

Engineering Thermodynamics (BME-12)

UNIT-III

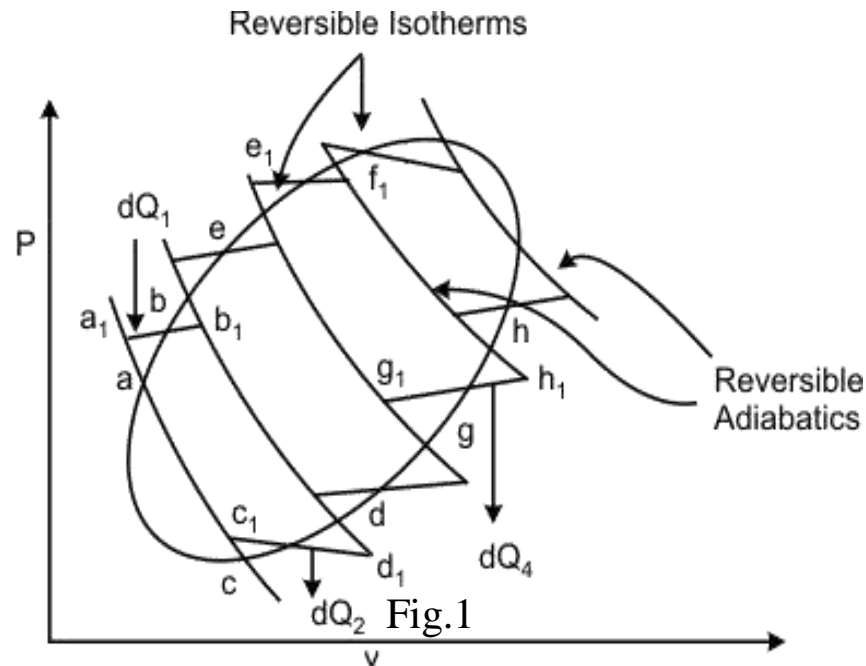
Lecture-1

The lecture contains

- Clausius Inequality

Clausius Inequality

Consider a system undergoing a reversible cycle. The given cycle may be subdivided by drawing a family of reversible adiabatic lines. Every two adjacent adiabatic lines may be joined by two reversible isotherms (refers to Figure 1)



Clausius Inequality cont.....

Now,

$$dQ_{a-b} = dQ_{a_1-b_1} \quad \text{and} \quad dQ_{cd} = dQ_{c_1-d_1}$$

Also, $a_1-b_1-d_1-c_1$ is a Carnot cycle which receives heat dQ_1 during the a_1b_1 process and rejects heat dQ_2 during the d_1c_1 process. Let the heat addition be at temperature T_1 and the heat rejection be at temperature T_2 . Then it is possible to write,

$$\eta = 1 - \frac{dQ_2}{dQ_1} = 1 - \frac{T_2}{T_1}$$

and

$$\frac{dQ_1}{dQ_2} = \frac{T_1}{T_2}$$

or,

$$\frac{dQ_1}{T_1} = \frac{dQ_2}{T_2}$$

Clausius Inequality cont.....

Since dQ_2 is negative, it reduces to

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = 0$$

Similarly for the cycle $e_1f_1h_1g_1$

$$\frac{dQ_3}{T_3} + \frac{dQ_4}{T_4} = 0$$

If similar equations are written for all the elementary cycles, then

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} + \frac{dQ_3}{T_3} + \frac{dQ_4}{T_4} = 0$$

or,

$$\oint_R \frac{dQ}{T} = 0$$

This is known as Clausius's theorem

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Clausius Inequality cont.....

Let us go back to the cycle a1b1d1c1

$$\eta_R = 1 - \frac{dQ_2}{dQ_1} = 1 - \frac{T_2}{T_1}$$

Now $\eta_{IR} < \eta_R$ where, $\eta_{IR} = \left[1 - \frac{dQ_2}{dQ_1} \right]$ and this is not equal to $\left[1 - \frac{T_2}{T_1} \right]$

For the irreversible cycle

$$1 - \frac{dQ_2}{dQ_1} < 1 - \frac{T_2}{T_1}$$

or,

$$\frac{dQ_2}{T_2} > \frac{dQ_1}{T_1} \quad \text{and} \quad \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} < 0$$

Because dQ_2 is negative.

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Clausius Inequality cont.....

Similarly, for the irreversible cycle $e_1g_1h_1f_1$

$$\frac{dQ_3}{T_3} + \frac{dQ_4}{T_4} < 0$$

Summing up all elementary cycles

$$\oint_{IR} \frac{dQ}{T} < 0$$

The above two conclusions about reversible and irreversible cycles can be generalized as

$$\oint \frac{dQ}{T} \leq 0$$

The equality holds good for a reversible cycle and the inequality holds good for an irreversible cycles. The complete expression is known as Clausius Inequality.

Lecture-2

The lecture contains

- Concept of Entropy

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UNIT-III (Lecture-2)

Concept of Entropy:-

Clausius inequality can be used to analyze the cyclic process in a quantitative manner. The second law became a law of wider applicability when Clausius introduced the property called entropy. By evaluating the entropy change, one can explain as to why spontaneous processes occur only in one direction.

