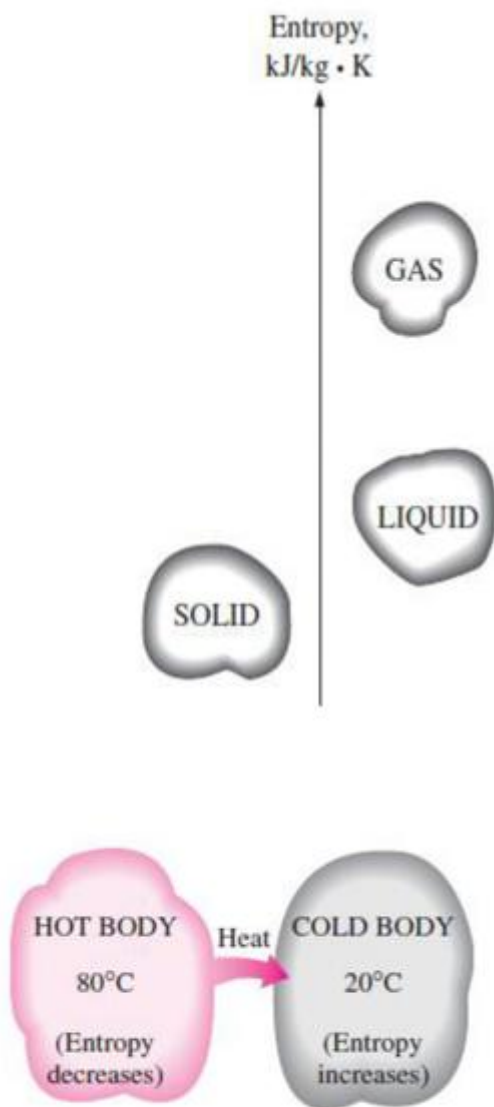


Unit - III

ENTROPY



Course Contents

- 4.1 Introduction
- 4.2 Entropy
- 4.3 Clausius Inequality
- 4.4 Clausius Theorem and its Proof
- 4.5 Entropy—a Property of a System
- 4.6 Entropy Change during Reversible Process
- 4.7 Entropy Change during Irreversible Process
- 4.8 Entropy Change for Universe
- 4.9 Entropy Change for Close System
- 4.10 Entropy Change of Universe during Mixing Process
- 4.11 Solved Numerical

4.1 Introduction

Up to this point, our study of the second law has been concerned primarily with what it says about systems undergoing thermodynamic cycles. In this chapter means are introduced for analyzing systems from the second law perspective as they undergo processes that are not necessarily cycles. The property entropy plays a prominent part in these considerations. The objective of the present chapter is to introduce entropy and show its use for thermodynamic analysis.

The word energy is so much a part of the language that you were undoubtedly familiar with the term before encountering it in early science courses. This familiarity probably facilitated the study of energy in these courses and in the current course in engineering thermodynamics. In the present chapter you will see that the analysis of systems from a second law perspective is conveniently accomplished in terms of the property entropy.

4.2 Entropy

Definition: "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.

Characteristics of Entropy

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

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{\text{Rev}}$$

Where the change in entropy for the system may positive, negative or zero depending on the heat absorption, rejection whether temperature changes or not.

4. Entropy is point function, independent on path of the process.
5. It remains unchanged in all adiabatic frictionless processes.
6. Entropy is extensive property.

4.3 Clausius Inequality

Clausius inequality is applied for both reversible and irreversible heat engine as explain below.

Case-(a) Reversible Heat Engine:

As shown in the Fig. 4.1 (a), the efficiency of reversible heat engine operating within the temperature limit T_1 and T_2 is given by,

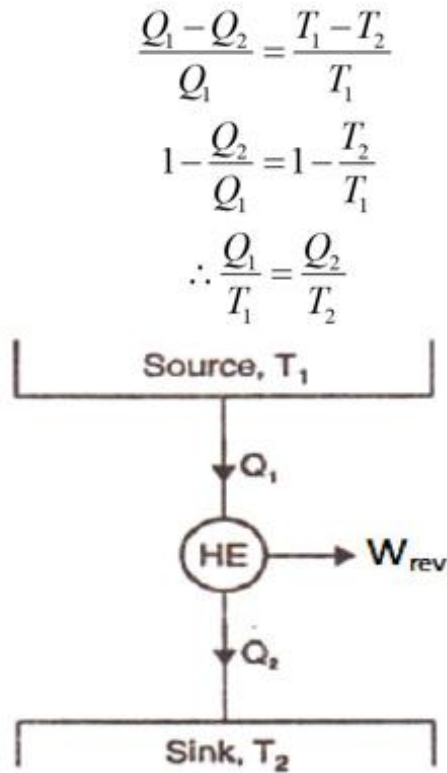


Fig. 4.1 (a) Reversible heat engine

With positive sign convention for heat absorption and negative sign for heat rejection,

$$\frac{Q_1}{T_1} - \frac{(-Q_2)}{T_2} = 0$$

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

$$\sum \frac{Q}{T} = 0 \quad (\text{Only for a reversible heat engine})$$

Therefore, algebraic summation of heat interaction to absolute temperature is equal to zero for reversible engine.

Case-(b) Irreversible Heat Engine:

As shown in Fig. 4.1 (b) the efficiency of irreversible heat engine is lower than operating within the same temperature limit T_1 and T_2 (according to the Carnot theorem) is given by,

$$\frac{Q_1 - Q_2'}{Q_1} < \frac{T_1 - T_2}{T_1}$$

$$1 - \frac{Q_2'}{Q_1} < 1 - \frac{T_2}{T_1}$$

$$\therefore \frac{Q_1}{T_1} < \frac{Q_2'}{T_2}$$

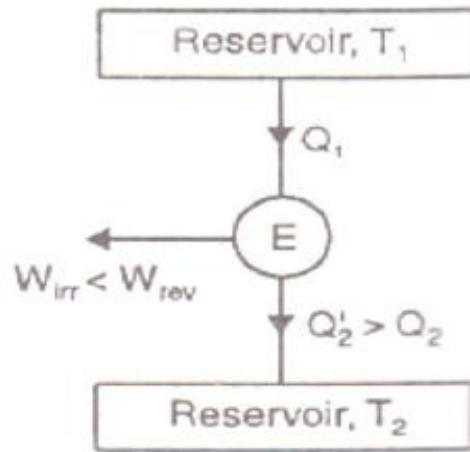


Fig. 4.1 (b) Reversible heat engine

With positive sign convention for heat absorption and negative sign for heat rejection,

$$\frac{Q_1}{T_1} - \frac{(-Q_2')}{T_2} < 0$$

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} < 0$$

$$\sum \frac{Q}{T} < 0 \quad (\text{Only for an irreversible heat engine})$$

Therefore, algebraic summation of heat interaction to absolute temperature is less than zero for irreversible heat engine.

Thus from case (a) and (b) together $\sum \frac{Q}{T} \leq 0$ is called *Clausius Inequality*.

Where equality sign is holds for reversible heat engine and less than sign is holds for irreversible heat engine.

Case-C Impossible Heat Engine:

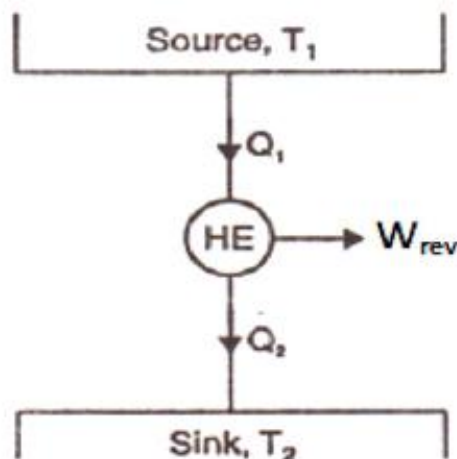


Fig. 4.1 (c) Impossible heat engine

As shown in Fig. 4.1 (c) if the efficiency of irreversible heat engine is more than operating within the same temperature limit T_1 and T_2 (violation of the Carnot theorem) is given by,

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

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

$$\therefore \frac{Q_1}{T_1} > \frac{Q_2'}{T_2}$$

With positive sign convention for heat absorption and negative sign for heat rejection,

$$\frac{Q_1}{T_1} - \frac{(-Q_2')}{T_2} > 0$$

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} > 0$$

$$\sum \frac{Q}{T} > 0 \quad (\text{For an impossible heat engine})$$

Therefore, algebraic summation of heat interaction to absolute temperature is less than zero for impossible heat engine.

4.4 Clausius Theorem and its Proof

Clausius Theorem

"The algebraic sum of the ratio of the heat interaction to the absolute temperature for a reversible heat engine is equal to zero."

Mathematically, $\oint_R \frac{\delta Q}{T} = 0$ where R refers to reversible cycle

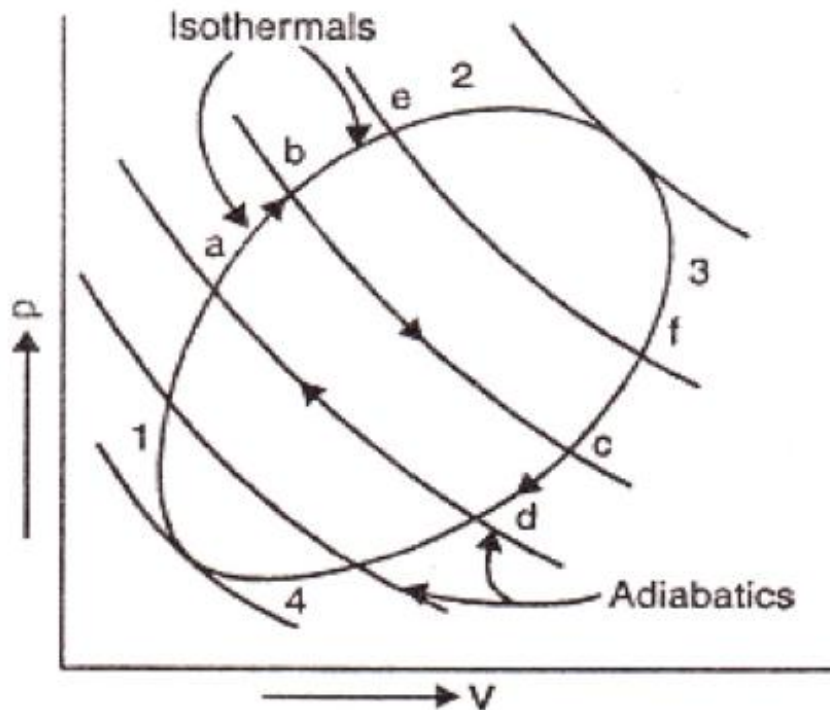


Fig. 4.2 Proof of Clausius Theorem

Proof of Clausius Theorem

As shown in Fig. 4.2 a system performing reversible cyclic process 1-2-3-4 on p - V diagram. Let the cycle be cut by a family of closely spaced adiabatics lines similar to

ad, be, ef etc. The elementary cycle $abed$ then consists of two adiabatics da and bc , and two elementary paths ab and cd . Since the adiabatics lie close to each other, the distance ab tends to be zero and accordingly the temperatures at points a and b can be thought to be equal. Likewise the points c and d would also be at another equal temperature. The elementary paths ab and cd then conform to isothermal conditions and the cycle $abcd$ constitutes an elementary Carnot cycle. Likewise $befc$ is another elementary Carnot cycle. Thus the given cycle 1-2-3-4 can be imagined to consist of a large number (say i) of Carnot cycles.

- For the Carnot cycle $abed$, the process be represents adiabatic expansion, and for the adjoining Carnot cycle $befc$ it represents an equal amount of adiabatic compression. As such for the composite reversible cycle 1-2-3-4, the adiabatics contribute neither towards work nor towards heat interactions. The work output from the engine is as a consequence of net heat transfer during the elementary isothermal processes.

