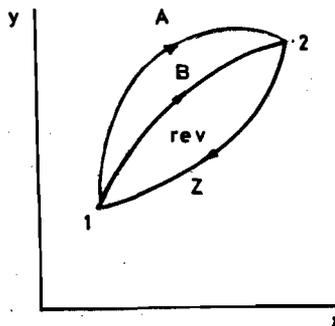

Fig. 8.3 : Diagram to show integral $\frac{\delta Q_R}{T}$ is independent of the path

$$\int_1^{2-A} \left(\frac{\delta Q_R}{T} \right) + \int_2^{1-Z} \left(\frac{\delta Q_R}{T} \right) = 0 \tag{i}$$

Now consider another reversible process B which can bring about the same state change as in process A. When process Z is carried out after the process B the system will execute a reversible cycle. For this cycle 1-B-2-Z-1, according to equation (8.2),

$$\oint \left(\frac{\delta Q_R}{T} \right) = 0 \text{ and hence}$$

$$\int_1^{2-B} \left(\frac{\delta Q_R}{T} \right) + \int_2^{1-Z} \left(\frac{\delta Q_R}{T} \right) = 0 \tag{ii}$$

Now, equation (i) minus equation (ii) gives

$$\int_1^{2-A} \left(\frac{\delta Q_R}{T} \right) + \int_1^{2-B} \left(\frac{\delta Q_R}{T} \right) = 0 \tag{8.3}$$

Thus $\int_1^2 \left(\frac{\delta Q_R}{T} \right)$ is same for the two reversible processes A and B between the states 1 and 2.

It can similarly be proved that for any other reversible path between 1 and 2 the value of the integral remains the same.

8.3. ENTROPY

It becomes obvious from the above statements that the quantity $\delta Q_R / T$ is unique in the sense that not only its change in a cyclic process is zero (equation (8.2)) but also its change between two state points is independent of the path between the two states (equation (8.3)). We already know that a magnitude related to a system is a property of a system if its change in a cyclic process is zero and its change between any two states is independent of the path

between the two states. Therefore, $\delta Q_R / T$ has to be a property of a system and this property is named as ENTROPY.

The entropy, S, of a system is a property whose change between two states 1 and 2 is given by,

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{\delta Q_R}{T}$$

(8.4)

or
$$dS = \frac{\delta Q_R}{T}$$

(8.5)

SAQ 1

According to Clausius Inequality statement $\oint \delta Q / T < 0$ for an irreversible thermodynamic cycle. Therefore there is a decrease in entropy of the system undergoing an irreversible cycle. Comment on this statement.

8.3.1 Remarks on Entropy

(i) Equation (8.4), or equation (8.5) in differential form, defines entropy ; to be precise it defines the change in entropy and not the absolute value of entropy.

(ii) The fact that only the difference in entropy is defined indicates that entropy, similar to energy, has to be measured with respect to a datum. If a value is fixed for entropy at an arbitrarily selected datum, the entropy at any other state, relative to the datum state, can be calculated by invoking the definition. Depending upon the state, relative to the datum state, a system can have either positive or negative values for entropy. It is worth recalling here similar statements made with respect to energy.

(iii) As the magnitude of heat transfer in any process depends on the mass of the system it is easy to infer from the definition of entropy that entropy has to be an extensive property. Therefore, specific entropy s is equal to S/m, where m is the mass of the system.

(iv) In accordance with its definition, the unit of entropy has to be J/K or kJ/K. The unit of specific entropy is kJ/kg K or J/kg K.

SAQ 2

1 kJ of heat is transferred from a reservoir at 300°C to a gas confined in a frictionless piston-cylinder mechanism and as a result of which the gas expands isothermally at 100°C. Is ΔS for the gas equal to $\int \delta Q / T$?

SAQ 3

The gas in SAQ 2 is now heated isothermally at the same temperature of 100°C but with the difference that the reservoir heating the gas is also at 100°C and that simultaneously the gas is stirred using a paddle wheel. Is ΔS for gas in this case equal to $\delta Q / T$?

8.3.2 Entropy as a Coordinate

Entropy, being a property, can be used as one of the coordinates for state diagrams. It shall be seen later that $T - s$ and $h - s$ diagrams are widely used in analysing several processes of practical interest in thermodynamics.

Shown on the $T - s$ diagram of figure 8.4 is a reversible process undergone by a system, in general, between an initial state 1 and a final state 2.
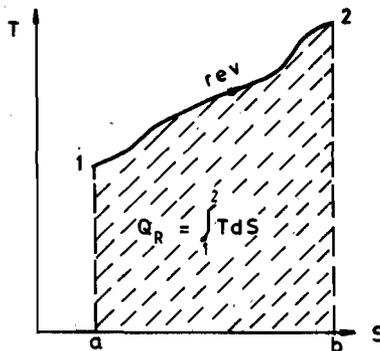

Fig. 8.4 : $T - s$ diagram in general

Draw ordinates at states 1 and 2. Consider the area (hatched) below the path of the reversible process bound by the two extreme ordinates: This area, a-1-2-b-a, according to mathematics, is equal to $\int y\, dx$. Temperature is represented on y-axis and entropy on x-axis and hence,

$$\text{Area a-1-2-b-a} = \int y\, dx = \int T\, dS$$

By the definition of entropy (equation (8.5)), $T\, dS = \delta Q_R$ and hence,

$$\int T\, dS = \int \delta Q_R = Q_R .$$

But $\int T\, ds$ is also equal to the area a-1-2-b-a. It can hence be said that the area bound by a reversible or quasi-static process and the two extreme ordinates on a $T - S$ diagram is equal to the net heat interaction the system has during the process.

It is worth emphasising here that $dS = \delta Q_R / T$ and that dS is not equal to $\delta Q / T$ in general. This fact is further elaborated below.
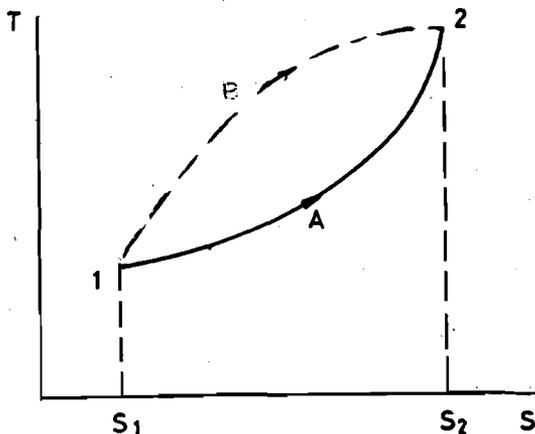

Fig. 8.5 : Diagram to distinguish between reversible and irreversible processes

Consider the reversible process 1-A-2 on the $T - S$ diagram in figure 8.5. The area below 1-A-2 is equal to the net heat transfer during the reversible process A and the entropy change during the process is given by,

$$S_2 - S_1 = \int_1^2 \frac{\delta Q_R}{T} \tag{8.4}$$

Now, consider an irreversible process B between the same two states 1 and 2. It is easy to see from the figure that change in entropy in this process is also equal to $S_2 - S_1$. But it

cannot be evaluated from $\int \delta Q / T$ along the irreversible process B, as $dS \neq \delta Q / T$. This fact reveals a method by which entropy change in an irreversible process can be calculated. Assume any convenient reversible process between the same end states as that of the irreversible process in question. Evaluate the value of $\int \delta Q_R / T$ along this assumed reversible process. Infer that the entropy change in the irreversible process is also the same. This is always true as entropy is a property and its change between two states is independent of the path between the two states.