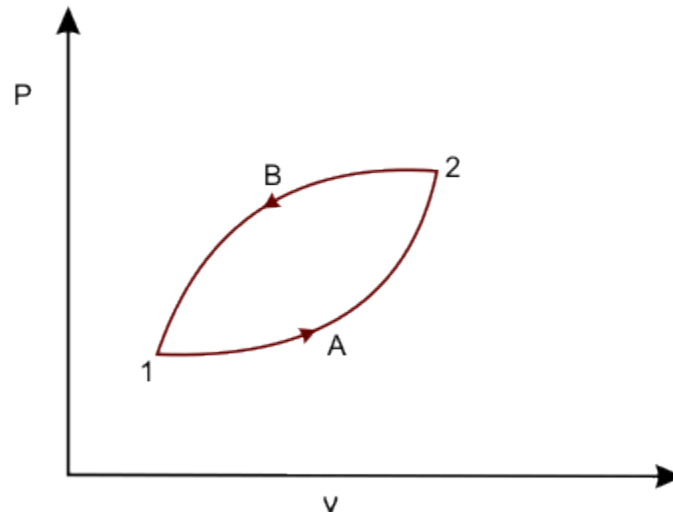


Fig.1

Consider a system in initial state 1. Let the system be taken from state 1 to state 2 along a reversible path 1-A-2, and then be restored to its initial state by following another reversible path 2BI (Figure 1). Then the two paths put together form a reversible cycle 1A2BI. Apply the Clausius inequality to this reversible cycle and obtain

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Concept of Entropy cont.....

$$\int_{1A2B1} \frac{dQ}{T} = 0$$

or,

$$\int_{1A2} \frac{dQ}{T} + \int_{2B1} \frac{dQ}{T} = 0$$

or,

$$\int_{1A2} \frac{dQ}{T} - \int_{2B1} \frac{dQ}{T} = \int_{1B2} \frac{dQ}{T}$$

Since path 2B1 is reversible, the limits of the integral can be reversed. That is, $\int \frac{dQ}{T}$ has the same value whether the path followed is 1A2 or 1B2. It is possible to connect the states 1 and 2 by several reversible paths and see that $\int \frac{dQ}{T}$ has the same value irrespective of the path as long as the paths are reversible. Therefore $(dQ/T)_R$ is an exact differential of some function which we identify as entropy. Hence it can be said that there exists a function S, called entropy, the change in entropy is expressed as

$$S_2 - S_1 = \Delta S = \int_1^2 dS = \int_1^2 (dQ/T)_R$$

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Concept of Entropy cont.....

This follows from the Clausius inequality as a consequence of the second law of thermodynamics. Therefore

$$ds = (dQ/T)_R \quad (\text{for reversible process only})$$

Calculation of Entropy Change

The following facts should be kept in mind while calculating the change in entropy for a process

1. $ds = (dQ/T)_R$ for a reversible process
2. Entropy is a state function. The entropy change of a system is determined by its initial and final states only, irrespective of how the system has changed its state.
3. In analyzing irreversible processes, it is not necessary to make a direct analysis of the actual process. **One can substitute the actual process by a reversible process connecting the final state to the initial state, and the entropy change for the imaginary reversible process can be evaluated.**

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UNIT-III (Lecture-2)

Concept of Entropy cont.....

Entropy change for some elementary processes

a. Absorption of energy by a constant temperature reservoir

A certain amount of heat is added to a constant temperature reservoir. The actual process can be replaced by a reversible path in which an equivalent amount of energy is added to the reservoir. Then, the entropy change of the reservoir is given by

$$\Delta s = (dQ/T)_R$$

b. Heating or Cooling of matter

The heating can be carried out either at constant pressure or at constant volume. From the first law of thermodynamics

$$Q = \Delta U \quad \text{for constant volume heating/cooling process}$$

$$Q = \Delta H \quad \text{for constant pressure heating/cooling process}$$

$$\Delta S = \int dQ/T = m \int_{T_1}^{T_2} c_p (dT/T) \quad \text{for a constant pressure process}$$

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Concept of Entropy cont.....

or,

$$\Delta S = mc_p \ln(T_2/T_1) \text{ for a constant pressure process}$$

Similarly,

$$\Delta S = \int dQ/T = m \int_{T_1}^{T_2} c_v (dT/T) \text{ for a constant volume process}$$

or,

$$\Delta S = mc_v \ln(T_2/T_1) , \text{ for a constant volume process}$$

(c) phase change at constant temperature and pressure

Melting : $S_{sf} = \int dq/T = h_{sf}/T$ [sf=solid to liquid]

Evaporation: $S_{fg} = \int dq/T = h_{fg}/T$ [fg = liquid to vapor]

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Concept of Entropy cont.....

(d) Change of state for an ideal gas

If an ideal gas undergoes a change of state from (P_1, v_1, T_1) to (P_2, v_2, T_2)

$$dQ = dU + PdV$$

or,

$$dq = du + Pdv$$

or,

$$ds = \left(\frac{dq}{T} \right)_R$$

or,

$$\Delta s = \int_1^2 \left(\frac{dq}{T} \right)_R = \int_1^2 \frac{(du + Pdv)}{T} = \int_1^2 \left\{ \frac{c_v dT}{T} + \frac{Rdv}{v} \right\}$$

or,

$$\Delta s = c_v \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{v_2}{v_1} \right)$$

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Concept of Entropy cont.....

Again, $H = U + PV$

or,

$$dH = dU + PdV + VdP$$

or,

$$dH = dQ + VdP$$

or,

$$dQ = dH - VdP$$

or,

$$dq = dh - v dP$$

or,

$$\Delta s = \int_1^2 \left(\frac{dq}{T} \right)_R = \int_1^2 \frac{(dh - v dP)}{T} = \int_1^2 \frac{c_p dT}{T} - \frac{R dP}{P}$$

or,

$$\Delta s = c_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right)$$

For a constant temperature process Δs is either $+ R \ln \left(\frac{v_2}{v_1} \right)$ or, $- R \ln \left(\frac{P_2}{P_1} \right)$

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Lecture-3

The lecture contains

- **Principle of entropy increase**

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UNIT-III (Lecture-3)

PRINCIPLE OF ENTROPY INCREASE:-

For any infinitesimal process undergone by a system, we have from Eq. for the total mass

$$dS \geq \frac{dQ}{T}$$

For an isolated system which does not undergo any energy interaction with the surroundings, $dQ = 0$.

Therefore, for an isolated system

$$dS_{\text{iso}} \geq 0$$

For a reversible process,

$$dS_{\text{iso}} = 0$$

or $S = \text{constant}$

For an irreversible process

$$dS_{\text{iso}} > 0$$

It is thus proved that *the entropy of an isolated system can never decrease*. It always increases and remains constant only when the process is reversible. This is known as the *principle of increase of entropy*, or simply the *entropy principle*. It is the quantitative general statement of second law from the macroscopic viewpoint.