Therefore, for the reversible cycle 1-2-3-4, we may write that,

$$\sum \frac{Q_i}{T_i} = 0 \quad \text{or} \quad \oint_R \frac{\delta Q}{T} = 0 \quad \text{where R refers to reversible cycle}$$

4.5 Entropy—a Property of a System or point function

- Let us consider a system undergoing a reversible process from state 1 to state 2 along path A and then from state 2 to the original state 1 along path B as shown in Fig. 4.3. Applying the Clausius theorem to this reversible cyclic process, we have,

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

(Where the subscript 'R' designates a reversible cycle)

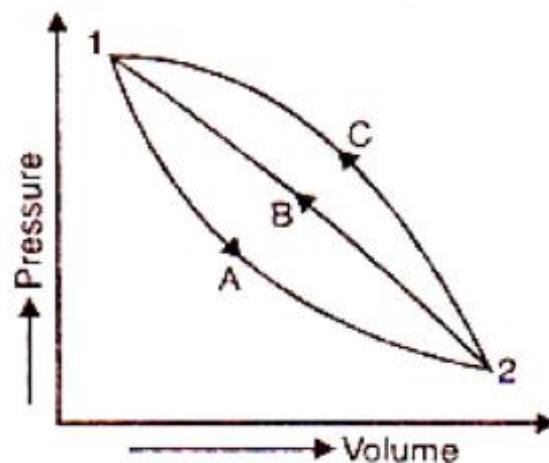


Fig. 4.3 Reversible cyclic process between two fixed end states

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

$$\int_1^2 \frac{\delta Q}{T} \bigg|_{(A)} + \int_2^1 \frac{\delta Q}{T} \bigg|_{(B)} = 0 \quad (4.1)$$

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

$$\int_1^2 \frac{\delta Q}{T} \bigg|_{(A)} + \int_2^1 \frac{\delta Q}{T} \bigg|_{(C)} = 0 \quad (4.2)$$

From above equation (4.1) and (4.2), we have,

$$\int_1^2 \frac{\delta Q}{T} \bigg|_{(B)} = \int_2^1 \frac{\delta Q}{T} \bigg|_{(C)}$$

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

4.6 Entropy Change during Reversible Process

(Refer Fig. 4.3 again)

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,

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_R \quad (4.3)$$

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 (4.3) may be written as,

$$dS = \left(\frac{\delta Q}{T} \right)_R \quad (4.4)$$

Where dS is exact differential

- Thus, from equation (4.4), we find that the change of entropy in a reversible process is equal to $\left(\frac{\delta Q}{T} \right)$ and this is the mathematical formulation of the second law of thermodynamics. It also indicates that when an inexact differential δQ is divided by an integrating factor T during a reversible process, it becomes an exact differential.

4.7 Entropy Change during Irreversible Process

- Consider a closed system undergoing a change from state 1 to state 2 by a reversible process 1-A-2 and returns from state 2 to the initial state 1 by an irreversible process 2-B-1 as shown in Fig. 4.4 on the thermodynamic coordinates, pressure and volume.
- Since entropy is a thermodynamic property, we can write,

$$\oint dS = \int_{1(A)}^2 (dS_R) + \int_{2(B)}^1 (dS_{IR}) = 0 \quad (4.5)$$

(Subscript IR represents the irreversible process)

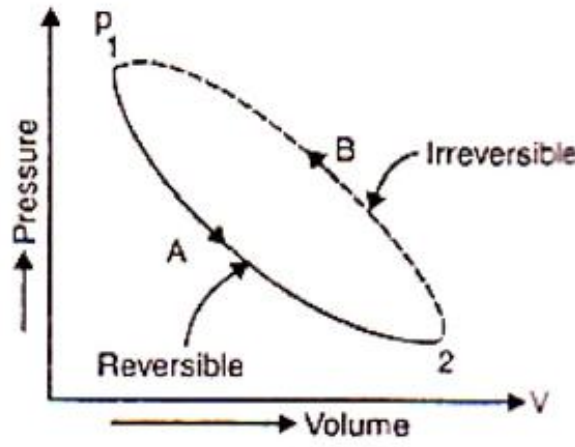


Fig. 4.4 A cycle composed of a reversible and an irreversible process

Now for a reversible process, we have,

$$\int_{1(A)}^2 (dS_R) = \left(\frac{\delta Q}{T} \right)_R \quad (4.6)$$

Substituting the value of $\int_{1(A)}^2 (dS_R)$ in above equation. We get,

$$\oint dS = \int_{1(A)}^2 \left(\frac{\delta Q}{T} \right)_R + \int_{2(B)}^1 (dS_{IR}) = 0 \quad (4.7)$$

Again, since the processes 1-A-2 and 2-B-1 together form an irreversible cycle, applying Clausius equality to this expression, we get

$$\oint \frac{\delta Q}{T} = \int_{1(A)}^2 \left(\frac{\delta Q}{T} \right)_R + \int_{2(B)}^1 \left(\frac{\delta Q}{T} \right)_{IR} < 0 \quad (4.8)$$

Now subtracting eqn. (4.8) from eqn. (4.7), we get

$$\int_{2(B)}^1 (dS_{IR}) > \int_{2(B)}^1 \left(\frac{\delta Q}{T} \right)_{IR}$$

$$\boxed{(dS_{IR}) > \left(\frac{\delta Q}{T} \right)_{IR}} \quad (4.9)$$

Eqn. (4.9) states that the change in entropy in an irreversible process is greater than $\frac{\delta Q}{T}$.

Combining eqns. (4.8) and (4.9), we can write the equation in the general form as,

$$\boxed{(dS_{IR}) \geq \left(\frac{\delta Q}{T} \right)} \quad (4.10)$$

Where equality sign stands for the reversible process and inequality sign stands for the irreversible process.

4.8 Entropy Change for the Universe or isolated System

- Let us now consider an *isolated system*, in which 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. (4.10), we get $dS_{isolated} \geq 0$

Entropy Principle: "It a state that the entropy of an isolated system either increases or remains constant is principle of increase in entropy."

Proof of entropy principle

- By including any system and its surrounding within a single boundary, as shown in Fig. 4.5, 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

$$dS_{universe} \geq 0 \quad \text{Where } dS_{universe} = dS_{sys} + dS_{surr}$$

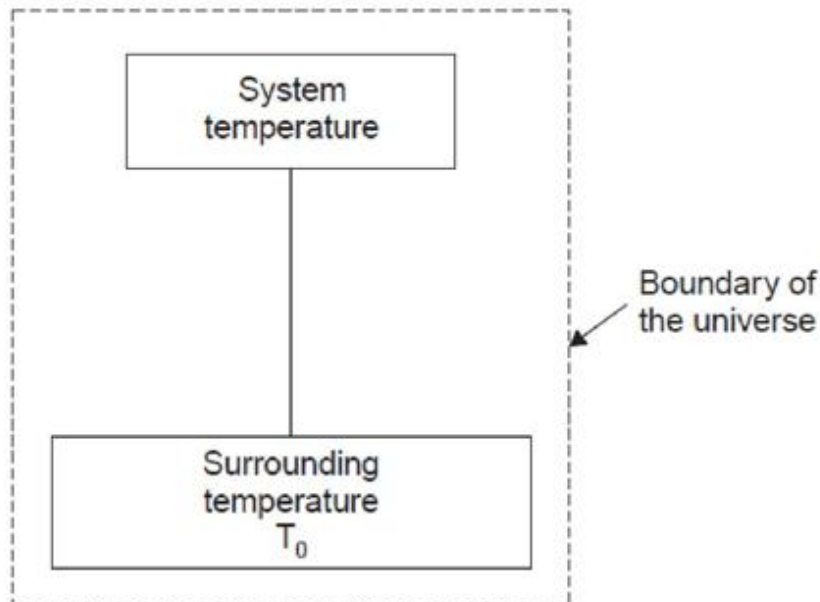


Fig. 4.5 Entropy change of universe

- In the combined closed system consider that a quantity of heat δQ is transferred from the system at temperature at T_{sys} to the surroundings at temperature T_{surr} OR T_0 . Entropy change for the system is,

$$dS_{sys} = -\frac{\delta Q}{T_{sys}}$$

$$dS_{surr} = +\frac{\delta Q}{T_{surr}}$$

Therefore, entropy change for the isolated system is,

$$dS_{isolated} = dS_{sys} + dS_{surr}$$

$$dS_{isolated} = \delta Q \left[\frac{1}{T_{surr}} + \frac{1}{T_{sys}} \right] \text{ where } T_{sys} > T_{surr}$$

Thus we may generalized and state that,

$$dS_{isolated} \geq 0$$

- Above equation states that the process involving the interaction of a system and the surroundings takes place only the net entropy of the combined system increases or in the limit remains constant when $T_{sys} = T_{surr}$. Since all natural processes are irreversible, the entropy is increasing continually.

4.9 Entropy Change for a Closed System

- In the absence of gravity, motion, electricity and magnetic effects, the first law of thermodynamics can be expressed as,

$$\delta q = du + \delta w \text{ for unit mass of substance}$$

If the process is reversible, $\delta w = p dv$

$$\therefore (\delta q)_{rev} = du + p dv$$

- From the second law of thermodynamics, $T ds = (\delta q)_{rev}$ and therefore,

$$\boxed{T ds = du + p dv}$$

Also, $h = u + pv$

By differentiating,

$$dh = du + p dv + v dp$$

$$\boxed{T ds = dh - v dp}$$

4.9.1 Heating of a Gas at Constant Volume Process

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 as shown in Fig. 4.6.

$$\delta q = C_v dT$$

Divided by T both the sides,

$$\frac{\delta q}{T} = C_v \frac{dT}{T}$$

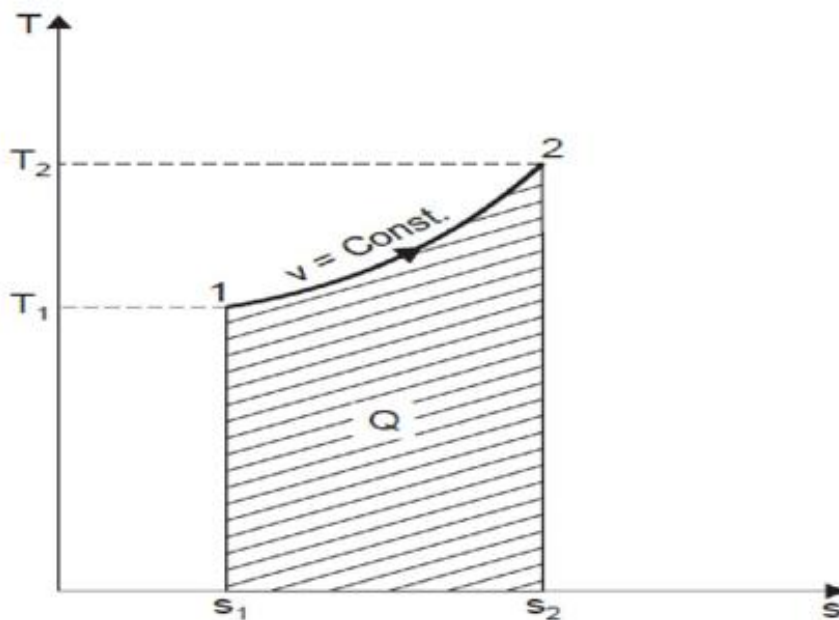


Fig. 4.6 T-s diagram of constant volume process

Integrating both the sides, we obtain

$$\int_1^2 ds = C_v \frac{dT}{T}$$

$$\boxed{s_2 - s_1 = C_v \ln \frac{T_2}{T_1} = C_v \ln \frac{P_2}{P_1}}$$

4.9.2 Heating of a Gas at Constant Pressure Process

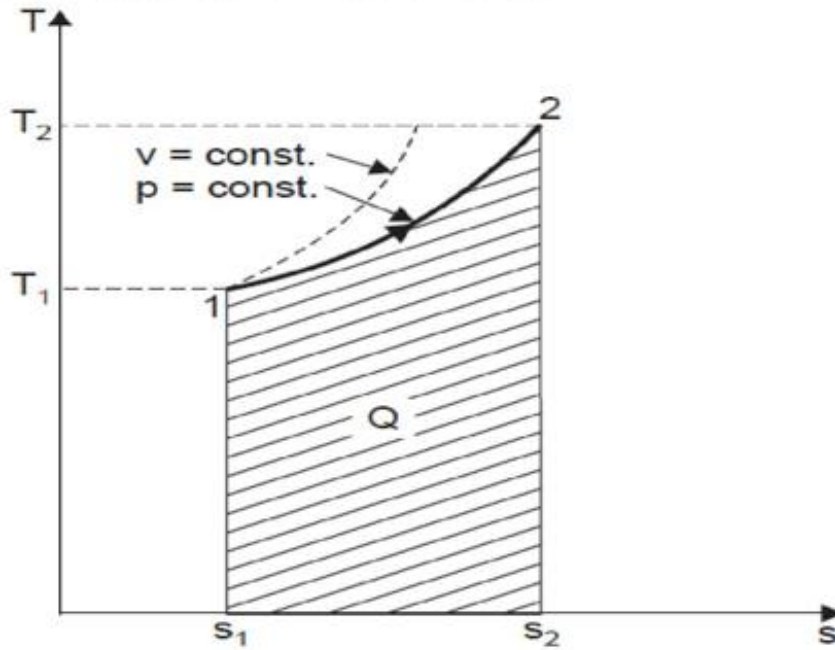


Fig. 4.7 T-s diagram of constant pressure process

Let 1 kg of gas be heated at constant pressure and let the change in entropy and absolute temperature be from s_1 to s_2 and T_1 to T_2 respectively as shown in Fig. 4.7.