8.3.3 Entropy as Quantitative Test for Irreversibility.

Consider the thermodynamic cycle 1-A-2-B-1 shown in $T - s$ diagram of figure 8.6. This is an irreversible cycle as process A is irreversible.
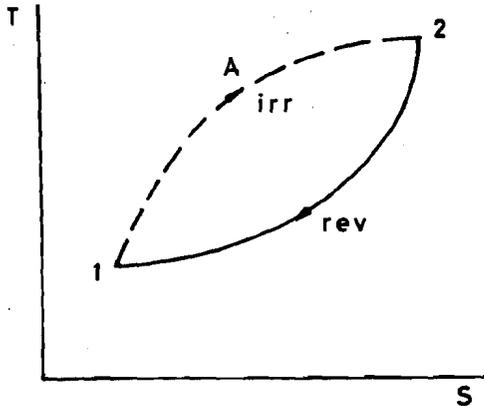

Fig. 8.6 : Quantitative test for irreversibility

According to Clausius Inequality, for this cycle,

$$\oint \frac{\delta Q}{T} < 0 \tag{8.1}$$

and therefore,

$$\int_{1}^{2 \rightarrow A} \frac{\delta Q}{T} + \int_{2}^{1 \rightarrow B} \frac{\delta Q}{T} < 0$$

Process B is reversible and hence the second term on the left hand side of the above equation, by the definition of entropy, has to be equal to $S_1 - S_2$ as, for this process 1 is the end state and 2 is the initial state. Therefore,

$$\int_{1}^{2 \rightarrow A} \frac{\delta Q}{T} + \left(S_1 - S_2\right) < 0, \text{ and hence}$$

$$S_2 - S_1 = \int_{1}^{2 \rightarrow A} \frac{\delta Q}{T} \tag{i}$$

Process A is one among the various irreversible processes that connect states 1 and 2. Thus, equation (i) is valid for all irreversible processes between states 1 and 2. It can now be generalised and stated that for all irreversible processes between two states 1 and 2,

$$S_2 - S_1 > \int_{1}^{2} \frac{\delta Q_R}{T} \tag{8.6}$$

However, by the definition of entropy,

$$S_2 - S_1 = \int_{1}^{2} \frac{\delta Q_R}{T} \tag{8.4}$$

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Equations (8.6) and (8.4) can be combined together as

$$S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T},$$

(8.7)

where the equality holds for reversible process and the inequality for any irreversible process.

The differential form of equation (8.7) is

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

(8.8)

Equations (8.7) or (8.8) can be used to find out whether a process is reversible or irreversible. If during a process the value of ΔS, the change in entropy, is equal to $\int \frac{\delta Q}{T}$ during the process, such a process must be reversible. If the change in entropy during a process is greater than the value of $\int \delta Q / T$, such a process must be an irreversible process.

8.3.4 Reversible and Irreversible Adiabatic Processes

If a process is reversible and adiabatic, $\delta Q_R = 0$ and hence entropy change during this process is zero, as $ds = \delta Q_R / T = 0$. Therefore, a reversible adiabatic process is one during which not only the heat transfer is zero but also the change in entropy is also zero. Therefore a reversible adiabatic process is also an isentropic process.

However, if a process is irreversible but adiabatic, $\delta Q = 0$ during this process. During this irreversible process $ds \neq \delta Q / T$ and hence $ds \neq 0$. In fact in an irreversible adiabatic process $ds > 0$. This can be verified by substituting zero for δQ in equation (8.6).

Thus, in general, for an adiabatic process,

$$ds \geq 0,$$

(8.9)

equality holding for reversible adiabatic process and the inequality for the irreversible process. This fact is embodied in the principle of increase of entropy.

SAQ 4

Shown in figure 8.7 are three different adiabatic expansion processes claimed to have been undergone by a system, each starting from the same state A and ending at B_1, B_2 and B_3 on the same pressure line on a T-s diagram. Identify the possible and impossible processes giving reasons.
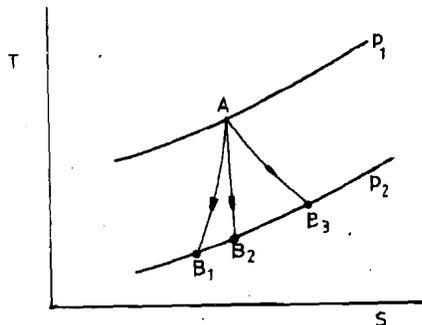

Fig. 8.7 : Diagram for SAQ 4

SAQ 5

Show on a T-s diagram the directions of possible adiabatic compression processes starting from any convenient state.

8.3.5 Principle of Increase of Entropy.

The principle of increase of entropy dictates that the change in entropy in an adiabatic process is always greater than zero or in the limiting case of a reversible adiabatic process it is equal to zero. Thus, in an adiabatic process the change in entropy can never be negative.

The fact that $ds \geq 0$ during an adiabatic process can be advantageously used to find out whether a given process is reversible or irreversible. The utility of this fact is not restricted to only adiabatic processes. It can also be used to assess the reversibility or irreversibility of any process, irrespective of whether there exists heat interaction during the process or not. All processes can be considered as adiabatic processes if the changes occurring in the system and the surroundings are considered together. The interactions in any process is only between the system and its surroundings. Therefore, in any situation, system + surroundings together is always an isolated system as nothing crosses this boundary. An isolated system is also an adiabatic system. The principle of increase of entropy can hence be generalised as,

$$ds_{system} + ds_{surroundings} \geq 0, \qquad (8.10)$$

where, the equality holds for reversible processes and the inequality for irreversible processes. It is obvious from equation 8.10 that, in a reversible process the change in entropy of the system is equal to the change in entropy of the surroundings with regard to their magnitudes, but their directions are opposite. In other words if the entropy of one system increases, the entropy of the other decreases by the same extent.

In an irreversible process the entropy change of the system and the surroundings are not the same. But the changes, in accordance with the principle of increase of entropy, will be such that their sum is always positive. Thus, the principle of increase of entropy when applied to the universe takes the form

$$\Delta S_{universe} > 0. \qquad (8.11)$$

The term universe connotes system and local surroundings.

One of the important questions raised at the beginning of the Unit on the second law of thermodynamics is 'how to decide the feasibility of a process quantitatively'. Equations (8.8) and (8.10) provide the answer to this question.

(a) A process is irreversible and possible if

$$S_2 - S_1 > \int_1^2 \frac{\delta Q}{T}$$

or $\Delta S_{system} + \Delta S_{surroundings} > 0,$

(b) A process is reversible and theoretically possible if

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}$$

or $\Delta S_{system} + \Delta S_{surroundings} = 0,$ and

(c) A process is impossible if

$$S_2 - S_1 < \int_1^2 \frac{\delta Q}{T}$$

or $\Delta S_{system} + \Delta S_{surroundings} < 0.$

SAQ 6

A rigid non-insulated vessel containing a mixture of fuel and air is surrounded by a large body of water at a particular temperature. The fuel is burnt. State whether the entropy change of the universe is +ve, -ve or 0.