An isolated system can always be formed by including any system and its surroundings within a single boundary Fig. Sometimes the original system which is then only a part of the isolated system is called a 'subsystem'.

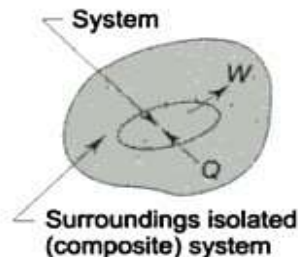


Fig. Isolated system

PRINCIPLE OF ENTROPY INCREASE cont.....

The system and the surroundings together (the universe or the isolated system) include everything which is affected by the process. For all possible processes that a system in the given surroundings can undergo

$$dS_{\text{univ}} \geq 0$$

or

$$dS_{\text{sys}} + dS_{\text{surr}} \geq 0$$

Entropy may decrease locally at some region within the isolated system, but it must be compensated by a greater increase of entropy somewhere within the system so that the net effect of an irreversible process is an entropy increase of

the whole system. The entropy increase of an isolated system is a measure of the extent of irreversibility of the process undergone by the system.

Rudolf Clausius summarized the first and second laws of thermodynamics in the following words:

- (a) Die Energie der Welt ist Constant.
- (b) Die Entropie der Welt strebt einem Maximum zu.
- [(a) The energy of the world (universe) is constant.
- (b) The entropy of the world tends towards a maximum.]

PRINCIPLE OF ENTROPY INCREASE cont.....

The entropy of an isolated system always increases and becomes a maximum at the state of equilibrium. If the entropy of an isolated system varies with some parameter x , then there is a certain value of x_e which maximizes the entropy

$\left(\text{when } \frac{dS}{dx} = 0 \right)$ and represents the equilibrium state Fig. The system is

then said to exist at the peak of the entropy hill, and $dS = 0$. *When the system is at equilibrium, any conceivable change in entropy would be zero.*

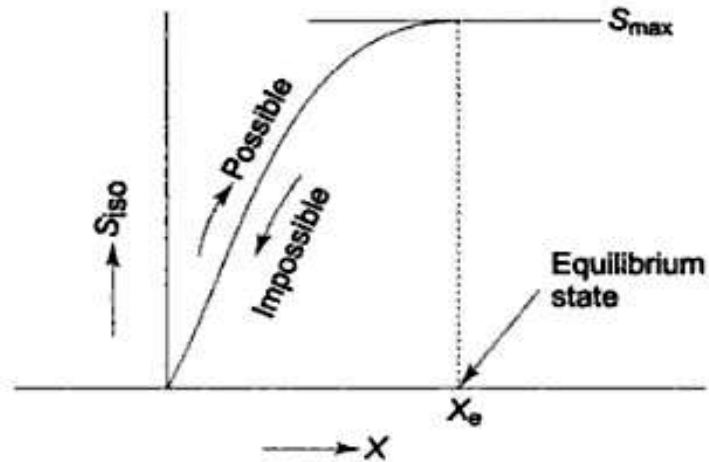


Fig. *Equilibrium state of an isolated system*

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Lecture-4

The lecture contains

Application of entropy principle

Application of entropy principle:-

The principle of increase of entropy is one of the most important laws of physical science. It is the quantitative statement of the second law of thermodynamics. Every irreversible process is accompanied by entropy increase of the universe, and this entropy increase quantifies the extent of irreversibility of the process. The higher the entropy increase of the universe, the higher will be the irreversibility of the process. A few applications of the entropy principle are illustrated in the following.

1 *Transfer of heat through a Finite Temperature Difference*

Let Q be the rate of heat transfer from reservoir A at T_1 to reservoir B at T_2 , $T_1 > T_2$ Fig.

For reservoir A , $\Delta S_A = -Q/T_1$. It is negative because heat Q flows out of the reservoir. For reservoir B , $\Delta S_B = +Q/T_2$. It is positive because heat flows into

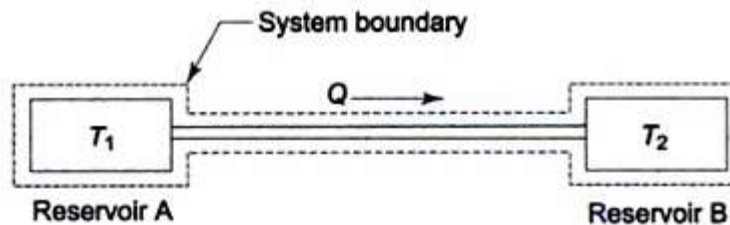


Fig. *Heat transfer through a finite temperature difference*

Application of entropy principle cont.....

the reservoir. The rod connecting the reservoirs suffers no entropy change because, once in the steady state, its coordinates do not change.

Therefore, for the isolated system comprising the reservoirs and the rod, and since entropy is an additive property

$$S = S_A + S_B$$

$$\Delta S_{\text{univ}} = \Delta S_A + \Delta S_B$$

or

$$\Delta S_{\text{univ}} = -\frac{Q}{T_1} + \frac{Q}{T_2} = Q \cdot \frac{T_1 - T_2}{T_1 T_2}$$

Since $T_1 > T_2$, ΔS_{univ} is positive, and the process is irreversible and possible. If $T_1 = T_2$, ΔS_{univ} is zero, and the process is reversible. If $T_1 < T_2$, ΔS_{univ} is negative and the process is impossible.

2 Mixing of Two Fluids

Subsystem 1 having a fluid of mass m_1 , specific heat c_1 , and temperature t_1 , and subsystem 2 consisting of a fluid of mass m_2 , specific heat c_2 , and temperature t_2 , comprise a composite system in an adiabatic enclosure Fig. When the partition is removed, the two fluids mix together, and at

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Application of entropy principle cont....