$$\delta q = C_p dT$$

Divided by T both the sides,

$$\frac{\delta q}{T} = C_p \frac{dT}{T}$$

Integrating both the sides, we obtain

$$\int_1^2 ds = C_p \int_1^2 \frac{dT}{T}$$

$$s_2 - s_1 = C_p \ln \frac{T_2}{T_1} = C_p \ln \frac{P_2}{P_1}$$

Show that Slope of Constant volume line is steeper than and constant pressure lines on T-s diagram between same temperature limit

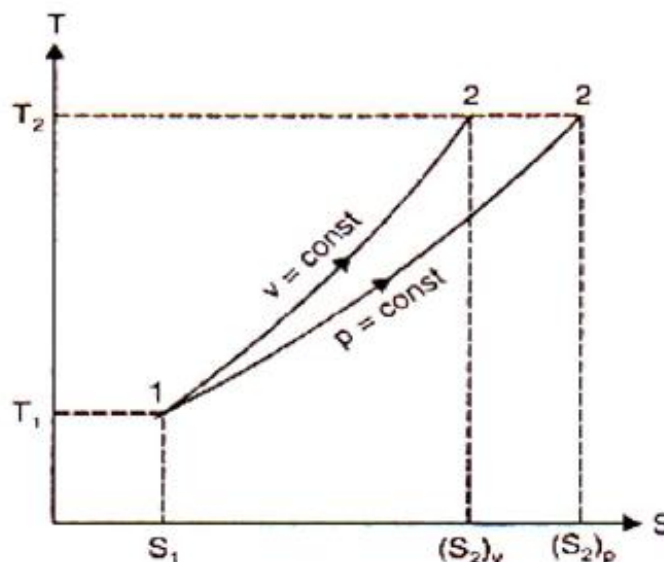


Fig. 4.8 Constant volume and constant pressure lines on T-s diagram

For unit mass of substance, the entropy changes are,

$$ds = C_v \frac{dT}{T} \text{ for constant volume process, and}$$

$$ds = C_p \frac{dT}{T} \text{ for constant pressure, and}$$

Thus, slope of the constant volume line on T-s diagram, (Fig. 4.7)

$$\frac{dT}{ds} = \frac{T}{C_v}$$

Thus, slope of the constant pressure on T-S diagram,

$$\frac{dT}{ds} = \frac{T}{C_p}$$

Since $C_p > C_v$, above expression indicates that above constant volume line on T-s diagram is steeper than and constant pressure lines working between the same temperature limits. Also C_p and C_v are constant, $\frac{dT}{ds} \propto T$ both the constant pressure and constant volume processes.

4.9.3 Heating of Gas at Isothermal Process

An isothermal expansion 1-2 at constant temperature T is shown in Fig. 4.9. Entropy changes from s_1 to s_2 when gas absorbs heat during expansion. The heat taken by the gas is given by the area under the line 1-2 which also represents the work done during expansion.

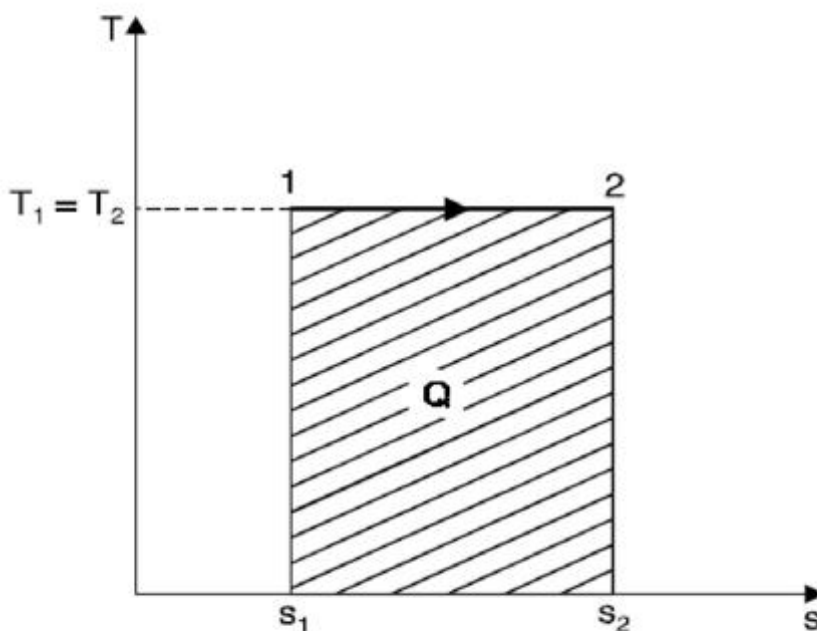


Fig. 4.9 T-s diagram of constant temperature process

$$\delta q = du + \delta w = C_v dT + \delta w \text{ for unit mass of substance}$$

If the process is reversible, $\delta w = p dv$

Since the temperature remains constant, $du = 0$ and therefore,

$$\delta q = p dv$$

Divided by T both the sides,

$$\therefore \frac{\delta q}{T} = \frac{pdv}{T} \text{ but } pv = RT \text{ for unit mass of the gas}$$

$$\frac{\delta q}{T} = \frac{pdv}{T}$$

$$\therefore ds = \frac{Rdv}{v}$$

Integrating both the sides, we obtain

$$\int_1^2 ds = R \frac{dv}{v}$$

$$s_2 - s_1 = R \ln \frac{v_2}{v_1} = R \ln \frac{P_1}{P_2}$$

4.9.4 Reversible Adiabatic Process (Isentropic Process)

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

$$\delta q = 0$$

Divided by T both the sides then,

$$\frac{\delta q}{T} = 0$$

$$ds = 0$$

$$s_2 = s_1$$

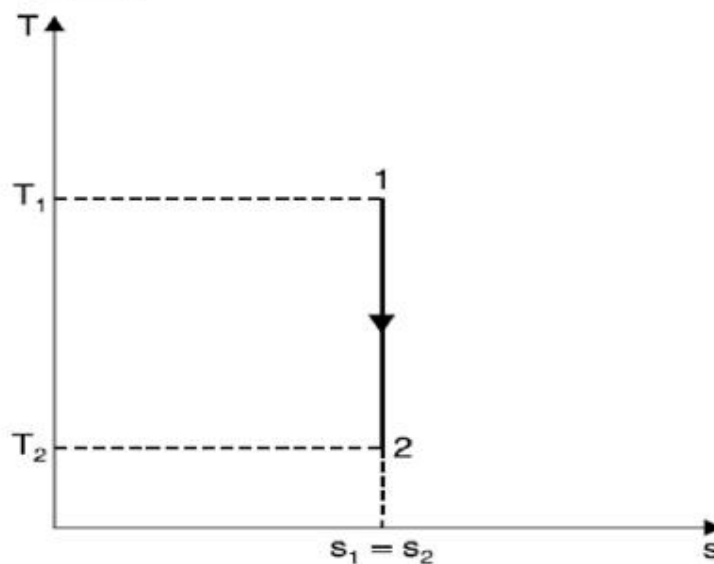


Fig. 4.10 T-s diagram of adiabatic process

This shows that there is no change in entropy and hence it is known as *isentropic process*. Fig. 4.10 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.

Show that Reversible adiabatic paths never intersect each other

- For a reversible adiabatic process, heat interaction is zero and so is the change in entropy. Two constant entropy curves S_1 and S_2 have been depicted on p - v diagram (Fig. 4.11). If we assume that these curves intersect at point A as shown, then at the

point of intersection, there will be two values of entropy. However, entropy is a property and point function, and therefore, cannot have two values at any point.

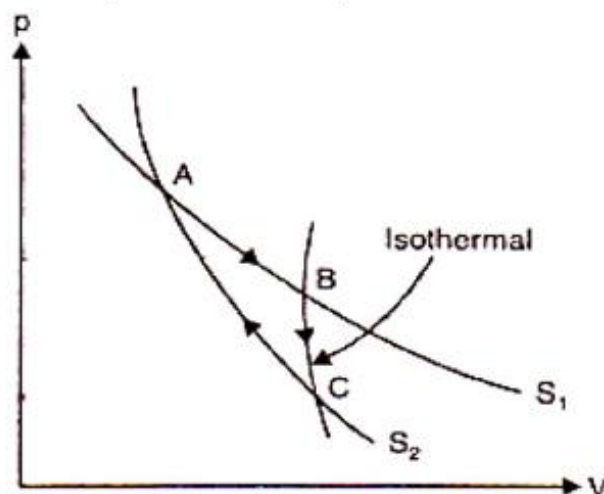


Fig. 4.11 Two reversible adiabatics intersecting each other

- Further, let a reversible isothermal be plotted on the p - v diagram and let it intersect the reversible adiabatics at B and C . The reversible processes AB , BC , CA then constitute a reversible cycle. The included area ABC represents the net work output. However, this work has been obtained from an engine which exchanges heat with a single thermal reservoir during the isothermal process BC (there is no heat interaction during the adiabatics AB and CB). This is violation of the Kelvin-Planck statement of the second law. Hence, our assumption of intersection of two reversible adiabatics is wrong. Through one point, there can pass only one reversible adiabatic.

4.9.5 Polytropic Process

(a) Entropy change in terms of temperature and volume:

$$\delta q = du + \delta w = C_v dT + \delta w \text{ for unit mass of substance}$$

$$\delta q = C_v dT + p dv$$

Divided by T both the sides,

$$\frac{\delta q}{T} = C_v \frac{dT}{T} + \frac{p}{T} dv \quad \text{But } pv = RT \text{ for unit mass of the gas}$$

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

Integrating both the sides between initial and final states, we obtain

$$\int_1^2 ds = C_v \int_1^2 \frac{dT}{T} + R \int_1^2 \frac{dv}{v}$$

$$s_2 - s_1 = C_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$

(b) Entropy change in terms of pressure and volume:

Apply characteristic gas equation,

$$\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}$$

$$\frac{T_2}{T_1} = \frac{P_2 v_2}{P_1 v_1}$$

Substitute the value of $\frac{T_2}{T_1}$ in above (4.11),

$$s_2 - s_1 = C_v \ln \frac{P_2 v_2}{P_1 v_1} + R \ln \frac{v_2}{v_1}$$

$$s_2 - s_1 = C_v \ln \frac{P_2}{P_1} + C_v \ln \frac{v_2}{v_1} + R \ln \frac{v_2}{v_1}$$

$$s_2 - s_1 = C_v \ln \frac{P_2}{P_1} + C_p \ln \frac{v_2}{v_1}$$

(c) Entropy change in terms of temperature and pressure:

Apply characteristic gas equation,

$$\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}$$

$$\frac{v_2}{v_1} = \frac{T_2 P_1}{T_1 P_2}$$

Substitute the value of $\frac{v_2}{v_1}$ in equation (4.11),

$$s_2 - s_1 = C_v \ln \frac{T_2}{T_1} + R \ln \frac{T_2 P_1}{T_1 P_2}$$

$$s_2 - s_1 = C_v \ln \frac{T_2}{T_1} + R \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

$$s_2 - s_1 = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

4.10 Entropy Change of Universe during Mixing Process Always Increases

- Consider an isolated system consists of sub-system 1 and sub-system 2 with their respective states as shown in Fig. 4.12. Both the systems are enclosed by adiabatic boundary, the system becomes isolated and no heat interaction with surrounding.
- Let m_1, T_1, C_{p1} = mass, temperature and specific heat of fluid in sub-system 1
 m_2, T_2, C_{p2} = mass, temperature and specific heat of fluid in sub-system 2

Let T_f is the final equilibrium temperature after mixing, then

Heat lost by fluid 1 = Heat gain by fluid 2

$$m_1 C_{p1} (T_1 - T_f) = m_2 C_{p2} (T_f - T_2)$$

$$T_f = \frac{m_1 C_{p1} T_1 + m_2 C_{p2} T_2}{m_1 C_{p1} + m_2 C_{p2}}$$

Entropy change of fluid 1 in sub-system 1 is,

$$dS_1 = \int_{T_1}^{T_f} \frac{\delta Q}{T} = \int_{T_1}^{T_f} \frac{m_1 C_{p1} dT}{T} = m_1 C_{p1} \ln \frac{T_f}{T_1} \quad (\because T_1 > T_f, dS_1 \text{ will be negative})$$

Entropy change of fluid 2 in sub-system 2 is,

$$dS_2 = \int_{T_2}^{T_f} \frac{\delta Q}{T} = \int_{T_2}^{T_f} \frac{m_2 C_{p2} dT}{T} = m_2 C_{p2} \ln \frac{T_f}{T_2} \quad (\because T_2 < T_f, dS_2 \text{ will be positive})$$

Entropy change of surrounding,

$$dS_{surr} = \frac{\delta Q}{T} = 0, \text{ for isolated system}$$

Thus, entropy change of universe,

$$dS_{uni} = dS_1 + dS_2 + dS_{surr}$$

$$dS_{uni} = m_1 C_{p1} \ln \frac{T_f}{T_1} + m_2 C_{p2} \ln \frac{T_f}{T_2} + 0$$

Put the value of T_f in above equation,

$$dS_{uni} = m_1 C_{p1} \ln \left[\frac{m_1 C_{p1} T_1 + m_2 C_{p2} T_2}{(m_1 C_{p1} + m_2 C_{p2}) T_1} \right] + m_2 C_{p2} \ln \left[\frac{m_1 C_{p1} T_1 + m_2 C_{p2} T_2}{(m_1 C_{p1} + m_2 C_{p2}) T_2} \right]$$

For same specific heats of fluids and same masses, ($\because C_{p1} = C_{p2}, m_1 = m_2 = m$)

$$dS_{uni} = m C_p \left[\ln \frac{T_1 + T_2}{2T_1} + \ln \frac{T_1 + T_2}{2T_2} \right]$$

$$dS_{uni} = m C_p \ln \left[\frac{(T_1 + T_2)^2}{4T_1 T_2} \right]$$

$$dS_{uni} = m C_p \ln \left[\frac{(T_1 + T_2)^2}{2\sqrt{T_1 T_2}} \right]^2$$

In above equation $\left(\frac{T_1 + T_2}{2} \right) > \sqrt{T_1 T_2}$, hence $dS_{uni} > 0$ and from principle of increase in entropy mixing process is irreversible.