8.4   CALCULATION OF ENTROPY

Equation (8.4) that defines entropy is not in a very convenient form to calculate entropy change in each and every process. This equation can be used only for either a reversible isothermal process or any other reversible process during which heat transfer is known as a function of temperature. Hence the utility of this relation is limited. Entropy is a property. From the two property rule for a pure substance it must be possible to calculate the entropy at any state in terms any two convenient independent properties. What follows is the explanation of such useful relations among properties.

Consider a reversible process undergone by a pure substance between states 1 and 2 as shown in the T - s diagram of figure 8.8. Applying the first law of thermodynamics to this process, in differential form $\delta Q - \delta W = dU$.
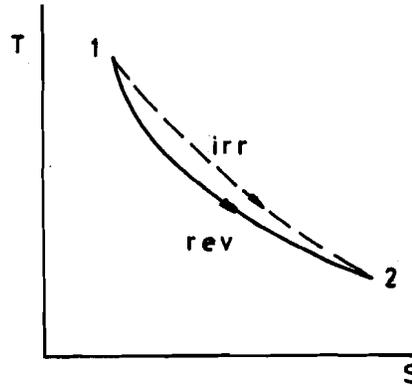

Fig. 8.8 : Reversible and irreversible processes on T - s diagram

As the process is reversible, $\delta Q = \delta Q_R$, and $\delta W = pdV$ and therefore,

$$\delta Q_R - pdV = dU.$$

By the definition of entropy, $\delta Q_R = TdS$ and hence,

$$TdS = dU + pdV.$$

This relation when written in terms of specific properties takes the form,

$$T \, ds = du + p \, dv \qquad (8.12)$$

By the definition of enthalpy, $h = u + pv$ and hence,

$$dh = du + pdv + vdp \quad \text{or} \quad du = dh - pdv - vdp.$$

Substituting for du in equation (8.12),

$$T \, ds = dh - pdv - vdp + pdv, \text{ or}$$

$$T \, ds = dh - v \, dp \qquad (8.13)$$

Equations (8.12) and (8.13) are called the Tds relations and are very important and useful relations that are very frequently used in calculating the entropy changes in majority of the cases. For the reversible process 1 - 2 in figure 8.8, from equation (8.12),

$$\Delta s = \int_1^2 ds = s_2 - s_1 = \int_1^2 du/T + \int_1^2 (p/T) \, dv \qquad (8.14)$$

Similarly from equation (8.13),

$$\Delta s = \int_1^2 ds = s_2 - s_1 = \int_1^2 dh/T - \int_1^2 (v/T) \, dp \qquad (8.14)$$

Now consider the irreversible process shown in figure 8.8. This process also occurs between
the same two end states as that of the reversible process. Hence, $s_2 - s_1$ is the same for both
the processes. Although equations (8.12) to (8.14) are derived for reversible processes it is
now easy to realise that the Tds relations can be used for calculating entropy changes in
irreversible processes as well. This can also be ascertained from the following point. There
is no factor in equations (8.12) to (8.14) which is path dependent. T, p, v, s, u and h are all
properties of the substance. Hence, the Tds relations can be used to find the entropy change
between two states in reversible as well as irreversible processes.

SAQ 7

Can a system undergo an isentropic process which is not reversible and adiabatic?

8.5 CARNOT CYCLE ON T - S DIAGRAM

In figure 8.9, a Carnot cycle is shown on p - v and T - s diagrams. The p - v diagram has
already been explained in the chapter on reversibility. An attempt is now made to explain
the Carnot cycle on T - s diagram. Corresponding state points on both the diagrams are
represented by the same alphabet and hence both the diagrams are compatible. In the
following analysis only the T - s diagram is considered.

During a - b, the system executing the cycle undergoes the reversible isothermal expansion
process. Hence, a - b is along the horizontal line such that $T_a = T_1 = T_b$. During this process
net heat transfer to the system at the constant temperature of T_1 is Q_1. For this process,

$$S_b - S_a = \int_a^b \frac{\delta Q_R}{T} = \frac{Q_1}{T_1}$$

$$\therefore Q_1 = T_1 \left(S_b - S_a\right) = T_1 \Delta S = \text{area } abfea \qquad (i)$$

As process b - c is reversible and adiabatic, $S_b = S_c$ and hence it is a vertical line.

Process $c - d$ is the reversible isothermal compression process during which the system
transfers out Q_2 at a steady temperature of T_2, such that $T_d = T_2 = T_c$. For this process,

$$S_d - S_c = \int_c^d \frac{\delta Q_R}{T} = \frac{Q_2}{T_2}$$

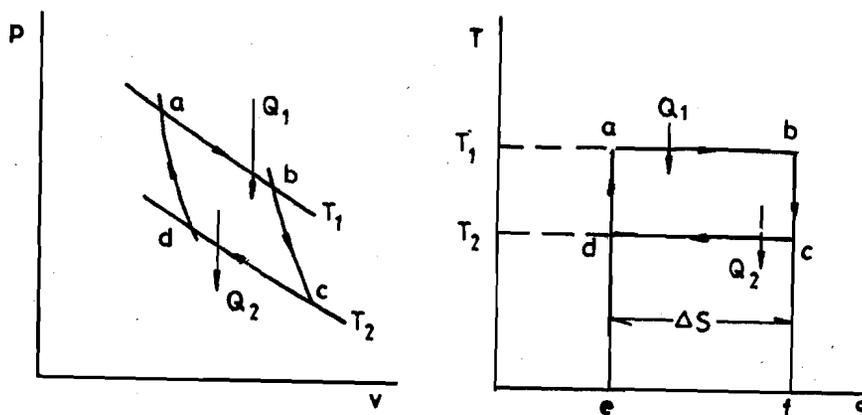$$\therefore Q_2 = T_2 (S_d - S_c) = \text{area } cdefc \qquad (ii)$$

Fig. 8.9 : Carnot cycle on p - v & T - s diagrams

In (ii) the entropy change is negative as heat is transferred out of the system. Thus the absolute value of Q_2 is

$$Q_2 = T_2 (S_c - S_d) = T_2 \ \Delta S. \tag{iii}$$

Process $d - a$ is reversible and adiabatic and hence it is along a vertical line as $S_d = S_a$. Thus, the Carnot cycle on a T - s diagram consists of two horizontal and two vertical lines and hence it is always a rectangle.

From equations (i) and (iii) net work W for the cycle is given by

$W = Q_1 - Q_2 = T_1 \Delta S - T_2 \Delta S =$ area of the diagram abcda.

$$\eta = \frac{(Q_1 - Q_2)}{Q_1} = \frac{(T_1 \Delta S - T_2 \Delta S)}{T_1 \Delta S} = \frac{(T_1 - T_2)}{T_1}.$$

The same expression for the efficiency of the reversible cycle was obtained in the Unit on Thermodynamic temperature scale.