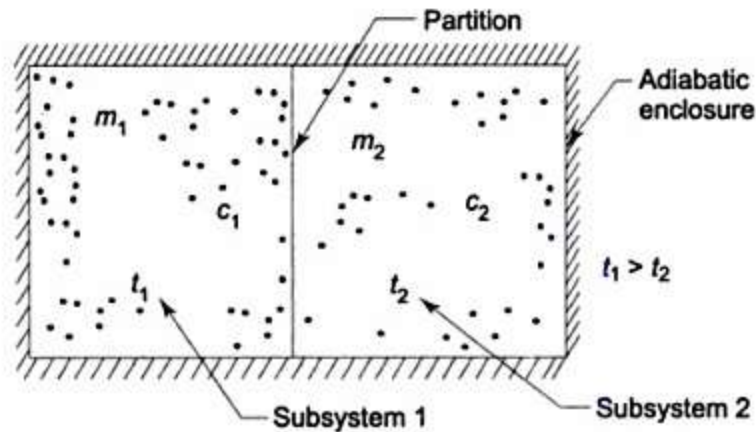


Fig. Mixing of two fluids

equilibrium let t_f be the final temperature, and $t_2 < t_f < t_1$. Since energy interaction is exclusively confined to the two fluids, the system being isolated

$$m_1 c_1 (t_1 - t_f) = m_2 c_2 (t_f - t_2)$$

$$\therefore t_f = \frac{m_1 c_1 t_1 + m_2 c_2 t_2}{m_1 c_1 + m_2 c_2}$$

Entropy change for the fluid in subsystem 1

$$\begin{aligned} \Delta S_1 &= \int_{T_1}^{T_f} \frac{dQ_{\text{rev}}}{T} = \int_{T_1}^{T_f} \frac{m_1 c_1 dT}{T} = m_1 c_1 \ln \frac{T_f}{T_1} \\ &= m_1 c_1 \ln \frac{t_f + 273}{t_1 + 273} \end{aligned}$$

This will be negative, since $T_1 > T_f$.

UNIT-III (Lecture-4)

Application of entropy principle

Entropy change for the fluid in subsystem 2

$$\Delta S_2 = \int_{T_1}^{T_f} \frac{m_2 c_2 dT}{T} = m_2 c_2 \ln \frac{T_f}{T_2} = m_2 c_2 \ln \frac{t_f + 273}{t_2 + 273}$$

This will be positive, since $T_2 < T_f$

$$\begin{aligned} \therefore \Delta S_{\text{univ}} &= \Delta S_1 + \Delta S_2 \\ &= m_1 c_1 \ln \frac{T_f}{T_1} + m_2 c_2 \ln \frac{T_f}{T_2} \end{aligned}$$

ΔS_{univ} will be positive definite, and the mixing process is irreversible.

Although the mixing process is irreversible, to evaluate the entropy change for the subsystems, the irreversible path was replaced by a reversible path on which the integration was performed.

If $m_1 = m_2 = m$ and $c_1 = c_2 = c$.

$$\Delta S_{\text{univ}} = mc \ln \frac{T_f^2}{T_1 \cdot T_2}$$

and

$$T_f = \frac{m_1 c_1 T_1 + m_2 c_2 T_2}{m_1 c_1 + m_2 c_2} = \frac{T_1 + T_2}{2}$$

$$\therefore \Delta S_{\text{univ}} = 2 mc \ln \frac{(T_1 + T_2)/2}{\sqrt{T_1 \cdot T_2}}$$

This is always positive, since the arithmetic mean of any two numbers is always greater than their geometric mean. This can also be proved geometrically. Let a semi-circle be drawn with $(T_1 + T_2)$ as diameter (Fig.).

Here, $AB = T_1$, $BC = T_2$ and $OE = (T_1 + T_2)/2$. It is known that $(DB)^2 = AB \cdot BC = T_1 T_2$.

$$\therefore DB = \sqrt{T_1 T_2}$$

Now,

$$OE > DB$$

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

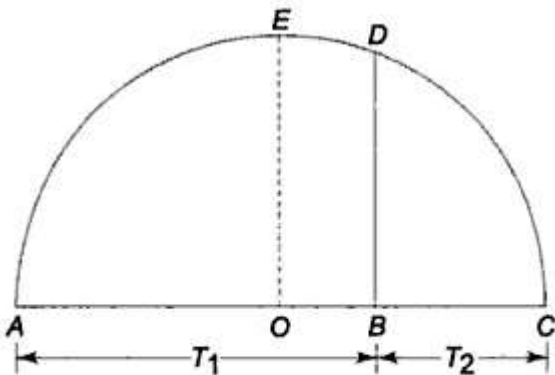


Fig. Geometrical proof to show that g.m < a.m.

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Lecture-5

The lecture contains

- **Temperature – Entropy Diagram**

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UNIT-III (Lecture-5)

Temperature – Entropy Diagram:-

The infinitesimal change in entropy dS due to reversible heat transfer dQ at temperature T is

$$dS = \frac{dQ_{rev}}{T}$$

If $dQ_{rev} = 0$, i.e., the process is reversible and adiabatic

$$dS = 0$$

and $S = \text{constant}$

A reversible adiabatic process is, therefore, an isentropic process.

Now

$$dQ_{rev} = TdS$$

or

$$Q_{rev} = \int_i^f TdS$$

The system is taken from i to f reversibly (Fig. 1). The area under the curve $\int_i^f T dS$ is equal to the heat transferred in the process.

For reversible isothermal heat transfer (Fig. 2), $T = \text{constant}$.

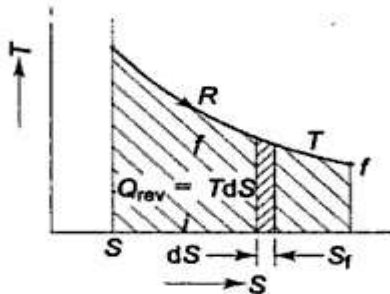


Fig. 1 Area under a reversible path on the T-s plot represents heat transfer

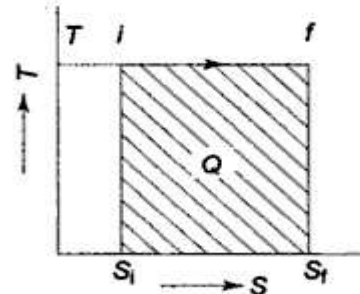


Fig. 2 Reversible isothermal heat transfer

Temperature – Entropy Diagram:-

$$\therefore Q_{\text{rev}} = T \int_i^f dS = T(S_f - S_i)$$

For a reversible adiabatic process, $dS = 0$, $S = C$ (Fig. 3).