4.11 Solved Numerical

Example 4.1 A lump of steel of mass 8 kg at 1000 K is dropped in 80 kg of oil at 300 K. Find out entropy change of steel, oil and the universe. Take specific heats of steel and oil as 0.5 kJ/kg K and 3.5 kJ/kg K respectively.

Solution:

Given data:

$$m_{st} = 8 \text{ kg}$$

$$T_{1(st)} = 1000\text{K}$$

$$m_{oil} = 80 \text{ kg}$$

$$T_{1(oil)} = 300\text{K}$$

$$C_{st} = 0.5 \text{ kJ/kg K}$$

$$C_{oil} = 3.5 \text{ kJ/kg K}$$

Find:

$$(1) dS_{st}$$

$$(2) dS_{oil}$$

$$(3) dS_{uni}$$

Let T_f is the final equilibrium temperature . then from principle of energy conservation,

heat lost by steel = heat gained by oil

$$mC_p dT_{steel} = mC_p dT_{oil}$$

$$8 \times 0.5 \times (1000 - T_f) = 80 \times 3.5 \times (T_f - 300)$$

$$T_f = 309.86 \text{ K}$$

Entropy change of steel,

$$dS_{steel} = mc_p \ln \frac{T_f}{T_1} = 8 \times 0.5 \times \ln \frac{309.86}{1000} = -4.686 \text{ kJ/K}$$

Entropy change of oil,

$$dS_{oil} = mc_p \ln \frac{T_f}{T_1} = 80 \times 3.5 \times \ln \frac{309.86}{300} = 9.0547 \text{ kJ/K}$$

Net change of entropy is,

$$dS_{Universe} = dS_{steel} + dS_{oil} = -4.686 + 9.0547 = 4.369 \text{ kJ/K (increase)}$$

Example 4.2 The connections of a reversible engine to three sources at 400 K, 300 K and 200 K. The engine draws 1200 kJ of heat from source at 400 K and produces 200 kJ of work. Determine: (1) The amount and directions of heat reservoirs with the other heat sources, (2) Make calculations for the entropy changes due to each of the heat interactions with the engine, (3) How much entropy change occurs for the cycle?

Solution:

Given data:

$$T_1 = 400\text{K}$$

$$T_2 = 300\text{K}$$

$$T_3 = 200\text{K}$$

$$Q_1 = 1200 \text{ kJ and } W = 200 \text{ kJ}$$

Find:

$$(1) Q_2 \text{ and } Q_3$$

$$(2) dS_1, dS_2, dS_3$$

$$(3) dS_{cycle}$$

Assuming the directions of heat interaction as shown in Fig. and noting that the engine is reversible.

Apply Clausius theorem $\oint \frac{\delta Q}{T} = 0$

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} = 0$$

$$\frac{1200}{400} + \frac{Q_2}{300} - \frac{Q_3}{200} = 0$$

$$2Q_2 - 3Q_3 = -1500 \dots (i)$$

Also from the law of conservation of energy,

$$Q_1 + Q_2 - Q_3 = W$$

$$1200 + Q_2 - Q_3 = 200$$

$$Q_2 = Q_3 - 1000 \dots (ii)$$

From expression (i) and (ii),

$$Q_3 = -200 \text{ kJ and } Q_2 = -1200 \text{ kJ}$$

The negative sign with Q_2 and Q_3 indicates that the directions of Q_2 and Q_3 are opposite to assumed direction.

$$ds_1 = -\frac{Q_1}{T_1} = -\frac{1200}{400} = -3 \text{ kJ/K}$$

$$ds_2 = +\frac{Q_2}{T_2} = +\frac{1200}{300} = 4 \text{ kJ/K}$$

$$ds_3 = \frac{Q_3}{T_3} = \frac{-200}{200} = -1 \text{ kJ/K}$$

Entropy change for the cycle

$$ds = ds_1 + ds_2 + ds_3 = -3 + 4 - 1 = 0$$

Thus entropy change for the cycle is zero because entropy is the property.

Example 4.3 1 m^3 of air is heated reversibly at constant pressure from 290 K to 580 K and is then cooled reversibly at constant volume back to initial temperature. If the initial pressure is 1 bar. Workout the net heat flow and overall (net) change in entropy. Represent the processes on T-s diagram. Take $C_p = 1.005 \text{ kJ/kg K}$ and $R = 0.287 \text{ kJ/kg K}$.

Solution:

Given data:

$$V_1 = 1 \text{ m}^3$$

$$P_1 = 1 \text{ bar}$$

$$T_1 = 290 \text{ K}$$

$$T_2 = 580 \text{ K}$$

$$C_p = 1.005 \text{ kJ/kg K}, R = 0.287 \text{ kJ/kg K}$$

Find:

$$(1) Q_{\text{net}}$$

$$(2) dS_{\text{net}}$$

$$\text{Mass of air, } m = \frac{p_1 v_1}{RT_1} = \frac{1 \times 10^5 \times 1}{287 \times 290} = 1.20 \text{ kg}$$

Total heat transfer,

$$\begin{aligned} Q &= Q_{1-2} + Q_{2-3} \\ &= mc_p (T_2 - T_1) + mc_v (T_3 - T_2) \\ &= mc_p (T_2 - T_1) + mc_v (T_1 - T_2) \\ &= m(T_2 - T_1)(c_p - c_v) \\ &= mR(T_2 - T_1) \\ &= 1.20 \times 287 \times (580 - 290) \\ &= 99876 = 99.876 \text{ kJ} \end{aligned}$$

Entropy change during constant pressure process 1-2,

$$\begin{aligned} S_2 - S_1 &= mc_p \ln \frac{T_2}{T_1} \\ &= 1.20 \times 1.005 \ln \frac{580}{290} \\ &= 0.8359 \text{ kJ/K} \end{aligned}$$

Entropy change during constant volume process 2-3,

$$\begin{aligned} S_3 - S_2 &= mc_v \ln \frac{T_3}{T_2} \\ &= m \times (c_v - R) \ln \frac{T_1}{T_2} \\ &= 1.20 \times (1.005 - 0.287) \ln \frac{290}{580} \\ &= -0.5972 \text{ kJ/K} \end{aligned}$$

Overall change in entropy,

$$\begin{aligned} &= (S_3 - S_2) + (S_2 - S_1) \\ &= 0.8359 + (-0.5972) \\ &= 0.2387 \text{ kJ/K} \end{aligned}$$

Example 4.4 3 kg of air at 150 kPa pressure and 360 K temperature is compressed polytropically to pressure 750 kPa according to the $pv^{1.2} = C$. Subsequently the air is cooled to initial temperature at constant pressure. This is followed by expansion at constant temperature till the original pressure of 150 kPa is reached. Sketch the cycle on p-v and T-s plot. Determine work done, heat transfer, and change in entropy during each process. Assuming the $C_p = 1.005 \text{ kJ/kg K}$, $C_v = 0.718 \text{ kJ/kg K}$ and $R = 0.287 \text{ kJ/kg K}$

Solution:Given data:

$$m = 3 \text{ kg}$$

$$P_1 = 150 \text{ kPa}$$

$$T_1 = 360 \text{ K}$$

$$P_2 = 750 \text{ kPa}$$

$$C_p = 1.005 \text{ kJ/kgK}$$

$$C_v = 0.718 \text{ kJ/kgK}$$

$$R = 0.287 \text{ kJ/kgK}$$

Find:

$$W_{1-2}, W_{2-3}, W_{3-1}$$

$$Q_{1-2}, Q_{2-3}, Q_{3-1}$$

$$dS_{1-2}, dS_{2-3}, dS_{3-1}$$

Process 1-2:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{n-1}{n}}$$

$$T_2 = 360 \times \left(\frac{750}{150} \right)^{\frac{1.2-1}{1.2}} = 471 \text{ K}$$

Work done,

$$\begin{aligned} W_{1-2} &= \frac{p_1 V_1 - p_2 V_2}{n-1} = \frac{mR(T_2 - T_1)}{n-1} \\ &= \frac{3 \times 0.287 \times (360 - 471)}{1.2 - 1} \\ &= -477.85 \text{ kJ} \end{aligned}$$

Heat transfer,

$$\begin{aligned} Q_{1-2} &= W_{1-2} + du_{1-2} = W_{1-2} + mc_v(T_2 - T_1) \\ &= -477.85 + 3 \times 0.718 \times (471 - 360) \\ &= -238.76 \text{ kJ} \end{aligned}$$

Entropy change

$$\begin{aligned} S_2 - S_1 &= mc_p \ln \frac{T_2}{T_1} + mR \ln \frac{P_1}{P_2} \\ &= 3 \times 1.005 \times \ln \frac{471}{360} + 3 \times 0.287 \ln \frac{150}{750} \\ &= -0.5762 \text{ kJ/K} \end{aligned}$$

Process 2-3

Work done,

$$\begin{aligned} W_{2-3} &= p_2(V_3 - V_2) = mR(T_3 - T_2) \\ &= 3 \times 0.287 \times (360 - 471) \\ &= -334.66 \text{ kJ} \end{aligned}$$

Heat transfer,

$$\begin{aligned} Q_{2-3} &= mc_p (T_3 - T_2) \\ &= 3 \times 1.005 \times (360 - 471) \end{aligned}$$

Entropy change

$$\begin{aligned} S_3 - S_2 &= mc_p \ln \frac{T_3}{T_2} \\ &= 3 \times 1.005 \times \ln \frac{360}{471} \\ &= -0.8104 \text{ kJ/k} \end{aligned}$$

Process 3-1

Work done,

$$W_{3-1} = p_3 V_3 mc_p \ln \frac{V_1}{V_3} = mRT_3 \ln \frac{p_3}{p_1} = 3 \times 0.287 \times 360 \ln \frac{750}{150} = 498.86 \text{ kJ}$$

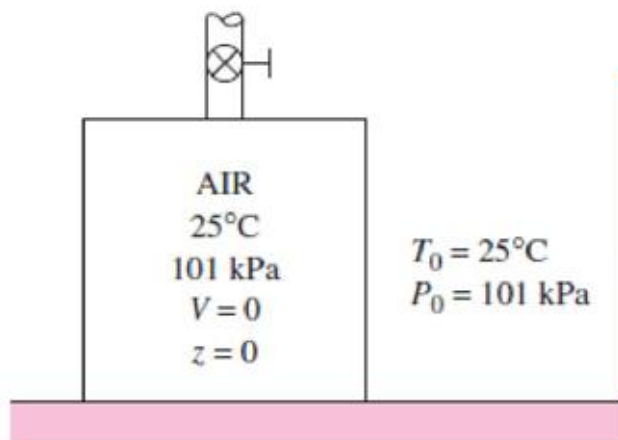
Heat transfer,

$$\begin{aligned} Q_{3-1} &= W_{3-1} + du_{3-1} = W_{3-1} + mc_v (T_1 - T_3) \\ &= 498.89 + 0 \quad (\because T_1 = T_3) \\ &= 498.89 \text{ kJ} \end{aligned}$$

$$\begin{aligned} S_1 - S_3 &= mR \ln \frac{p_3}{p_1} \\ &= 3 \times 0.287 \times \ln \frac{750}{150} \\ &= 1.3857 \text{ kJ/k} \end{aligned}$$