8.6 AVAILABLE AND UNAVAILABLE ENERGY

Consider a heat transfer of magnitude Q_1 from a given high temperature reservoir at T_1K to a heat engine. The magnitude of work produced by the heat engine depends upon (i) T_2 the temperature of the low temperature reservoir to which the engine rejects heat and (ii) the nature of the engine - whether it is reversible or irreversible. The work produced increases with a decrease in T_2. The naturally available lowest temperature is the temperature of the surroundings at any place, say T_0. Thus, an engine rejecting heat to the surroundings at T_0 gives maximum work. Also, of all engines operating between T_1 and T_0 the reversible engine gives the maximum work for a given Q_1. Thus, only a reversible engine, operating between T_1, the temperature of the given high temperature reservoir, and T_0, the temperature of the surroundings, can convert the heat transfer to it to the maximum work, W_{max}. Under these conditions while W_{max} is called the available energy of Q_1, Q_0 the heat rejected to the surroundings at T_0 is called the unavailable energy of Q_1. This nomenclature is quite logical and meaningful as W_{max}, the maximum work realisable is the useful part of Q_1, while Q_0 the heat rejected to the surroundings is lost for ever and hence is the useless part of Q_1. The unavailable energy is also equal to $(Q_1 - W_{max})$. It can now be generalised and stated as follows.

Energy from any given high temperature reservoir is made up of two parts namely the available energy (useful part) and the unavailable energy (useless part). Available Energy is that part of the energy which can be converted to work by a reversible engine operating between the given high temperature reservoir and the low temperature reservoir at the surroundings temperature. Unavailable Energy is the energy rejected to the surroundings by this reversible heat engine.
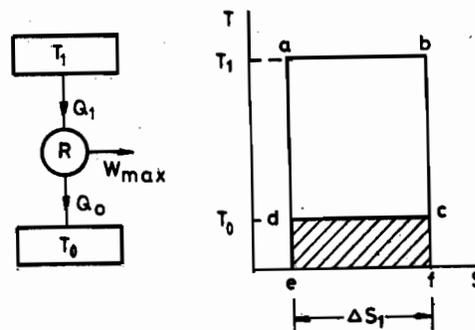

Fig. 8.10 : Available and unavailable energy

Referring to figure 8.10, which shows the schematic and the T - s diagram of a reversible engine operating between T_1 and T_0.

Available Energy of $Q_1 = W_{max} = Q_1 \times \eta_{max} = Q_1 \times \left[1 - \left(\frac{T_0}{T_1} \right) \right]$ (8.15)

= Area of the cycle 'abcda' on T - s diagram.

Unavailable Energy of $Q_1 = Q_0 = Q_1 - W_{max}$ (8.16)

= Area 'cdefc' on T - s diagram = $T_0 \times \Delta S_1$,

where ΔS_1 = increase in entropy of the surroundings, which in magnitude is also equal to the decrease in entropy of the high temperature reservoir which is evident from the T - s diagram.

As a **first example** suppose $Q_1 = 100$ kJ, $T_1 = 1000$ K and $T_0 = 300$ K.
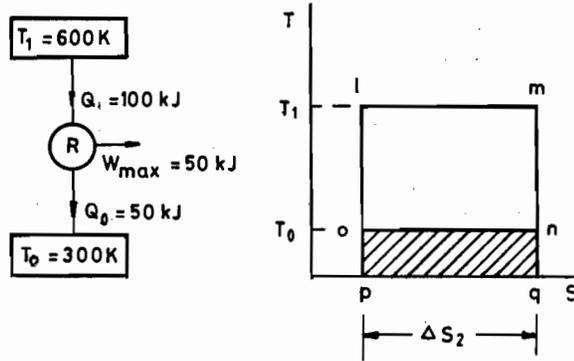

Fig. 8.11 : Available energy as a function of temperature

From equation (8.15). Available Energy of 100 kJ $= 100 \times \left[1 - \left(\dfrac{300}{1000} \right) \right] = 70$ kJ, and from equation (8.16),

Unavailable energy of 100 kJ $= 100 - 70 = 30$ kJ = area *cdefc*.

As a second example, let $T_1 = 600$ K, and $Q_1 = 100$ kJ, $T_0 = 300$ K (same as in the previous example). In this case, as shown in Figure 8.11, the Available Energy of 100 kJ $= 100[1 - (300 / 600)] = 50$ kJ and the Unavailable Energy is $= Q_1 - W_{max} = 50$ kJ = hatched area 'nopqn' $= T_0 \times \Delta S_2$, , where ΔS_2 is the increase in entropy of the surroundings.

It is worth noting from these two examples that while the Available Energy of 100 kJ from the reservoir at 1000 K is 70 kJ, the available energy of the same 100 kJ from a reservoir at a lower temperature of 600 K is only 50 kJ. As the temperature of the high temperature reservoir decreases the available part of the energy supplied by it also gets decreased. It is for this reason that the energy at a higher temperature is said to be more valuable than the same magnitude of energy at a lower temperature.

Let us now consider a **third example**. Let 100 kJ of heat be transferred from the reservoir at 1000 K to a reversible engine through an intermediate reservoir at 600 K as represented by the schematic and T - s diagrams in Fig.8.12. Although the input to the engine is from the
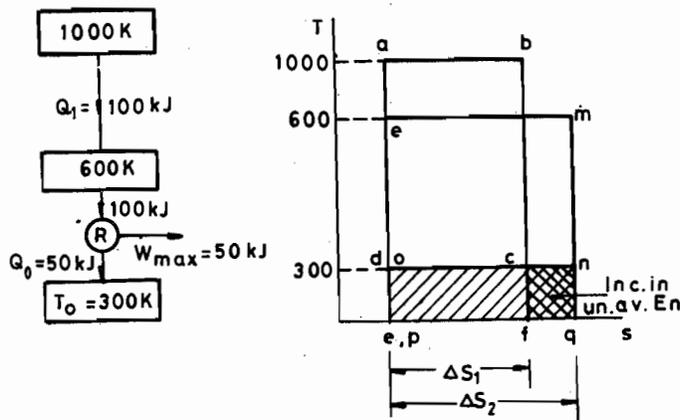

Fig. 8.12 : Increase in unavailable energy

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reservoir at 1000 K, the engine is operating between the reservoirs at 600 K and 300 K. Hence the work output of the engine is = 100 [1 - (300/600)] = 50 kJ which is equal to that in Example 2 and not 70 kJ as in Example 1. This reduction is because the 100 kJ from 1000 K is first transferred to another reservoir at 600 K before it is transferred to the engine. The heat transfer between the two reservoirs at 1000 K and 600 K is irreversible. This irreversibility reflects in the decrease of the available energy by 70 - 50 = 20 kJ. This reduction manifests itself in the increase of unavailable energy by the same extent of 20 kJ. It can thus be stated that irreversibility due to heat transfer with finite temperature difference always increases the unavailable energy.

An important relation between the increase in unavailable energy and entropy can now be deduced. In the $T - s$ diagram of figure 8.12, the unavailable energy, in the absence of the intermediate reservoir, according to Example 1, is equal to 30 kJ which is represented by the single hatched area 'cdefc' (also the same area shown in figure 8.10). Because of the introduction of the intermediate reservoir the unavailable energy, according to Example 2, has increased to 50 kJ as represented by the area 'nopqn' (same area shown separately in figures 8.11 and 8.12). It can be seen from the $T - s$ diagram in figure 8.12 that this area 'nopqn' is equal to the sum of the single hatched area 'cdefc' and the double hatched area 'ncfqn'.