The *Carnot cycle* comprising two reversible isotherms and two reversible adiabatics forms a rectangle in the T - S plane (Fig. 4). Process 4-1 represents reversible isothermal heat addition Q_1 to the system at T_1 from an external

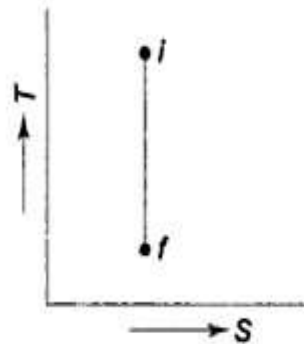


Fig. 3 Reversible adiabatic isentropic

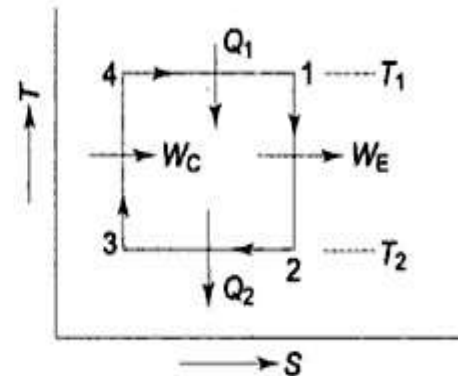


Fig. 4 Carnot cycle

Temperature – Entropy Diagram:-

source, process 1–2 is the reversible adiabatic expansion of the system producing W_E amount of work, process 2–3 is the reversible isothermal heat rejection from the system to an external sink at T_2 , and process 3–4 represents reversible adiabatic compression of the system consuming W_c amount of work. Area 1 2 3 4 represents the net work output per cycle and the area under 4–1 indicates the quantity of heat added to the system Q_1 .

$$\begin{aligned} \therefore \eta_{\text{Carnot}} &= \frac{Q_1 - Q_2}{Q_1} = \frac{T_1(S_1 - S_4) - T_2(S_2 - S_3)}{T_1(S_1 - S_4)} \\ &= \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1} \end{aligned}$$

and

$$W_{\text{net}} = Q_1 - Q_2 = (T_1 - T_2)(S_1 - S_4)$$

Engineering Thermodynamics (BME-12)
UNIT-III

Lecture-6

The lecture contains

- **TdS Equations**
- Statement of the third law of thermodynamics.

Engineering Thermodynamics (BME-12)
UNIT-III (Lecture-6)

TdS Equations:-

For a closed system containing a pure compressible substance undergoing a reversible process.

$$dU = \delta Q_{rev} - \delta W_{rev} = Tds - PdV$$

$$Tds = dU + PdV, \quad \text{or} \quad Tds = du + Pdv \quad (\text{per unit mass})$$

This is the famous **Gibbsian equation**.

- Eliminate du by using the definition of enthalpy $h = u + Pv$

Thus, $dh = du + Pdv + \frac{vdP}{\gamma}$ $du + Pdv = dh - vdP$

$$Tds = du + Pdv \quad \text{Also,} \quad Tds = dh - vdP$$

Important: These equations relate the entropy change of a system to the changes in other **properties** : dh,du,dp,dv Therefore, they are **independent of the process** .

These relations can be used for reversible as well as irreversible processes.

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(Lecture-6)

Statement of the third law of thermodynamics:-

- ‘Third law of thermodynamics’, an independent principle uncovered by ‘Nernst’ and formulated by ‘Planck’, states that the “Entropy of a pure substance approaches zero at absolute zero temperature.” This fact can also be corroborated by the definition of entropy which says it is a measure of molecular disorderness. At absolute zero temperature substance molecules get frozen and do not have any activity, therefore it may be assigned zero entropy value at crystalline state. Although the attainment of absolute zero temperature is impossible practically, however theoretically it can be used for defining absolute entropy value with respect to zero entropy at absolute zero temperature. Second law of thermodynamics also shows that absolute zero temperature can’t be achieved. Third law of thermodynamics is of high theoretical significance for the sake of absolute property definitions and has found great utility in thermodynamics.

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UNIT-III

(Problem)

Example 1 One kg of ice at -5°C is exposed to the atmosphere which is at 20°C . The ice melts and comes into thermal equilibrium with the atmosphere. (a) Determine the entropy increase of the universe. (b) What is the minimum amount of work necessary to convert the water back into ice at -5°C ? c_p of ice is 2.093 kJ/kg K and the latent heat of fusion of ice is 333.3 kJ/kg .

Solution Heat absorbed by ice Q from the atmosphere (Fig.)

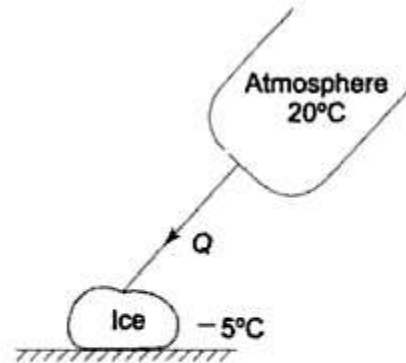


Fig.

$$\begin{aligned} &= \text{Heat absorbed in solid phase} + \text{Latent heat} \\ &\quad + \text{Heat absorbed in liquid phase} \\ &= 1 \times 2.093 \times [0 - (-5)] + 1 \times 333.3 + 1 \times 4.187 \times (20 - 0) \\ &= 427.5 \text{ kJ} \end{aligned}$$

Engineering Thermodynamics (BME-12)

UNIT-III

(Problem)

Entropy change of the atmosphere.

$$(\Delta S)_{\text{atm}} = -\frac{Q}{T} = -\frac{427.5}{293} = -1.46 \text{ kJ/K}$$