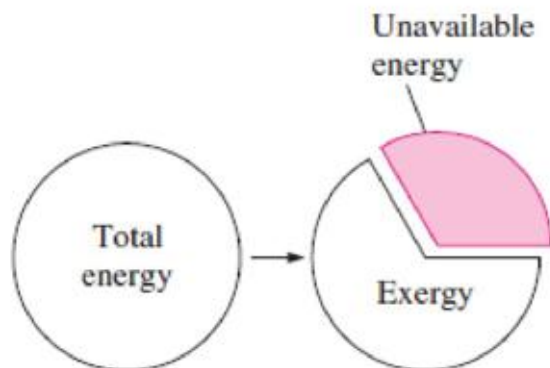
Net entropy change during cycle,

$$\begin{aligned} \oint ds &= (S_2 - S_1) + (S_3 - S_2) + (S_1 - S_3) \\ &= -0.5762 + 0.8104 + 1.3857 \\ \oint ds &= 0 \end{aligned}$$



Course Contents

- 5.1 Introduction
- 5.2 Basic Definitions
- 5.3 Available Energy Referred to a Cycle
- 5.4 Decrease in Available Energy When Heat is transferred Through a Finite Temperature Difference
- 5.5 Availability of the Closed System (Non Flow System)
- 5.6 Availability of the Open System (Steady Flow System)
- 5.7 Effectiveness (Second law efficiency), Reversible Work and Irreversibility
- 5.8 Solved Numerical



5.1 Introduction

- The increased awareness that the world's energy resources are limited has caused many countries to reexamine their energy policies and take drastic measures in eliminating waste. It has also sparked interest in the scientific community to take a closer look at the energy conversion devices and to develop new techniques to better utilize the existing limited resources. The first law of thermodynamics deals with the *quantity* of energy and asserts that energy cannot be created or destroyed. This law merely serves as a necessary tool for the bookkeeping of energy during a process and offers no challenges to the engineer. The second law, however, deals with the *quality* of energy. More specifically, it is concerned with the degradation of energy during a process, the entropy generation, and the lost opportunities to do work; and it offers plenty of room for improvement.
- When a new energy source, such as a geothermal well, is discovered, the first thing the explorers do is estimate the amount of energy contained in the source. This information alone, however, is of little value in deciding whether to build a power plant on that site. What we really need to know is the *work potential* of the source—that is, the amount of energy we can extract as useful work. The rest of the energy is eventually discarded as waste energy and is not worthy of our consideration. Thus, it would be very desirable to have a property to enable us to determine the useful work potential of a given amount of energy at some specified state. This property is *exergy*, which is also called the *availability* or *available energy*.
- **Exergy (Work Potential) Associated with Kinetic and Potential Energy**

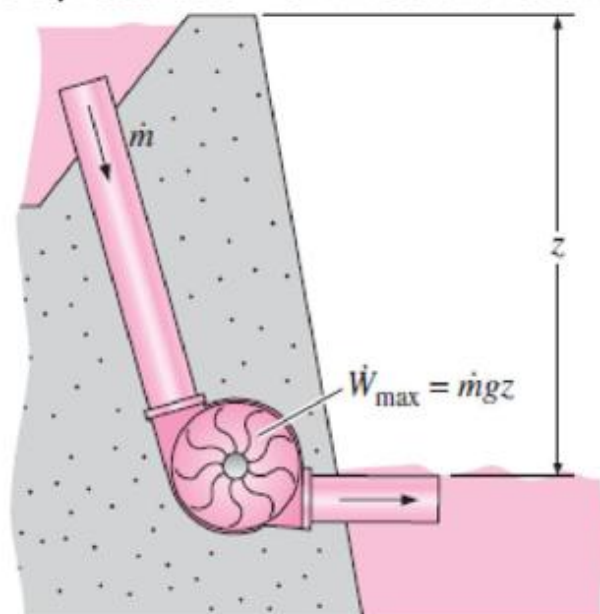


Fig. 5.1 The work potential or exergy of potential energy is equal to the potential energy itself

Kinetic energy is a form of mechanical energy, and thus it can be converted to work entirely. Therefore, the work potential or exergy of the kinetic energy of a system is equal to the kinetic energy itself regardless of the temperature and pressure of the environment. That is,

Exergy of kinetic energy: $ke = \frac{V^2}{2} \text{ kJ/kg}$

Where V is the velocity of the system relative to the environment.

- **Potential energy** is also a form of mechanical energy, and thus it can be converted to work entirely. Therefore, the exergy of the potential energy of a system is equal to the potential energy itself regardless of the temperature and pressure of the environment (Fig.5.1). That is,

Exergy of potential energy:

$$pe = gz \text{ kJ/kg}$$

where g is the gravitational acceleration and z is the elevation of the system relative to a reference level in the environment. Therefore, the exergies of kinetic and potential energies are equal to themselves, and they are entirely available for work. However, the internal energy u and enthalpy h of a system are not entirely available for work.

5.2 Basic Definitions

1. Available Energy

It is the portion of thermal energy input in cyclic engine which converted into useful mechanical work is called available energy.



Fig. 5.2 The atmosphere contains a tremendous amount of energy, but no exergy

2. Unavailable Energy

It is the portion of thermal energy which is not utilizable and is rejected to the sink is called unavailable energy. (Fig. 5.2)

3. High Grade Energy

Energy that can be completely transformed in to shaft work without any loss and hence it is fully utilizable is called high grade energy. *Examples:* mechanical and electrical work, water, wind and tidal power, kinetic energy of the jet, animal and manual power.

4. Low Grade Energy

Energy from which only a certain portion can be converted in to mechanical work is called low grade energy. *Examples:* heat or thermal energy, heat from nuclear fission or fusion, heat from combustion of fuels such as coal, wood, oil etc.

5. Dead State

When system comes to complete equilibrium with its environment there is no energy difference exists to promote further work is called dead state.

6. Law of Degradation of Energy

The concept of available energy provides a useful measure of the quality of energy. Energy is said to be degraded each time it flows through a finite temperature difference. The second law may, therefore, be referred to as *law of degradation of energy*. Whereas the first law tells that energy is always conserved quantity wise, the second law emphasizes that energy always degrades quality wise. Energy is always conserved but its quality is always degraded.

5.3. Available Energy Referred to a Cycle

- As shown in Fig. 5.3 represents a reversible engine that operates between a constant temperature reservoir at temperature T and a sink at temperature T_0 . Heat Q supplied by the reservoir and the available work W_{\max} .

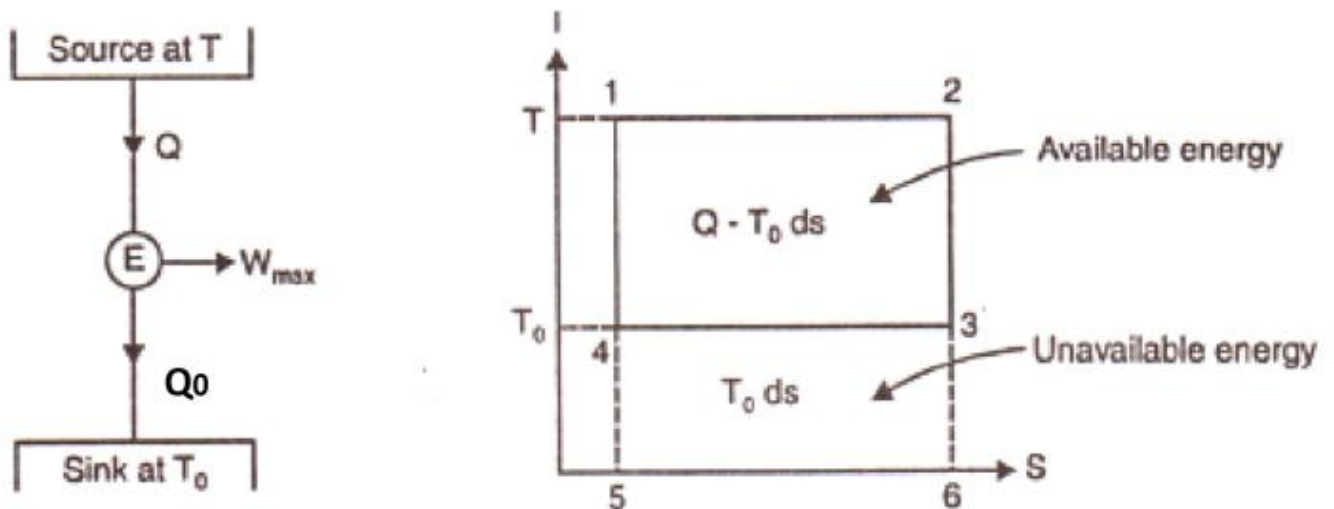


Fig. 5.3 Available and unavailable energy: heat withdrawn from an infinite reservoir

Efficiency of the reversible heat engine,

$$\eta_{\text{rev}} = \frac{T - T_0}{T} = \frac{W_{\max}}{Q}$$

$$W_{\max} = Q \left(\frac{T - T_0}{T} \right) = Q \left(1 - \frac{T_0}{T} \right) = Q - \frac{Q}{T} T_0 = Q - T_0 dS$$

- W_{\max} is the availability and on T - S diagram it is given by the area 1-2-3-4. The area 3-4-5-6 represents the unavailable portion of the heat supplied to the engine.
- Unavailable energy is the energy rejected from the engine, and hence represents the portion of heat supplied that cannot be converted into work. The unavailable energy equals the product of the lowest temperature of heat rejection and the change of entropy of the system during the process of heat supply (unavailable energy = $T_0 dS$)

5.4 Decrease in Available Energy When Heat is transferred Through a Finite Temperature Difference

Consider certain quantity of heat Q transfer from a system at constant temperature T_1 to another system at constant temperature T_2 ($T_1 > T_2$) as shown in Fig. 5.4. Before heat is transfer, the energy Q is available at T_1 and ambient temperature is T_0 .

Initial available energy is given by,

$$(AE)_1 = Q \left(1 - \frac{T_0}{T_1} \right)$$

After heat transfer, the energy Q is available at T_2 and again the ambient temperature is T_0 .

Final available energy is given by,

$$(AE)_2 = Q \left(1 - \frac{T_0}{T_2} \right)$$

$$\begin{aligned} \text{Change in available energy} &= (AE)_1 - (AE)_2 \\ &= Q \left(1 - \frac{T_0}{T_1} \right) - Q \left(1 - \frac{T_0}{T_2} \right) \\ &= T_0 \left[-\frac{Q}{T_1} + \frac{Q}{T_2} \right] \\ &= T_0 (dS_1 + dS_2) \end{aligned}$$

$$\text{Change in available energy} = T_0 dS_{net}$$

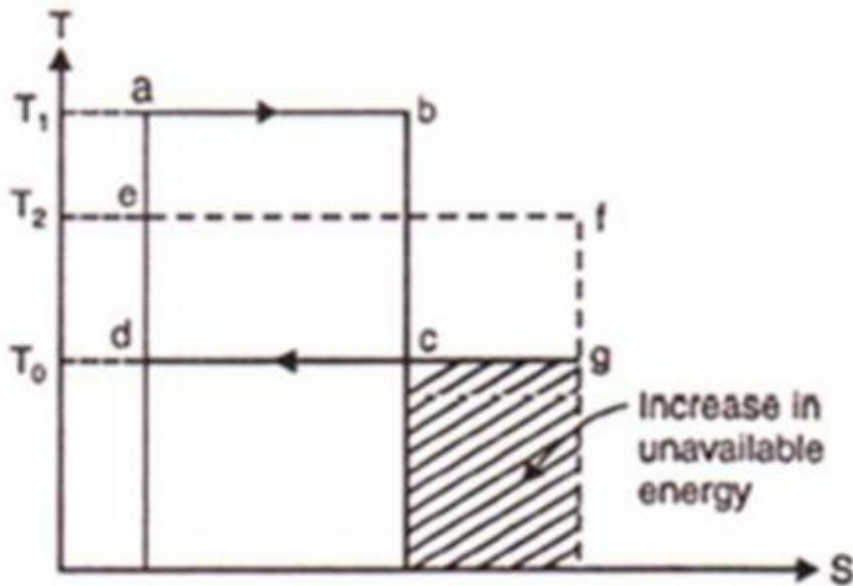


Fig. 5.4 Decrease in available energy due to heat transfer through a finite temperature difference

Where, dS_{net} is the net change in the entropy of the combination of the two interacting systems. This total entropy change is called entropy of universe or entropy production. Since the heat transfer has been through a finite temperature difference, the process is irreversible, i.e., $dS_{net} > 0$ and hence there is loss or decrease of available energy.