Thus, the increase in unavailable energy is equal to the latter area which is given by :

$$T_0 \ [\Delta S_2 - \Delta S_1] = T_0 \ \Delta S_{net}, \text{ where} \tag{8.17}$$

Δs_{net} = Entropy increase of the universe due to irreversibility in the problem. With reference to the schematic and $T - s$ diagram of figure 8.12, entropy increase of the universe

$$\Delta S_{net} = \Delta S_{resr.at\ 1000K} + \Delta S_{resr.at\ 600K} + \Delta S_{engine} + \Delta S_{low\ temp.resr.}$$

$$= -\frac{100}{1000} + \left(\frac{100}{600} - \frac{100}{600}\right) + 0 + \frac{50}{300}$$

$$= -0.1 + 0.1667 = 0.0667.$$

Increase in un.av.energy = $T_0 \ \Delta S_{net} = 300 \times 0.0667 = 20$ kJ.

The above example and the analysis therein have a great practical importance. High temperature reservoirs are realised in practice by burning fuel, fossil or nuclear. The heat transferred from the burning fuel is used to run a heat engine. During the heat addition process the substance that undergoes the cycle is usually at a temperature lower than the reservoir temperature. This is a necessity for the following two reasons : (i) In the absence of such temperature difference the heat transfer rates are small and thus the power from the engine is bound to be very small being of no practical use ; and (ii) if the substance were to be at the same temperature as that of the high temperature reservoir, there will be the problem of the material of the container of the substance during the heat addition process. At such high temperatures the materials are bound to melt and damage the engine. Hence although the reservoir that supplies energy can be at any high temperature (similar to 1000 K in the above examples) the heat addition to the heat engine occurs at a low temperature (similar to 600 K in the above examples). As a ready example the reader can easily recall here that the water in a steam power plant boils at a low temperature in the boiler, although the furnace, where the fuel is burnt, is at a very high temperature.

The concept of available and unavailable energies are not restricted to heat transfers from reservoirs (constant temperature systems) alone. It is general and can also be used for energies from finite systems whose temperature may decrease with the supply of heat. In such a case it is not possible to imagine a single externally reversible engine that can take the heat from the system reversibly at a fixed temperature. Instead it can be assumed that the heat is supplied to a series of tiny Carnot engines, each taking heat at a particular temperature T. As an example suppose a system changes from 1_s to 2_s as it supplies heat Q reversibly. This heat rejection process is represented by the process $1_s - 2_s$ in the $T - s$ diagram of figure 8.13 and Q is equal to the area below $1_s - 2_s$. To find the available and unavailable parts of Q, it is necessary to imagine an engine that takes in Q reversibly and also rejects heat to T_0. If the heat transfer to the engine is reversible then the temperature of the system supplying heat must be equal to the temperature of the working substance of the engine at any instant. Thus in figure 8.13 while $1_s - 2_s$ represents the process of heat

rejection by the system, $1_c - 2_c$ must be the process of heat addition to the cycle. Let this be imagined to be possible through successive heat transfers to a series of Carnot engines. Let δQ be the heat transfer to one such tiny Carnot cycle at a Temperature T. Then $\delta Q = Tds$. Unavailable energy of $\delta Q = T_0 \, dS$ = area hatched horizontally, and available energy of

$\delta Q = \delta Q - T_0 \, dS$ = double hatched area. Therefore, as $Q = \int \delta Q$ = area below $1c$ - $2c$,

unavailable energy of $Q = \int T_0 \, dS = T_0 \, \Delta S.$ = area '$abcda$' and available energy of

$Q = Q - T_0 \, \Delta S$.

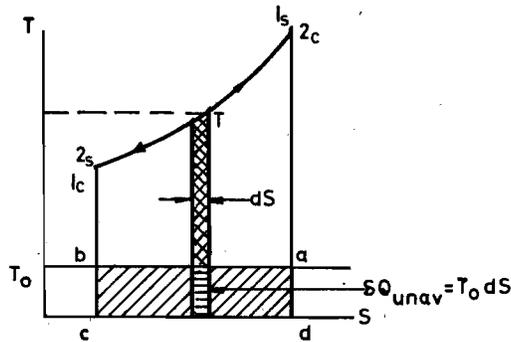The illustrative problems 8.7 to 8.8 further clarify these concepts.

Fig. 8.13 : Available and unavailable energy - finite system

SAQ 8

Shown in Figure 8.14 is a heat engine operating between 500 K and 350 K at a place where surroundings temperature is 300 K. According to the data provided in the figure the available energy of Q_1 is 250 kJ and its unavailable part is 750 kJ. Do you agree with this ? If not what is the available and unavailable energy of Q_1 ?
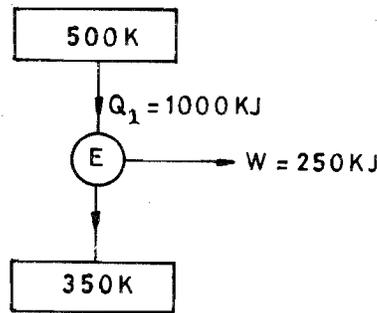

Fig. 8.14 : Diagram for SAQ 8

8.7   ILLUSTRATIVE PROBLEMS

Example 8.1 :

Analyse Prob.7.2 using Clausius' inequality statement.

Solution :

Refer to figure 7.6. For engine A, $Q_1 = 1000$ and from I law

$$Q_{2A} = Q_1 - W = 1000 - 600 = 400 \text{ kJ}.$$

With respect to the system undergoing the thermodynamic cycle, while Q_1 is positive Q_{2A} is negative. Also during the two heat interactions, namely the heat addition process and the heat rejection process the temperature of the system is given to remain constant at

$T_1 = 1000$ K and $T_2 = 300$ K respectively. Hence for each process $\int \delta Q / T = Q_{net} / T$.

$\oint (\delta Q / T) = \int (\delta Q / T)$ for the heat addition process at $T_1 + \int (\delta Q / T)$ for the heat rejection process at T_2.

$$= \left(\frac{Q_1}{T_1}\right) + \left(\frac{Q_{2A}}{T_2}\right)$$

$$= \frac{1000}{1000} + \left(-\frac{400}{300}\right) > -0.333 \text{ kJ} / \text{K}.$$

i.e. $\oint \frac{\delta Q}{T} < 0$ and hence, according to Clausius Inequality, the heat engine A is irreversible.

Similarly, for engine B,

$\oint \frac{\delta Q}{T} = \frac{Q_1}{T_1} + \frac{Q_{2B}}{T_2} = \frac{1000}{1000} + \left(\frac{-300}{300}\right) = 0$ and hence hence, according to Clausius Inequality, engine B is reversible.

For engine C,

$$\oint \frac{\delta Q}{T} = \frac{Q_1}{T_1} + \frac{Q_{2C}}{T_2} = \frac{1000}{1000} + \left(\frac{-200}{300}\right) = +0.33 > 0,$$

and hence, according to Clausius Inequality, engine C is impossible.

Example 8.2 :

(a) In a certain reversible process the rate of heat transfer to the system per unit temperature rise is constant and is given by $dQ / dT = 1.5$ kJ / deg. Find the increase in entropy of the system as its temperature increases from 300 to 500 K.

(b) In a second process between the same end states, the temperature rise is accomplished by stirring plus heat addition half as that in (a). What is the entropy increase in this case ?

Solution :

(a) Increase in entropy $\Delta S = \int \frac{\delta Q_R}{T}$.