Entropy change of the system (ice) as it gets heated from -5°C to 0°C

$$\begin{aligned}(\Delta S_{\text{I}})_{\text{system}} &= \int_{268}^{273} mc_p \frac{dT}{T} = 1 \times 2.093 \ln \frac{273}{268} = 2.093 \times 0.0186 \\ &= 0.0389 \text{ kJ/K}\end{aligned}$$

Entropy change of the system as ice melts at 0°C to become water at 0°C

$$(\Delta S_{\text{II}})_{\text{system}} = \frac{333.3}{273} = 1.22 \text{ kJ/K}$$

Entropy change of water as it gets heated from 0°C to 20°C

$$(\Delta S_{\text{III}})_{\text{system}} = \int_{273}^{293} mc_p \frac{dT}{T} = 1 \times 4.187 \ln \frac{293}{273} = 0.296 \text{ kJ/K}$$

Total entropy change of ice as it melts into water

$$\begin{aligned}(\Delta S)_{\text{total}} &= \Delta S_{\text{I}} + \Delta S_{\text{II}} + \Delta S_{\text{III}} \\ &= 0.0389 + 1.22 + 0.296 \\ &= 1.5549 \text{ kJ/K}\end{aligned}$$

The entropy-temperature diagram for the system as ice at -5°C converts to water at 20°C is shown in Fig. 2

\therefore Entropy increase of the universe

$$\begin{aligned}(\Delta S)_{\text{univ}} &= (\Delta S)_{\text{system}} + (\Delta S)_{\text{atm}} \\ &= 1.5549 - 1.46 = 0.0949 \text{ kJ/K}\end{aligned}$$

Ans. (a)

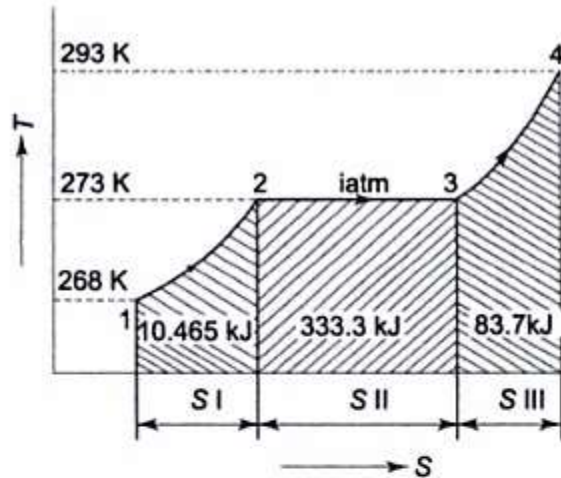


Fig. 2

(b) To convert 1 kg of water at 20°C to ice at -5°C, 427.5 kJ of heat have to be removed from it, and the system has to be brought from state 4 to state 1 (Fig. Ex. 2). A refrigerator cycle, as shown in Fig. Ex. 3, is assumed to accomplish this.

The entropy change of the system would be the same, i.e. $S_4 - S_1$, with the only difference that its sign will be negative, because heat is removed from the system (Fig. Ex. 7.3.2).

$$(\Delta S)_{\text{system}} = S_1 - S_4$$

(negative)

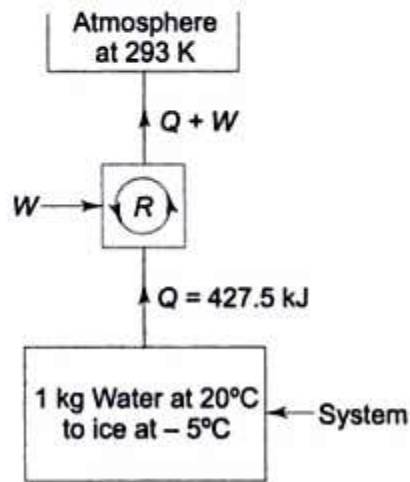


Fig. 3

The entropy change of the working fluid in the refrigerator would be zero,

Engineering Thermodynamics (BME-12)

UNIT-III (Problem)

since it is operating in a cycle, i.e.,

$$(\Delta S)_{\text{ref}} = 0$$

The entropy change of the atmosphere (positive)

$$(\Delta S)_{\text{atm}} = \frac{Q + W}{T}$$

∴ Entropy change of the universe

$$\begin{aligned} (\Delta S)_{\text{univ}} &= (\Delta S)_{\text{system}} + (\Delta S)_{\text{ref}} + (\Delta S)_{\text{atm}} \\ &= (S_1 - S_4) + \frac{Q + W}{T} \end{aligned}$$

By the principle of increase of entropy

$$(\Delta S)_{\text{univ or isolated system}} \geq 0$$

$$\therefore \left[(S_1 - S_4) + \frac{Q + W}{T} \right] \geq 0$$

$$\therefore \frac{Q + W}{T} \geq (S_4 - S_1)$$

$$W \geq T(S_4 - S_1) - Q$$

$$\therefore W_{(\text{min})} = T(S_4 - S_1) - Q$$

$$\text{Here } Q = 427.5 \text{ kJ}$$

$$T = 293 \text{ K}$$

$$S_4 - S_1 = 1.5549 \text{ kJ/K}$$

$$\begin{aligned} \therefore W_{(\text{min})} &= 293 \times 1.5549 - 427.5 \\ &= 28.5 \text{ kJ} \end{aligned}$$

Engineering Thermodynamics (BME-12)

UNIT-III (Problem)

Example 2 A fluid undergoes a reversible adiabatic compression from 0.5 MPa, 0.2 m³ to 0.05 m³ according to the law, $pv^{1.3} = \text{constant}$. Determine the change in enthalpy, internal energy and entropy, and the heat transfer and work transfer during the process.