Description

- $abcd$ is the power cycle when heat is available at T_1 . Area under cd then represents the unavailable portion of energy.
- $efgd$ is the power cycle when heat is available at T_2 . Area under dg then represents the unavailable energy.
- Increase in unavailable energy due to irreversible heat transfer is then represented by the shaded area under eg . The increase in unavailable energy equals the decrease in available energy, and is given by the product of the ambient temperature and the net increase in the entropy of the interacting systems.

Conclusion

- Whenever heat is transferred through a finite temperature difference, there is always a loss of available energy.
- Greater the temperature difference $T_1 - T_2$, the more net increase in entropy and, therefore, loss of available energy.
- The available energy of a system at a higher temperature is more than at a lower temperature, and decreases progressively as the temperature falls. Stated in other words, quality of energy of a fluid at higher temperature is superior to that at lower temperature; a high temperature fluid has capacity to do more work under the same identical conditions.

5.5 Availability of the Closed System (Non Flow System)

- Let us consider a system consisting of piston- cylinder arrangement in which the fluid expanding reversibly from initial condition of p_1 and T_1 to final atmospheric conditions of p_0 and T_0 . (Fig. 5.5)

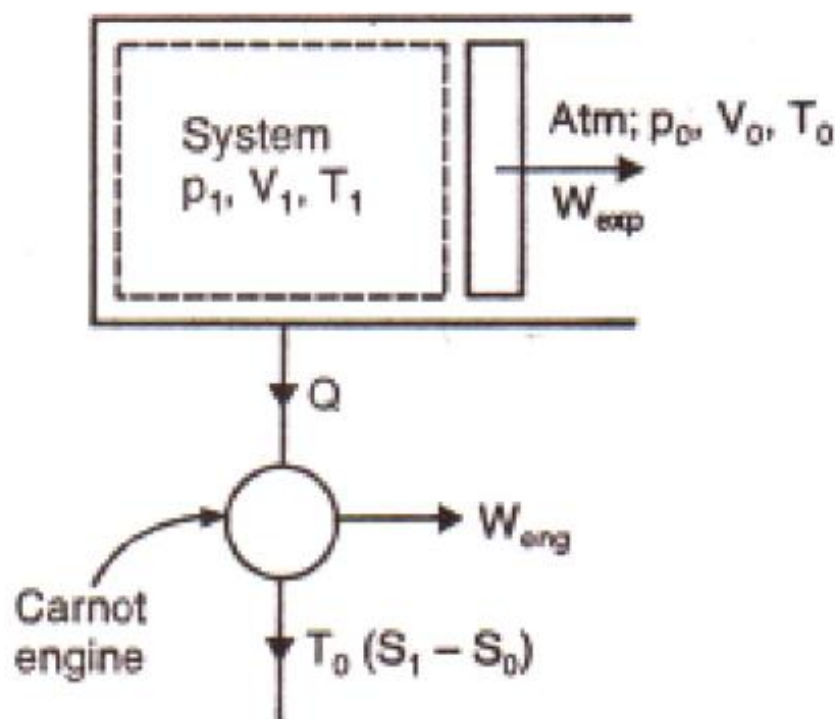


Fig. 5.5 Availability of non flow (closed) system

- Following are the heat and work interactions take place in given system:

Expansion work (W_{exp}):

The fluid expands and expansion work W_{exp} is obtained. From the principal of energy conservation,

$$\delta Q = \delta W + du$$

$$-Q = W_{\text{exp}} + (u_0 - u_1)$$

Negative sign indicate that heat leaves the system

$$W_{\text{exp}} = (u_1 - u_0) - Q$$

Engine work (W_{eng}):

Heat rejected by piston cylinder assembly may be utilized to run reversible heat engine which receives. The work done by the engine is given by,

$$W_{\text{eng}} = Q \left(1 - \frac{T_0}{T_1} \right) = Q - T_0 (S_1 - S_0)$$

Maximum work (W_{max}):

The summation of expansion work W_{exp} and the engine work W_{eng} gives maximum obtainable from the given arrangement,

$$W_{\text{max}} = (u_1 - u_0) - Q + Q - T_0 (S_1 - S_0)$$

$$W_{\text{max}} = (u_1 - u_0) - T_0 (S_1 - S_0)$$

Surrounding work (W_{surr}):

When the piston moving outwards has to spend a work in pushing the atmosphere against its own pressure. This work, which may be called as the surroundings work is simply dissipated, and such is not useful. It is given by,

$$W_{\text{surr}} = P_0 (V_0 - V_1)$$

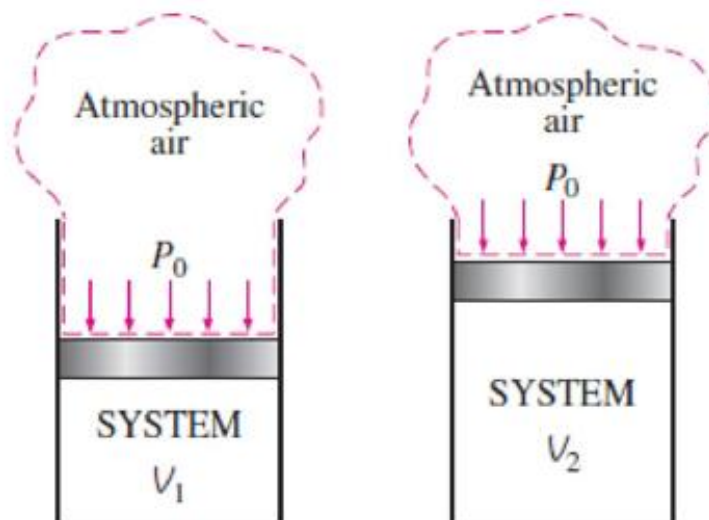


Fig. 5.6 As a closed system expands, some work needs to be done to push the atmospheric air out of the way

[Note FYI: When a system is compressed, however, the atmospheric pressure helps the compression process, and *thus* W_{surr} represents a gain. Note that the work done by or against the atmospheric pressure has significance only for systems whose volume changes during the process (i.e., systems that involve moving boundary work). It has no

significance for cyclic devices and systems whose boundaries remain fixed during a process such as rigid tanks and steady-flow devices (turbines, compressors, nozzles, heat exchangers, etc.)]

Net work (W_{net}):

The energy available for work transfer less work absorbed in moving the environment is called the useful work or net work.

Maximum available useful work or net work is given by,

$$W_{net} = W_{max} - W_{surr}$$

$$W_{net} = (u_1 - u_0) - T_0(S_1 - S_0) - p_0(V_0 - V_1)$$

$$W_{net} = (u_1 + p_0V_1 - T_0S_1) - (u_0 + p_0V_0 - T_0S_0)$$

$$\boxed{W_{net} = A_1 - A_0}$$

Where $A = u + p_0V - T_0S$ is known as non-flow availability function. It is composite property of the system and surroundings as it consists of three extensive properties of the system (u, V, S) and two intensive properties of the surroundings (p_0, T_0).

When system undergoes change from state 1 to state 2 without reaching the dead state, then

$$(W_u)_{max} = W_{net} = (A_1 - A_0) - (A_2 - A_0) = A_1 - A_2$$

Change in entropy for the closed system:

From the property relation,

$$Tds = du + pdV$$

Upon integration between the initial and final states, we obtain,

$$\int_1^2 dS = \int_1^2 \frac{mC_v dT}{T} + \int_1^2 \frac{pdV}{T} = mC_v \int_1^2 \frac{dT}{T} + mR \int_1^2 \frac{dV}{V} \quad \left(\because \frac{p}{T} = \frac{mR}{V} \right)$$

$$\boxed{S_2 - S_1 = mC_v \ln \frac{T_2}{T_1} + mR \ln \frac{V_2}{V_1}}$$

5.6 Availability of the Open System (Steady Flow System)

Consider a steady flow system and let it is assumed that the flowing fluid has the following properties and characteristics: (Fig. 5.7)

$u_1, v_1, h_1, p_1, C_1, z_1$ = Internal energy, specific volume, enthalpy, pressure, velocity and elevation at inlet

Q = Heat rejected by the system

W_s = Work delivers by the system

u_0, v_0, h_0, p_0, C_0 and z_0 = Fluid properties at the outlet respectively refers to surroundings.

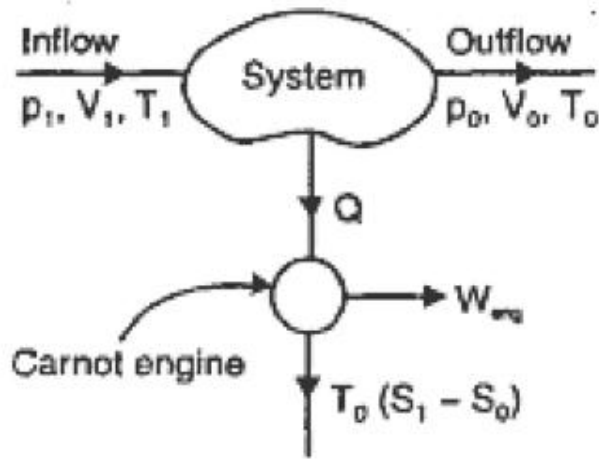


Fig. 5.7 Availability of non flow (closed) system

Steady flow energy equation may be written as,

$$u_1 + p_1 v_1 + \frac{C_1^2}{2} + gz_1 = u_0 + p_0 v_0 + \frac{C_0^2}{2} + gz_0$$

Neglecting kinetic and potential energy changes,

$$u_1 + p_1 v_1 - Q = u_0 + p_0 v_0 + W_s$$

$$H_1 - Q = H_0 + W_s$$

$$\text{Shaft work, } W_s = (H_1 - H_0) - Q$$

The heat Q rejected by the system may be utilized to run a reversible heat engine. The work output from this engine is,

$$W_{eng} = Q \left(1 - \frac{T_0}{T_1} \right) = Q - T_0 (S_1 - S_0)$$

Maximum available useful work or net work is given by,

$$W_{net} = W_s + W_{eng}$$

$$W_{net} = (H_1 - H_0) - Q + Q - T_0 (S_1 - S_0)$$

$$W_{net} = (H_1 - T_0 S_1) - (H_0 - T_0 S_0)$$

$$W_{net} = B_1 - B_0$$

Where $B = H - T_0 S$ is known as steady flow availability function or Darrieus and the Keenan function. It is a composite property of the system and surroundings as it consists of three extensive properties of the system (H, S) and one intensive property of the surroundings T_0 .

When a system undergoes change from state 1 to state 2 without reaching the dead state, then

$$(W_u)_{\max} = W_{net} = dB = (B_1 - B_0) - (B_2 - B_0) = B_1 - B_2$$

Change in entropy for the closed system:

From the property relation,

$$T ds = dh - v dp$$

Upon integration between the initial and final states, we obtain,

$$\int_1^2 dS = \int_1^2 \frac{mC_p dT}{T} - \int_1^2 \frac{Vdp}{T} = mC_p \int_1^2 \frac{dT}{T} - mR \int_1^2 \frac{dP}{P} \quad \left(\because \frac{p}{T} = \frac{mR}{V} \right)$$

$$S_2 - S_1 = mC_p \ln \frac{T_2}{T_1} - mR \ln \frac{p_2}{p_1}$$

5.7 Effectiveness (Second law efficiency), Reversible Work and Irreversibility

5.7.1 Effectiveness (Second law efficiency)

"It is defined as the fraction of maximum useful work $(W_u)_{\max}$ actually utilized and is expressed as the ratio of useful work (W_u) to the maximum useful work $(W_u)_{\max}$.

$$\varepsilon = \frac{W_u}{(W_u)_{\max}} = \frac{\text{gain in availability of the environment}}{\text{loss of availability of the system}}$$

Where useful work is given by,

$$W_u = W_{\exp} - W_{\text{surr}} = W_{\exp} - p_0 dV$$

Likewise the maximum useful work is given by,

$$(W_u)_{\max} = W_{\max} - p_0 dV$$

In steady flow system, there is no change in volume of the system; no work is done on the atmosphere thus term $p_0 dV$ is zero.

$$(W_u)_{\max} = W_{\max}$$

For reversible process $(W_u)_{\max} = W_u$ and thus ε will be unity.

For heating or compression process,

$$\varepsilon = \frac{W_u}{(W_u)_{\max}} = \frac{\text{loss in availability of the system}}{\text{gain of availability of the environment}}$$

[Note FYI: We defined the *thermal efficiency* and the *coefficient of performance* for devices as a measure of their performance. They are defined on the basis of the first law only, and they are sometimes referred to as the *first-law efficiencies*. The first law efficiency, however, makes no reference to the best possible performance, and thus it may be misleading.