It is given that the process is reversible and that $dQ / dT = 1.5$ kJ/deg and therefore

$$\frac{\delta Q}{T} = 1.5 \frac{dT}{T}$$

$$\Delta S = \int_1^2 1.5 \frac{dT}{T} = 1.5 \ln (T_2 / T_1).$$

From data $T_1 = 300$ K and $T_2 = 500$ K and therefore

$$\Delta S = 1.5 \ln (500 / 300) = 0.766 \text{ kJ} / \text{K}.$$

(b) In this problem the state change is the same as in (a). The system is also the same. But the manner in which the state change is achieved is different. Actually the process here is irreversible because of stirring work. Entropy being a property its change is independent of the path between any two given states. Thus the entropy change in this case is also the same as that in (a) being equal to 0.766 kJ/K.

Example 8.3 :

A certain pure substance of constant c_p ($= 0.6$ kJ/kg K) undergoes a change of state from 1 to 2 because of heating accompanied by stirring. The mass of the system is 2.5 kg and the temperatures at the two states are $t_1 = 30°C$, $t_2 = 80°C$. At the end of this process the substance is subjected to a reversible constant pressure cooling process which restores it to the initial state. Find the increase in entropy in the first process.

Solution :

The first process and the second process are between the same two state points. Thus the entropy change in both the processes must be the same but for their direction. The process

from 1 to 2 is irreversible because of stirring work. The process from 2 to 1 is given to be reversible and hence entropy change can be evaluated along this path.

$$ds = \frac{dh}{T} - \left(\frac{v}{T}\right)dp \qquad (8.14)$$

For the process 2 - 1, p is constant and therefore

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

For the substance c_p is a constant and therefore $dh = c_p\, dT$

$$\therefore\ ds = c_p\frac{dT}{T}\ \text{or}\ s_1 - s_2 = \int c_p\frac{dT}{T} = c_p\ \ln(T_1/T_2)$$

Here $T_1 = 30 + 273 = 303$ K and $T_2 = 80 + 273 = 353$ K.

$$\therefore\ s_1 - s_2 = 0.6\ \ln(303/353) = -0.0916\ \text{kJ/kg K}$$

$\therefore$ The entropy increase in the first process $= s_2 - s_1$

$$= -(s_1 - s_2) = 0.0916\ \text{kJ/kg K}$$

Net Entropy change $= m \times 0.0916 = 2.5 \times 0.0916 = 0.229$ kJ/K.

Example 8.4 :

(a) one kg water in open vessel at 30°C is brought in contact with a reservoir at 100°C. After steady state has been established, what is the entropy change of water ? Of the reservoir ? Assume for water $dh = cdT$ where c is a constant $= 4.2$ kJ/kg K.

(b) What would be the entropy increase of the universe had the water been heated from 30°C to 100°C by first bringing it in contact with a reservoir at 65°C and then with the reservoir at 100°C ?

Solution :

(a) For water $ds = \dfrac{dh}{T} - \left(\dfrac{v}{T}\right)dp$ $\qquad (8.14)$

Heating of water in an open vessel is a constant pressure process as the pressure is steady at the atmospheric value and hence in equation (8.14) $dp = 0$ (Alternatively the process can also be considered as a constant volume process as water is an incompressible medium for which $c_v = c_p$ and hence $dh = du$).

$$\therefore\ ds = c\,dT/T\ \text{or}\ \Delta s_{\text{water}} = s_2 - s_1 = c\ \ln(T_2/T_1)$$

$$= 4.2\ \ln\left[\frac{(273+100)}{(273+30)}\right] = 0.873\ \text{kJ/kg K}.$$

Heat transfer Q to water, by the first law is given by $Q = \Delta u + W$, where the work $W = 0$ as the process is also a constant volume process, and $\Delta u = c(t_2 - t_1)$

$\therefore\ Q = 4.2(100 - 30) = 294$ kJ/kg. This heat is transferred from the reservoir to the water. Heat transfer from the reservoir is internally reversible as its temperature is always the same.

$$\Delta S_{\text{resr}}\ \text{at}\ 100 = \int \frac{\delta Q_{\text{rev}}}{T} = \frac{Q}{T} = -\frac{294}{(273+100)}$$

$$= -0.788\ \text{kJ/kg water K}.$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{water}} + \Delta S_{\text{reservoir}}$$

$$= 0.873 + (-0.788) = 0.085\ \text{kJ/kg water K}.$$

(Note: During this process the entropy of the universe has increased. Hence the process is irreversible. In the chapter on reversibility it had been qualitatively stated that heat transfer with finite temperature difference makes a process irreversible. The same is proved quantitatively here with the use of entropy).

(b) Water is heated in two stages namely, from 30 to 65°C in the I stage with heat transfer from the reservoir at 65°C and from 65 to 100°C in the II stage with heat transfer from the reservoir at 100°C.

Following the same sequence of calculations as in (a)

$$(\Delta S_{\text{water}})_I = c \ln \left(\frac{T_2}{T_1}\right)_{\text{Istage}} = 4.2 \ln \frac{(273 + 65)}{(273 + 30)} = 0.459 \text{ kJ / kg K.}$$

Heat transfer to water $= Q_I = c\,(t_2 - t_1) = 4.2\,(65 - 30) = 147 \text{ kJ / kg.}$

$$(\Delta S_{\text{resr}})_I = \int \frac{\delta Q}{T} = \frac{Q}{T} = \frac{-147}{(273 + 65)} = -0.435 \text{ kJ / kg water K}$$

Similarly $(\Delta s_{\text{water}})_{II} = c \ln [(T_2 / T_1)]_{\text{IIstage}} = 4.2 \ln \frac{(273 + 100)}{(273 + 65)} = 0.414 \text{ kJ / kg K.}$

$Q_{II} = c\,(t_2 - t_1) = 4.2(100 - 65) = 147 \text{ kJ / kg.}$

$$(\Delta s_{\text{resr.}})_{II} = \int \frac{\delta Q}{T} = \frac{Q}{T} = \frac{-147}{(273 + 100)} = -0.394 \text{kJ kg water K.}$$

$(\Delta s_{\text{universe}}) = (\Delta s_{\text{water}})_I + (\Delta s_{\text{resr.}})_I + (\Delta s_{\text{water}})_{II} + (\Delta s_{\text{resr.}})_{II}$

$= 0.459 + (-0.435) + 0.414 + (-0.394) = 0.044 \text{ kJ / kg water K.}$

(Note: Entropy increase of the universe in case (b) is less than that in case (a). This is because the irreversibility in (b) is less than that in (a) - although the heating in both cases is from an initial temperature of 30°C to the final temperature of 100°C. Step heating in (b) decreases the finite temperature difference causing heat transfer in each stage thereby reducing the irreversibility).