Solution

$$TdS = dH - Vdp$$

For the reversible adiabatic process (Fig. 2)

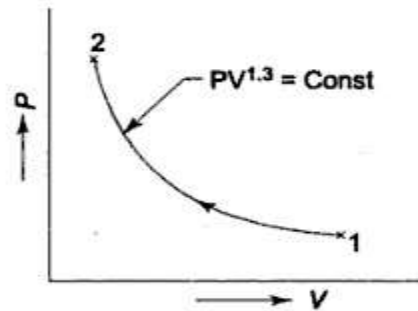


Fig. 2

$$dH = Vdp$$

$$p_1 = 0.5 \text{ MPa}, V_1 = 0.2 \text{ m}^3$$

$$V_2 = 0.05 \text{ m}^3, p_1 V_1^n = p_2 V_2^n$$

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

$$= 0.5 \times \left(\frac{0.20}{0.05} \right)^{1.3} \text{ MPa}$$

$$= 0.5 \times 6.061 \text{ MPa}$$

$$= 3.0305 \text{ MPa}$$

$$p_1 V_1^n = p V^n$$

$$\therefore V = \left(\frac{p_1 V_1^n}{p} \right)^{1/n}$$

$$\int_{H_1}^{H_2} dH = \int_{p_1}^{p_2} V dp$$

$$H_2 - H_1 = \int_{p_1}^{p_2} \left[\left(\frac{p_1 V_1^n}{p} \right)^{1/n} \right] dp$$

$$= (p_1 V_1^n)^{1/n} \left(\frac{p_1^{1-1/n} - p_2^{1-1/n}}{1-1/n} \right)$$

$$= \frac{n(p_2 V_2 - p_1 V_1)}{n-1}$$

$$= \frac{1.3(3030.5 \times 0.05 - 500 \times 0.2)}{1.3-1}$$

$$= 223.3 \text{ kJ}$$

$$H_2 - H_1 = (U_2 + p_2 V_2) - (U_1 + p_1 V_1)$$

$$= (U_2 - U_1) + (p_2 V_2 - p_1 V_1)$$

$$U_2 - U_1 = (H_2 - H_1) - (p_2 V_2 - p_1 V_1)$$

$$= 223.3 - 51.53$$

$$= 171.77 \text{ kJ}$$

Ans.

$$S_2 - S_1 = 0$$

Ans.

$$Q_{1-2} = 0$$

Ans.

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

$$W_{1-2} = U_1 - U_2 = -171.77 \text{ kJ}$$

Ans.

Engineering Thermodynamics (BME-12)
UNIT-III

Lecture-7

The lecture contains

- **Available Energy**

Engineering Thermodynamics (BME-12)
UNIT-III (Lecture-7)

Available Energy:-

The sources of energy can be divided into two groups, viz. high grade energy and low grade energy. The conversion of high grade energy to shaft work is exempted from the limitations of the second law, while conversion of low grade energy is subject to them.

The examples of two kinds of energy are:

High grade energy

- (a) Mechanical work
- (b) Electrical energy
- (c) Water power
- (d) Wind power
- (e) Kinetic energy of a jet
- (f) Tidal power

Low grade energy

- (a) Heat or thermal energy
- (b) Heat derived from nuclear fission or fusion
- (c) Heat derived from combustion of fossil fuels

The bulk of the high grade energy in the form of mechanical work or electrical energy is obtained from sources of low grade energy, such as fuels, through the medium of the cyclic heat engine. The complete conversion of low grade energy, heat, into high grade energy, shaft-work, is impossible by virtue of the second law of thermodynamics. That part of the low grade energy which is available for conversion is referred to as available energy, while the part which, according to the second law, must be rejected, is known as *unavailable energy*.

Available Energy Referred to a Cycle

The maximum work output obtainable from a certain heat input in a cyclic heat engine (Fig. 1) is called the *available energy* (A.E.), or the available part of the energy supplied. The minimum energy that has to be rejected to the sink by the second law is called the *unavailable energy* (U.E), or the unavailable part of the energy supplied.

Therefore, $Q_1 = \text{A.E.} + \text{U.E.}$

or $W_{\max} = \text{A.E.} = Q_1 - \text{U.E.}$

For the given T_1 and T_2 ,

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

For a given T_1 , η_{rev} will increase with the decrease of T_2 . The lowest practicable temperature of heat rejection is the *temperature of the surroundings*, T_0

$$\therefore \eta_{\max} = 1 - \frac{T_0}{T_1}$$

and $W_{\max} = \left(1 - \frac{T_0}{T_1}\right) Q_1$

Let us consider a finite process $x-y$, in which heat is supplied reversibly to a heat engine (Fig. 2). Taking an elementary cycle, if δQ_1 is the heat received by the engine reversibly at T_1 , then

$$\delta W_{\max} = \frac{T_1 - T_0}{T_1} \delta Q_1 = \delta Q_1 - \frac{T_0}{T_1} \delta Q_1 = \text{A.E.}$$

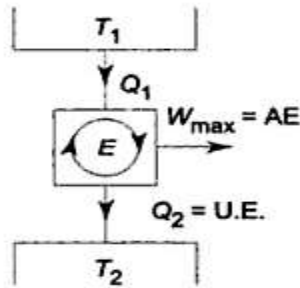


Fig. 1 Available and unavailable energy in a cycle

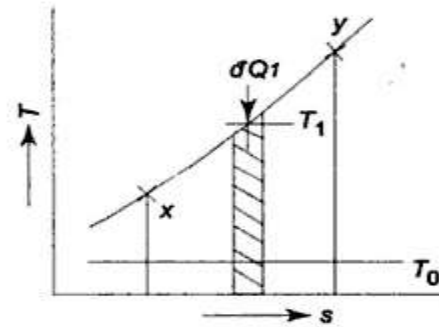


Fig. 2 Availability of energy

For the heat engine receiving heat for the whole process $x-y$, and rejecting heat at T_0

$$\int_x^y dW_{\max} = \int_x^y dQ_1 - \int_x^y \frac{T_0}{T_1} dQ_1$$

$$\begin{aligned} \therefore W_{\max} &= A.E. \\ &= Q_{xy} - T_0 (s_y - s_x) \\ \text{or U.E.} &= Q_{xy} - W_{\max} \\ \text{or U.E.} &= T_0 (s_y - s_x) \end{aligned}$$

The unavailable energy is thus the product of the lowest temperature of heat rejection, and the change of entropy of the system during the process of supplying heat (Fig. 3). The available energy is also known as *exergy* and the unavailable energy as *energy*, the words first coined by Rant (1956).