- Consider two heat engines, both having a thermal efficiency of 30 %, as shown in Fig.5. 8 (a). One of the engines (engine A) is supplied with heat from a source at 600 K, and the other one (engine B) from a source at 1000 K. Both engines reject heat to a medium at 300 K. At first glance, both engines seem to convert to work the same fraction of heat that they receive; thus they are performing equally well. When we take a second look at these engines in light of the second law of thermodynamics, however, we see a totally different picture. These engines, at best, can perform as reversible engines, in which case their efficiencies would be,

$$\eta_{rev,A} = \left(1 - \frac{T_L}{T_H}\right)_A = 1 - \frac{300\text{ K}}{600\text{ K}} = 50\%$$

$$\eta_{rev,B} = \left(1 - \frac{T_L}{T_H}\right)_B = 1 - \frac{300\text{ K}}{1000\text{ K}} = 70\%$$

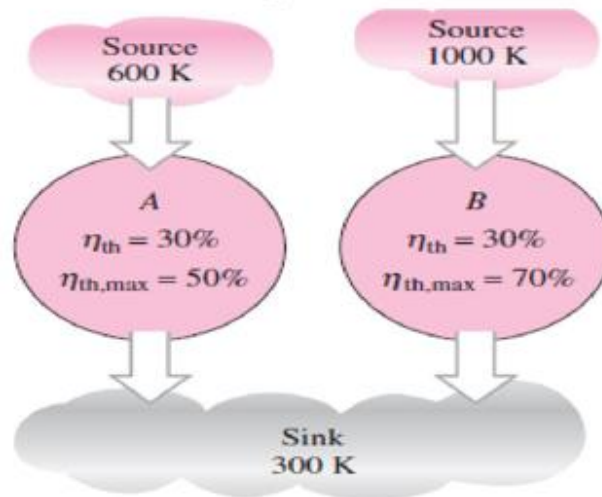


Fig.5.8 (a) Two heat engines that have the same thermal efficiency, but different maximum thermal efficiencies

- Now it is becoming apparent that engine *B* has a greater work potential available to it (70 % of the heat supplied as compared to 50% for engine *A*), and thus should do a lot better than engine *A*. Therefore, we can say that engine *B* is performing poorly relative to engine *A* even though both have the same thermal efficiency. It is obvious from this example that the first-law efficiency alone is not a realistic measure of performance of engineering devices. To overcome this deficiency, we define second-law efficiency.
- “Second-law efficiency is defined as the ratio of the actual thermal efficiency to the maximum possible (reversible) thermal efficiency under the same conditions” (Fig. 5.8 b)

$$\eta_{II} = \frac{\eta_{th}}{\eta_{th,rev}} \text{ (heat engines)}$$

- Based on this definition, the second-law efficiencies of the two heat engines discussed above are,

$$\eta_{rev,A} = 1 - \frac{0.30}{0.50} = 0.60$$

$$\eta_{rev,B} = 1 - \frac{0.30}{0.70} = 0.43$$

- The second-law efficiency can also be expressed as the ratio of the useful work output and the maximum possible (reversible) work output:

$$\eta_{II} = \frac{W_u}{W_{rev}} \text{ (work producing device)}$$

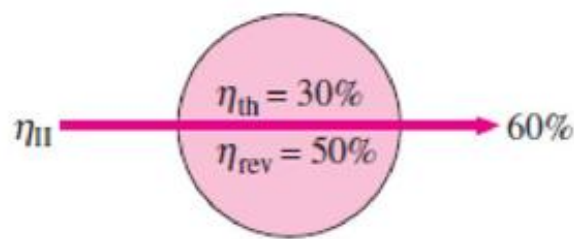


Fig.5.8 (b) Second-law efficiency is a measure of the performance of a device relative to its performance under reversible conditions

- We can also define second-law efficiency for work-consuming non-cyclic (such as compressors) and cyclic (such as refrigerators) devices as the ratio of the minimum (reversible) work input to the useful work input:

$$\eta_{II} = \frac{W_u}{W_{rev}} \text{ (work consuming device)}$$

- For cyclic devices such as refrigerators and heat pumps, it can also be expressed in terms of the coefficients of performance as,

$$\eta_{II} = \frac{COP}{COP_{rev}} \text{ (refrigerators and heat pumps)}$$

- The definitions above for the second-law efficiency do not apply to devices that are not intended to produce or consume work. The second-law efficiency is intended to serve as a measure of approximation to reversible operation, and thus its value should range from zero in the worst case (complete destruction of exergy) to one in the best case (no destruction of exergy). With this in mind, we define the second-law efficiency of a system during a process as,

$$\eta_{II} = \frac{\text{Exergy recovered}}{\text{Exergy supplied}}$$

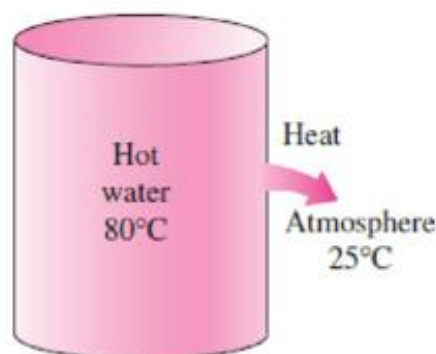


Fig. 5.9 The second-law efficiency of naturally occurring processes is zero if none of the work potential is recovered

- Therefore, when determining the second-law efficiency, the first thing we need to do is determine how much exergy or work potential is consumed during a process. In a reversible operation, we should be able to recover entirely the exergy supplied during the process, and the irreversibility in this case should be zero. The second-law efficiency is zero when we recover none of the exergy supplied to the system. Note that the exergy can be supplied or recovered at various amounts in various forms such as heat, work, kinetic energy, potential

energy, internal energy, and enthalpy. At all times, however, the exergy recovered and the exergy destroyed (the irreversibility) must add up to the exergy supplied.

- For a *heat engine*, the exergy supplied is the decrease in the exergy of the heat transferred to the engine, which is the difference between the exergy of the heat supplied and the exergy of the heat rejected. (The exergy of the heat rejected at the temperature of the surroundings is zero.) The net work output is the recovered exergy.
- For a *refrigerator* or *heat pump*, the exergy supplied is the work input since the work supplied to a cyclic device is entirely available. The recovered exergy is the exergy of the heat transferred to the high-temperature medium (which is the reversible work) for a heat pump, and the exergy of the heat transferred from the low-temperature medium for a refrigerator.
- For a heat exchanger with two unmixed fluid streams, normally the exergy supplied is the decrease in the exergy of the higher-temperature fluid stream, and the exergy recovered is the increase in the exergy of the lower temperature fluid stream.]

5.7.2 Reversible work and Irreversibility OR Guoy-Stodola equation

(A) Reversible work (W_{rev})

- “It is defined as the maximum amount of useful work that can be produced (or the minimum work that needs to be supplied) as a system undergoes a process between the specified initial and final states.” This is the useful work output (or input) obtained (or expended) when the process between the initial and final states is executed in a totally reversible manner.
- When the final state is the dead state, the reversible work equals exergy. For processes that require work, reversible work represents the minimum amount of work necessary to carry out that process.

(B) Irreversibility

“It is defined as difference between the reversible work W_{rev} and the useful work W_u is due to the irreversibilities present during the process, and this difference is called irreversibility.”

Irreversibility refers to closed system:

It is defined as the difference between the maximum work output from the system and the expansion work. That is,

$$I = [(u_1 - T_0 S_1) - (u_2 - T_0 S_2)] - [-Q - (u_2 - u_1)]$$

$$I = T_0 (S_2 - S_1) + Q$$

$$I = T_0 (dS)_{sys} + Q$$

Change in entropy of environment due to addition of heat Q at constant atmospheric temperature T_0 ,

$$dS_{surr} = \frac{Q}{T_0} \quad ; \quad Q = T_0 dS_{surr}$$

$$I = T_0 \left[(dS)_{sys} + (dS)_{surr} \right] = T_0 (dS)_{net}$$

$$I = T_0 (dS)_{univ}$$

Irreversibility refers to steady flow system:

$$I = \left[(h_1 - T_0 S_1) - (h_2 - T_0 S_2) \right] - \left[(h_1 - h_2) - Q \right]$$

$$I = T_0 (S_2 - S_1) + Q$$

$$I = T_0 (dS)_{sys} + T_0 (dS)_{surr} = T_0 (dS)_{net}$$

$$I = T_0 (dS)_{univ}$$

Above equation refers to as the Gouy-Stodola equation.

5.8 Solved Numerical

Example 5.1 A system at 450 K receives 225 kJ/s of heat energy from a source at 1500 K, and the temperatures of both the system and source remains constant during heat transfer process. Represent process on T-s diagram. Determine, (1) the net change in entropy, (2) available energy of heat source and system, and (3) decrease in available energy.

Solution:

Given data:

$$T_1 = 1500 \text{ K}$$

$$Q = 225 \text{ kJ/s}$$

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

$$T_0 = 300 \text{ K}$$

Find:

$$dS_{\text{net}}$$

$$A_1$$

$$A_2$$

$$A_1 - A_2$$

Entropy change of heat source,

$$dS_{\text{source}} = -\frac{Q}{T_1} = -\frac{225}{1500} = -0.150 \text{ kJ/s K}$$

Entropy change of system,

$$dS_{\text{system}} = -\frac{Q}{T_2} = -\frac{225}{450} = 0.5 \text{ kJ/s K}$$

Net change in entropy,

$$\begin{aligned} dS_{\text{net}} &= dS_{\text{source}} + dS_{\text{system}} \\ &= -0.15 + 0.5 = 0.25 \text{ kJ/s K} \end{aligned}$$

Available energy of heat source,

$$\begin{aligned} A_1 &= Q - T_0 dS_{\text{source}} \\ &= 225 - 300 \times 1.5 \\ &= 180 \text{ kJ/s} \end{aligned}$$

Available energy of heat system,

$$\begin{aligned} A_2 &= Q - T_0 dS_{\text{system}} \\ &= 225 - 300 \times 0.5 \\ &= 75 \text{ kJ/s} \end{aligned}$$

Decrease in available energy,

$$= A_1 - A_2 = 180 - 75 = 105 \text{ kJ/s}$$

Decrease in available energy can be determined using following relation,

$$= T_0 dS_{\text{net}} = 300 \times 0.5 = 105 \text{ kJ/s}$$

Example 5.2 20 kg of water at 90°C is mixed with 30 kg of water at 30°C and the pressure remains constant during the mixing operation. Calculate the decrease in

available energy. It may be presumed that the surroundings are at 10°C temperature and for water $C_{pw} = 4.187 \text{ kJ/kg K}$.

Solution:

Given data:

$$m_{w_1} = 20 \text{ kg}$$

$$T_{w_1} = 90^\circ \text{C}$$

$$m_{w_2} = 30 \text{ kg}$$

$$T_{w_2} = 30^\circ \text{C}$$

$$T_0 = 10^\circ \text{C}$$

$$C_{pw} = 4.187 \text{ kJ/kg K}$$

Find:

Decrease in AE

The available energy of system of mass m , specific heat c_p and at temperature T is given by,

$$AE = mc_p \int_{T_0}^T \left(1 - \frac{T_0}{T} \right) dT$$

where T_0 is the temperature of surroundings.

Now available energy of 20 kg of water at 90°C (363 K)

$$\begin{aligned} AE_1 &= 20 \times 4.18 \int_{283}^{363} \left(1 - \frac{283}{T} \right) dT \\ &= 83.6 \left[(363 - 283) - 283 \ln \frac{363}{283} \right] \\ &= 798.4 \text{ kJ} \end{aligned}$$

Available energy of 30 kg of water at 30°C (303 K)

$$\begin{aligned} AE_2 &= 30 \times 4.18 \int_{283}^{303} \left(1 - \frac{283}{T} \right) dT \\ &= 125.4 \left[(303 - 283) - 283 \ln \frac{303}{283} \right] \\ &= 85.3 \text{ kJ} \end{aligned}$$

Total available energy,

$$AE_{\text{total}} = 798.4 + 85.3 = 883.7 \text{ kJ}$$

Let T_f is the final equilibrium temperature after the mixing process.