Example 8.5 :

As shown in Figure 8.15 a certain gas with a constant c_v of 0.7 kJ/kg K is expanded reversibly and adiabatically from 0.0625 m³/kg, 500 K to 0.1875 m³/kg. During this process the temperature drops by 178 degrees. In another irreversible but adiabatic process of the same gas from the same initial state to the same final specific volume the drop in temperature is reported to be only 38 degrees. Find the change in entropy in the second process.
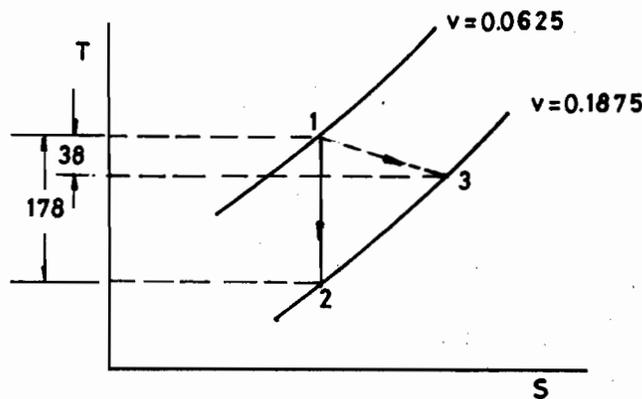
Solution :

Fig. 8.15 : Diagram for Illustrative Prob. 8.5

Refer to figure 8.15 in which the reversible adiabatic process 1 - 2 and the irreversible adiabatic process 1 - 3, both starting at the same initial state and ending at the same final specific volume, are shown on T - s diagram. Entropy change in the process $1 - 2$ is zero as it is reversible and adiabatic. $1 - 3$ is irreversible but adiabatic and hence $s_3 - s_1 > 0$. It may be thought that $s_3 - s_1$ can be calculated using the Tds relations (equation 8.14). But the data is not sufficient to adapt this method. Hence an indirect method is used. It can be seen from figure 8.15 that $s_3 - s_1 = (s_3 - s_2) + (s_2 - s_1) = (s_3 - s_2) + 0$

2 – 3 is on the constant volume line, $v = 0.1875$ m³/kg. From equation (8.14), for the constant volume process, $ds = du / T = c_v \, dT / T$ or $s_3 - s_1 = c_v \ln (T_3 / T_2)$

$$= 0.7 \ln \left[\frac{(500 - 38)}{(500 - 178)} \right] = 0.2527 \text{ kJ / kg K}$$

$$\therefore \ s_3 - s_1 = s_3 - s_2 = 0.2527 \text{ kJ / kg K.}$$

Example 8.6 :

As shown in figure 8.16 a reversible engine is operating having heat interactions with three reservoirs at temperatures of $T_1 = 500$ K, $T_2 = 300$ K and $T_3 = 250$ K. When Q_1, the heat transfer to the heat engine from T_1 is 500 kJ the work output of the engine is reported to be 175 kJ. Find the magnitudes and directions of Q_2 and Q_3

Solution :

Refer to Figure 8. 16. As we already know the heat engine is a system operating in a thermodynamics cycle. Therefore, from the first law, $\Sigma Q = \Sigma W$, i.e., $Q_1 + Q_2 + Q_3 = \Sigma W$,
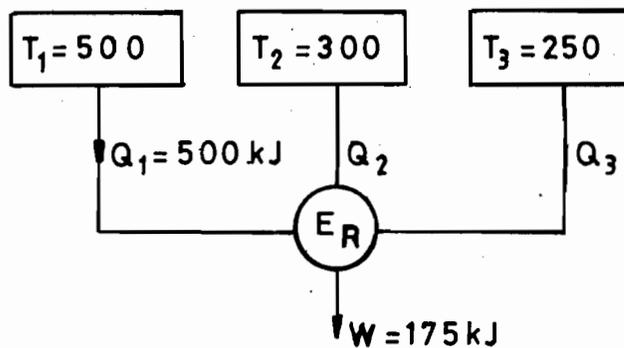

Fig. 8.16 : Diagram for Illustrative Prob. 8.6

where, from data, $Q_1 = + 500$ kJ and $\Sigma W = + 175$ kJ.

$$\therefore \ 500 + Q_2 + Q_3 = 175 \text{ or } Q_2 + Q_3 = - 325 \tag{i}$$

As the heat engine (cycle) is reversible, according to Clausius' Inequality, $\oint \dfrac{\delta Q}{T} = 0$ and

hence, $\dfrac{Q_1}{T_1} + \dfrac{Q_2}{T_2} + \dfrac{Q_3}{T_3} = 0$

$$\therefore \ \frac{500}{500} + \frac{Q_2}{300} + \frac{Q_3}{250} = 0$$

$$\text{or} \quad \frac{Q_2}{300} + \frac{Q_3}{250} = - 1 \tag{ii}$$

Solving for Q_2 and Q_3 between (i) and (ii)

$Q_2 = - 450$ kJ and $Q_3 = 125$ kJ. i.e., while 450 kJ is rejected by the engine to the reservoir at 300 K, 125 kJ is transferred to the engine from the reservoir at 250 K.

Example 8.7 :

Exhaust gases leave an internal combustion engine at 750°C and 1 atm, after having done 450 kJ work per kg gas in the engine cylinder. Assume that the enthalpy of the gas is a function of temperature only and that $c_p = 1.1$ kJ / kg K. Assume the temperature of the surroundings to be 27°C. Calculate (a) The available and unavailable parts of the energy in every kg gas discharged to the surroundings and (b) The ratio of the lost available energy to the engine work.
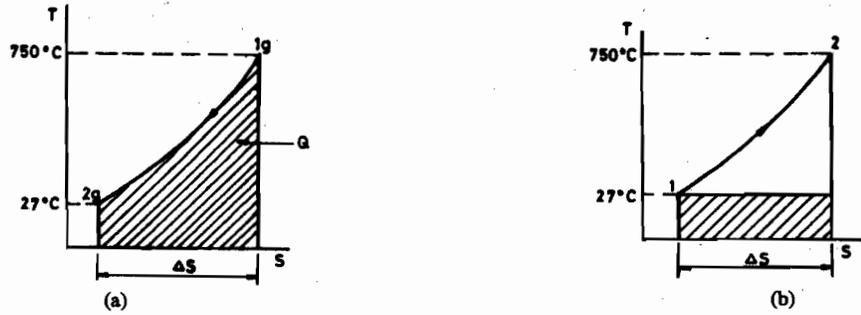
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Solution :

Fig. 8.17 : T - s diagrams for Prob. 8.7

(a) The exhaust gases leaving the engine at 750°C can be made to pass through a heat exchanger where it can cool to the surrounding temperature before being discharged to the atmosphere. During this constant pressure process the heat transferred from the gases $Q = \Delta h$. For the gases $h = h(T)$ only and c_p is a constant and therefore

$$Q = \Delta h = c_p(t_2 - t_1) = 1.1 \times (750 - 27) = 795.3 \text{ kJ / kg gas.}$$

This process of constant pressure cooling of the gases is shown by the path $1_g - 2_g$ in figure 8.17 (a). The area below the path is equal to Q. The change in entropy during this process Δs can be evaluated from $ds = c_p \dfrac{dT}{T} - \left(\dfrac{v}{T}\right)\dfrac{dp}{p}$ where $dp = 0$ and hence

$$\Delta s = c_p \ln (T_2 / T_1) = 1.1 \ln \left[\frac{(273 + 27)}{(273 + 750)}\right] = -1.349 \text{ kJ / kg K.}$$

If the heat transfer from the gas could be used in a reversible heat engine the heat addition process would be exactly similar to the cooling process in figure 8.17 (a) with the same Δs but in opposite direction. This is shown by the process $1 - 2$ in figure 8.17(b). When this engine rejects heat to the surroundings at 27°C the magnitude of heat rejected (hatched area) is the unavailable part of the energy in the gases.

Unavailable energy = $T_0 \Delta s = (273 + 27) \times 1.349 = 404.7$ kJ/kg gas.

Available energy = $Q - T_o \Delta s = 795.3 - 404.7 = 390.6$ kJ.