Then from principle of energy conversion,

$$\text{heat lost by water at } 90^\circ \text{C} = \text{heat gain by water at } 30^\circ \text{C}$$

$$20 \times 4.18 (363 - T_f) = 30 \times 4.18 (T_f - 303)$$

$$T_f = 327 \text{ K}$$

Total mass after mixing = 20 + 30 = 50 kg

Available energy of 50 kg of water at 327 K

$$\begin{aligned} AE &= 50 \times 4.18 \int_{283}^{327} \left(1 - \frac{283}{T} \right) dT \\ &= 209 \left[(327 - 283) - 283 \ln \frac{327}{283} \right] \\ &= 650 \text{ kJ} \end{aligned}$$

Decrease in available energy due to mixing

$$\begin{aligned} &= \text{total energy before mixing} - \text{total energy after mixing} \\ &= 883.7 - 650 = 233.7 \text{ kJ} \end{aligned}$$

Example 5.3 One kg of air is contained in a piston cylinder assembly at 10 bar pressure and 500 K temperature. The piston moves outwards and the air expands to 2 bar pressure and 350 K temperature. Calculate: (1) the availability in the initial and final states, (2) the maximum useful work, and (3) the irreversibility for the system. Assume that system is insulated and the environment conditions are 1 bar and 290 K. Further for air, $R = 0.287 \text{ kJ/kg K}$, $C_v = 0.718 \text{ kJ/kg K}$.

Solution:

Given data:

$$\begin{aligned} m &= 1 \text{ kg} \\ p_1 &= 10 \text{ bar} \\ T_1 &= 500 \text{ K} \\ p_2 &= 2 \text{ bar} \\ T_2 &= 350 \text{ K} \end{aligned}$$

Find:

$$\begin{aligned} &A_1 \text{ (Initial state), } A_2 \text{ (Final state)} \\ &A_1 - A_2 \\ &I \end{aligned}$$

(i) Availability at the initial state

$$A_1 = (u_1 - u_0) + p_0(V_1 - V_0) - T_0(S_1 - S_0)$$

$$\text{Now, } (u_1 - u_0) = mc_v(T_1 - T_0) = 1 \times 0.718(500 - 290) = 150.78 \text{ kJ}$$

$$V_1 = \frac{mRT_1}{p_1} = 0.1435 \text{ m}^3 \text{ and } V_0 = \frac{mRT_0}{p_0} = 0.8323 \text{ m}^3$$

$$\therefore p_0(V_1 - V_0) = 1 \times 10^5 (0.1435 - 0.8323) = -68880 \text{ J} = -68.88 \text{ kJ}$$

further,

$$\begin{aligned} S_0 - S_1 &= mc_v \ln \frac{T_0}{T_1} + mR \ln \frac{V_0}{V_1} \\ &= 1 \times 0.718 \times \ln \frac{290}{500} + 1 \times 0.287 \ln \frac{0.8323}{0.1435} \\ &= 0.1134 \text{ kJ/K} \end{aligned}$$

$$\therefore T_0(S_1 - S_0) = 290 \times (-0.1134) = -32.77 \text{ kJ}$$

Accordingly:

$$A_1 = 150.78 + (-68.88) - (-32.87) = 114.77 \text{ kJ}$$

Availability at the final state

$$A_2 = (u_2 - u_0) + p_0(V_2 - V_0) - T_0(S_2 - S_0)$$

$$\text{Now, } (u_2 - u_0) = mc_v(T_2 - T_0) = 1 \times 0.718(350 - 290) = 43.08 \text{ kJ}$$

$$V_2 = \frac{mRT_2}{p_2} = 0.5022 \text{ m}^3 \text{ and } V_0 = \frac{mRT_0}{p_0} = 0.8323 \text{ m}^3$$

$$\therefore p_0(V_2 - V_0) = 1 \times 10^5(0.5022 - 0.8323) = -33010 \text{ J} = -33.01 \text{ kJ}$$

further,

(ii) For non flow process, the maximum useful work obtainable is given by change in availability,

$$W_{\text{net}} = A_1 - A_2 = 114.78 - 12.97 = 101.81 \text{ kJ}$$

(iii) The irreversibility is given by,

$$I = T_0(dS)_{\text{univ}} = T_0[(dS)_{\text{sys}} + (dS)_{\text{surr}}]$$

Change in entropy of system is given by,

$$\begin{aligned}(dS)_{\text{sys}} &= mc_p \ln \frac{T_2}{T_1} - mR \ln \frac{p_2}{p_1} \\ &= 1 \times 1.005 \ln \frac{350}{500} - 1 \times 0.287 \ln \frac{2}{10} \\ &= 0.104 \text{ kJ/K}\end{aligned}$$

Since the system is insulated, there will be no heat interaction with the surrounding, thus

$$(dS)_{\text{surr}} = 0$$

then, irreversibility is given by,

$$I = T_0(dS)_{\text{net}} = T_0[(dS)_{\text{sys}} + (dS)_{\text{surr}}] = 290 \times 0.104 = 30.16 \text{ kJ}$$

11.2 Maxwell's Equations

A pure substance existing in a single phase has only two independent variables. Of the eight quantities p , V , T , S , U , H , F (Helmholtz function), and G (Gibbs function) *any one may be expressed as a function of any two others.*

For a pure substance undergoing an infinitesimal reversible process

$$(a) \quad dU = TdS - pdV$$

$$(b) \quad dH = dU + pdV + Vdp = TdS + Vdp$$

$$(c) \quad dF = dU - TdS - SdT = -pdV - SdT$$

$$(d) \quad dG = dH - TdS - SdT = Vdp - SdT$$

Since U , H , F and G are thermodynamic properties and exact differentials of the type

$$dz = M dx + N dy, \text{ then}$$

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

Applying this to the four equations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (11.4)$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \quad (11.5)$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad (11.6)$$

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \quad (11.7)$$

These four equations are known as *Maxwell's equations*.

11.3 TdS Equations

Let entropy S be imagined as a function of T and V . Then

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

$$\therefore TdS = T \left(\frac{\partial S}{\partial T} \right)_V dT + T \left(\frac{\partial S}{\partial V} \right)_T dV$$

Since $T \left(\frac{\partial S}{\partial T} \right)_V = C_v$, heat capacity at constant volume, and

$$\left(\frac{\partial S}{\partial T} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V, \text{ Maxwell's third equation,}$$

$$TdS = C_v dT + T \left(\frac{\partial p}{\partial T} \right)_V dV \quad (11.8)$$

This is known as the *first TdS equation*.

If $S = S(T, p)$

$$dS = \left(\frac{\partial S}{\partial T} \right)_p dT + \left(\frac{\partial S}{\partial p} \right)_T dp$$

$$\therefore TdS = T \left(\frac{\partial S}{\partial T} \right)_p dT + T \left(\frac{\partial S}{\partial p} \right)_T dp$$

Since $T \left(\frac{\partial S}{\partial T} \right)_p = C_p$, and $\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p$

$$\text{then } TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp \quad (11.9)$$

This is known as the *second TdS equation*.

11.4 Difference in Heat Capacities

Equating the first and second TdS equations

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp = C_v dT + T \left(\frac{\partial p}{\partial T} \right)_V dV$$

$$(C_p - C_v) dT = T \left(\frac{\partial p}{\partial T} \right)_V dV + T \left(\frac{\partial V}{\partial T} \right)_p dp$$

$$\therefore dT = \frac{T \left(\frac{\partial p}{\partial T} \right)_V}{C_p - C_v} dV + \frac{T \left(\frac{\partial V}{\partial T} \right)_p}{C_p - C_v} dp$$

Again
$$dT = \left(\frac{\partial T}{\partial V} \right)_p dV + \left(\frac{\partial T}{\partial p} \right)_V dp$$

$$\therefore \frac{T \left(\frac{\partial p}{\partial T} \right)_V}{C_p - C_v} = \left(\frac{\partial T}{\partial V} \right)_p \text{ and } \frac{T \left(\frac{\partial V}{\partial T} \right)_p}{C_p - C_v} = \left(\frac{\partial T}{\partial p} \right)_V$$

Both these equations give

$$C_p - C_v = T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p$$

But
$$\left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_p \left(\frac{\partial V}{\partial p} \right)_T = -1$$

$$\therefore C_p - C_v = -T \left(\frac{\partial V}{\partial T} \right)_p^2 \left(\frac{\partial p}{\partial V} \right)_T \quad (11.10)$$

This is a very important equation in thermodynamics. It indicates the following important facts.

(a) Since $\left(\frac{\partial V}{\partial T} \right)_p^2$ is always positive, and $\left(\frac{\partial p}{\partial V} \right)_T$ for any substance is negative, $(C_p - C_v)$ is always positive. Therefore, C_p is always greater than C_v .

(b) As $T \rightarrow 0$ K, $C_p \rightarrow C_v$ or at absolute zero, $C_p = C_v$.

(c) When $\left(\frac{\partial V}{\partial T} \right)_p = 0$ (e.g., for water at 4°C , when density is maximum, or specific volume minimum), $C_p = C_v$.

(d) For an ideal gas, $pV = mRT$

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{mR}{p} = \frac{V}{T}$$

and

$$\left(\frac{\partial p}{\partial V} \right)_T = -\frac{mRT}{V^2}$$

$$\therefore C_p - C_v = mR$$

or
$$c_p - c_v = R$$

Equation (11.10) may also be expressed in terms of volume expansivity (β), defined as

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

and isothermal compressibility (k_T), defined as

$$k_T = - \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_T$$

$$C_p - C_v = \frac{TV \left[\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \right]^2}{-\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T}$$

$$\therefore C_p - C_v = \frac{TV \beta^2}{k_T} \quad (11.11)$$

11.5 Ratio of Heat Capacities

At constant S , the two TdS equations become

$$C_p dT_s = T \left(\frac{\partial V}{\partial T} \right)_p dp_s$$

$$C_v dT_s = -T \left(\frac{\partial p}{\partial T} \right)_v dV_s$$

$$\therefore \frac{C_p}{C_v} = - \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial T}{\partial p} \right)_v \left(\frac{\partial p}{\partial V} \right)_s = \frac{\left(\frac{\partial p}{\partial V} \right)_s}{\left(\frac{\partial p}{\partial V} \right)_T} = \gamma$$

Since $\gamma > 1$,

$$\left(\frac{\partial p}{\partial V} \right)_s > \left(\frac{\partial p}{\partial V} \right)_T$$

Therefore, the slope of an isentrope is greater than that of an isotherm on p - v diagram (Fig. 11.1). For reversible and adiabatic compression, the work done is

$$\begin{aligned} W_s &= h_{2s} - h_1 = \int_1^{2s} v dp \\ &= \text{Area } 1-2s-3-4-1 \end{aligned}$$

For reversible and isothermal compression, the work done would be

$$\begin{aligned} W_T &= h_{2T} - h_1 = \int_1^{2T} v dp \\ &= \text{Area } 1-2T-3-4-1 \end{aligned}$$

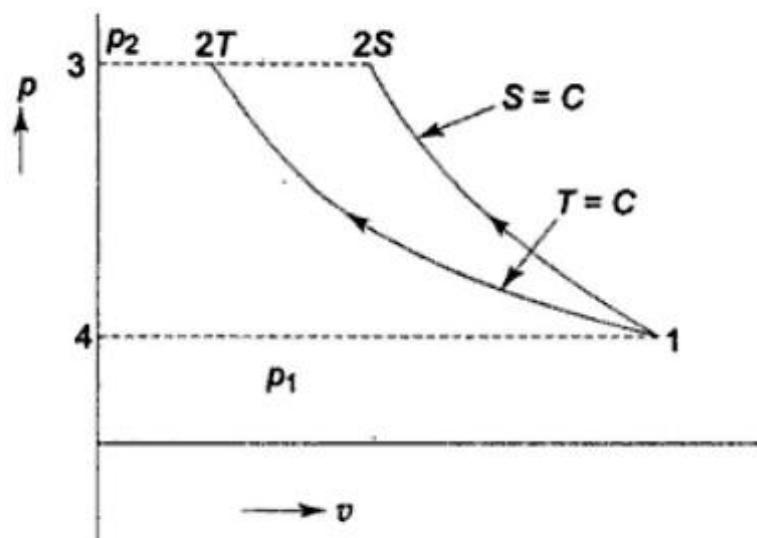


Fig. 11.1 Compression work in different reversible processes

$$\therefore W_T < W_s$$

For polytropic compression with $1 < n < \gamma$, the work done will be between these two values. So, isothermal compression requires minimum work. (See Sec. 10.4).

The adiabatic compressibility (k_s) is defined as

$$k_s = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_s$$

$$\therefore \frac{C_p}{C_v} = \frac{-\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T}{-\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_s} = \gamma$$

$$\text{or} \quad \gamma = \frac{k_T}{k_s} \quad (11.12)$$

11.6 Energy Equation

For a system undergoing an infinitesimal reversible process between two equilibrium states, the change of internal energy is

$$dU = T dS - p dV$$

Substituting the first $T dS$ equation

$$\begin{aligned} dU &= C_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dV - p dV \\ &= C_v dT + \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] dV \end{aligned} \quad (11.13)$$

$$\text{If} \quad U = U(T, V)$$