(b) The required ratio = $\dfrac{390.6}{450} = 0.868$

The useful part of energy in the exhaust gases is 86.8 % of the work developed by the engine per every kg gas. This analysis shows that it is worth attempting to recover this energy which otherwise is thrown as waste to the atmosphere.

Example 8.8 :

In a certain power station a binary vapour cycle employing mercury and water as the working substance is used for power generation. In this cycle the condensing mercury vapour at 272°C is used to vaporise water at 252°C. Assuming the surroundings to be at 27°C calculate the increase in unavailable energy due to irreversible heat transfer between the mercury and water. Obtain the results based on 1 kg water evaporated. The heat transfer required for vaporising 1 kg water = 1700 kJ.
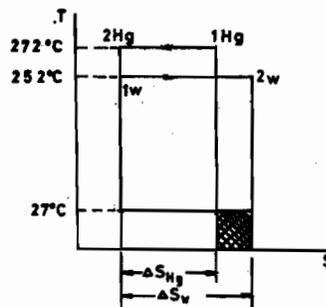
Solution :

Fig. 8.18 : Diagram for Illustrative Prob. 8.8

Refer to figure 8.18, in which 1_{Hg} - 2_{Hg} represents the process of mercury condensation and 1_w - 2_w represents evaporation of water. Area below 1_w - 2_w is equal to heat transfer to water and this, from data, is equal to 1700 kJ/kg water. This amount of heat transfer to water

must have come from the condensing mercury and hence area below 1_{Hg} - 2_{Hg} is also equal to 1700 kJ/kg water evaporated.

$$\Delta s_{water} = \left(\frac{Q}{T}\right)_{water} = \frac{1700}{(273 + 252)} = 3.24 \text{ kJ/kg K.}$$

$$\Delta s_{Hg} = \left(\frac{Q}{T}\right)_{Hg} = \frac{-1700}{(273 + 272)} = -3.12 \text{ kJ/kg water K}$$

Increase in unavailable energy = $T_o (\Delta s)_{net}$

$$= \text{double hatched area} = T_o(\Delta s_w + \Delta s_{Hg})$$

$$= (273 + 27)(3.24 - 3.12) = 36 \text{ kJ/kg water.}$$

8.8 SUMMARY

Clausius Inequality statement dictates that for a reversible cycle $\oint \delta Q / T = 0$, for an irreversible cycle $\oint \delta Q / T < 0$ and that $\oint \delta Q / T > 0$ is an impossibility in any cycle.

Entropy is a property of a system and it is defined by

$$\Delta S = \int \frac{\delta Q_{rev}}{T}$$

$\delta Q / T$ and $\delta Q_R / T$ for a given change of state are, in general, not the same. Also, the relation $ds = \delta Q / T$ is valid for an internally reversible process and it is not in contravention of the second law of thermodynamics.

For a reversible non-cyclic process $\Delta S = \int \delta Q / T$ (by definition) while for an irreversible process $\Delta S > \int \delta Q / T$, from which it follows that, while $\Delta S = 0$ for a reversible adiabatic process, it is > 0 for an irreversible adiabatic process.

The 'Tds' relations that are extensively used in evaluating the changes in entropy of pure substances are:

$$Tds = du + pdv \text{ and } Tds = dh - vdp.$$

In any process the net entropy change of the system and surroundings is ≥ 0 and this is the principle of increase of entropy

When heat transfer occurs across a finite temperature difference, there is a decrease in the available part of the energy and this decrease reflects itself as the increase in the unavailable part of the energy.

8.9 ANSWERS/SOLUTIONS TO SAQs

SAQ 1

$ds = \delta Q_R / T$ and not $\delta Q / T$. Hence, although $\delta Q / T < 0$ there can be no decrease in entropy of the system executing an irreversible cycle. In a cycle, whether it is reversible or irreversible, there can be no change in any property. Entropy is a property of a system and hence its change in any cycle has to be zero.

SAQ 2

Although heat transfer occurs irreversibly, for the system it is an internally reversible process in the sense that it behaves as though heat were transferred to it reversibly. Hence ΔS for the system is equal to $\int \delta Q / T$ and its value is equal to $1 / (100 + 273)$ kJ / K.

SAQ 3

Heat is transferred reversibly here as the source and the system are at the same temperature. Yet the process is internally irreversible because of fluid friction and hence ΔS is not equal to $\int \delta Q/T$. In fact $\Delta S > \int \delta Q/T$.

SAQ 4

Process AB_1 is not possible. There can be no decrease in entropy in an adiabatic process. Process AB_2 is reversible and adiabatic, as there is no change in entropy, and may be possible. Process AB_3 is irreversible, as entropy in this adiabatic process is increasing, and hence it is a possible process.

SAQ 5

In an adiabatic process entropy can only increase, or in the limiting case of a reversible process remains constant, and hence the direction of possible compression processes are AB_1 and AB_2. AB_3 is **impossible**. These are shown in figure 8.19.
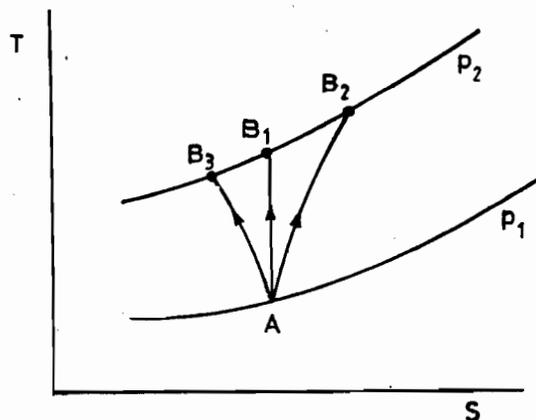

Fig. 8.19 : Adiabatic compression processes

SAQ 6

Combustion makes a process irreversible. Hence the entropy change of the universe is +ve.

SAQ 7

Yes

SAQ 8

The available energy is defined as that part of the energy which is converted to work by a reversible engine operating between the given high temperature reservoir and the low temperature reservoir at the surroundings temperature. A reversible engine operating between 500 K and 300 K has an efficiency of 0.4. Thus, available energy of Q_1 (= 1000 kJ) is 400 kJ and the unavailable energy = 1000 - 400 = 600 kJ.

The engine shown in figure 8.14 converts 1000 kJ to 250 kJ operating between 500 K and 350 K. Hence 250 is not the available energy but it is only the actual work produced by the engine under the given conditions.

8.10 GLOSSARY

Clausius' Inequality : The integral of $\dfrac{\delta Q}{T}$ in a cycle is less than or equal to zero.

Entropy : An extensive property whose change in any reversible process is given by integral $\dfrac{\delta Q}{T}$.

Tds Relations : Relations used to calculate the change in entropy in any process, viz : $Tds = du + pdv$; $Tds = dh - vdp$

Principle of increase of : (i) Entropy of the universe is always on the increase ;
entropy   (ii) Entropy of an adiabatic system can never decrease ;
     (iii) Entropy change of system plus surroundings in any process
     is ≥ 0 .

Isentropic Process   : A process with no change in entropy.

Available Energy   : That part of the energy supplied to an externally reversible heat
engine which is converted to work while the engine rejects heat
at the local surroundings temperature. Also called the useful part
of the energy.

Unavailable energy   : Difference between the energy supplied and the available
energy. This is also equal to the energy rejected by the reversible
heat engine to the surroundings. Also the useless part of the
energy.

FURTHER SUGGESTED READING

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