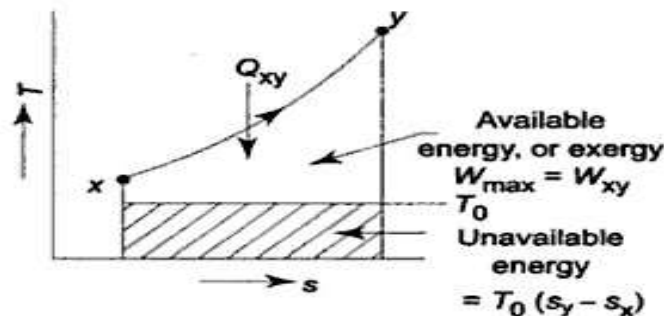


Fig. 3 Unavailable energy by the second law

Decrease (loss) in Available Energy when heat is transferred through a Finite Temperature Difference:-

Whenever heat is transferred through a finite temperature difference, there is a decrease in the availability of energy so transferred.

Let us consider a reversible heat engine operating between T_1 and T_0 (Fig. 4). Then

$$Q_1 = T_1 \Delta s, \quad Q_2 = T_0 \Delta s, \quad \text{and} \quad W = \text{A.E.} = (T_1 - T_0) \Delta s$$

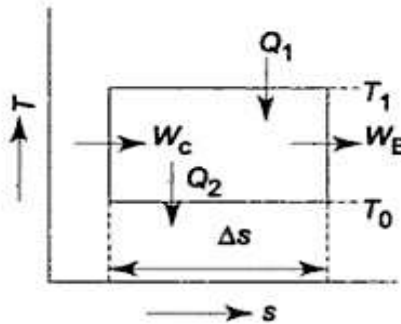


Fig. 4 Carnot cycle

Let us now assume that heat Q_1 is transferred through a finite temperature difference from the reservoir or source at T_1 to the engine absorbing heat at T'_1 , lower than T_1 (Fig. 5). The availability of Q_1 as received by the engine at T'_1

lower than T_1 (Fig. 5). The availability of Q_1 as received by the engine at T'_1 can be found by allowing the engine to operate reversibly in a cycle between T'_1 and T_0 receiving Q_1 and rejecting Q_2 .

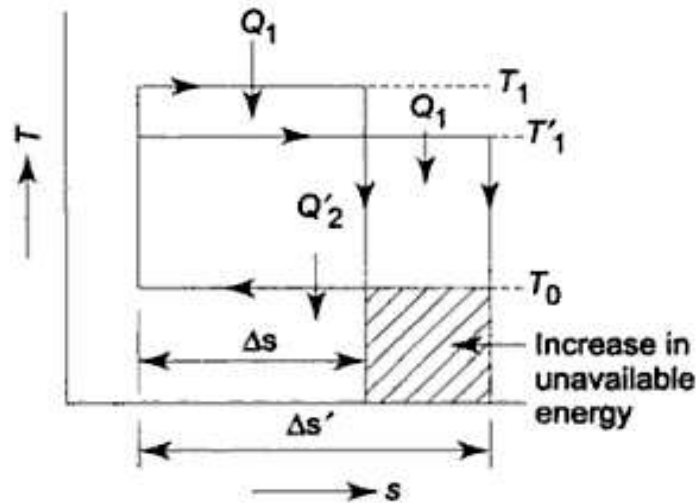


Fig. 5 Increase in unavailable energy due to heat transfer through a finite temperature difference

Now
 since

$$Q_1 = T_1 \Delta s = T'_1 \Delta s'$$

$$T_1 > T'_1, \therefore \Delta s' > \Delta s$$

$$Q_2 = T_0 \Delta s$$

$$Q'_2 = T_0 \Delta s'$$

Since

$$\Delta s' > \Delta s \quad \therefore \quad Q'_2 > Q_2$$

\therefore

$$W' = Q_1 - Q'_2 = T_1 \Delta s' - T_0 \Delta s'$$

and

$$W = Q_1 - Q_2 = T_1 \Delta s - T_0 \Delta s$$

\therefore

$$W' < W, \text{ because } Q'_2 > Q_2$$

Available energy or exergy lost due to irreversible heat transfer through finite temperature difference between the source and the working fluid during the heat addition process is given by

$$\begin{aligned}W - W' &= Q'_2 - Q_2 \\ &= T_0 (\Delta s' - \Delta s)\end{aligned}$$

or, decrease in A.E. = $T_0 (\Delta s' - \Delta s)$

The decrease in available energy or exergy is thus the product of the lowest feasible temperature of heat rejection and the additional entropy change in the system while receiving heat irreversibly, compared to the case of reversible heat transfer from the same source.

The greater is the temperature difference ($T_1 - T'_1$), the greater is the heat rejection Q'_2 and the greater will be the unavailable part of the energy supplied or energy (Fig. 5). Energy is said to be degraded each time it flows through a finite temperature difference.

Lecture-8

The lecture contains

- **Dead state**
- **Availability**
- **Availability in a Steady flow Process**
- **Availability in a Non flow Process**

Dead state:-

If the state of a system departs from that of the surroundings, an opportunity exists for producing work (Fig. 1). However, as the system changes its state towards that of the surroundings, this opportunity diminishes, and it ceases to exist when the two are in equilibrium with each other. When the system is in equilibrium with the surroundings, it must be in pressure and temperature equilibrium with the surroundings, i.e., at p_0 and T_0 . It must also be in chemical equilibrium with the surroundings, i.e., there should not be any chemical reaction or mass transfer. The system must have zero velocity and minimum potential energy. This state of the system is known as the *dead state*, which is designated by affixing subscript '0' to the properties. Any change in the state of the system from the dead state is a measure of the available work that can be extracted from it. Farther the initial point of the system from the dead state in terms of p, t either above or below it, higher will be the available energy or exergy of the system (Fig. 1). All spontaneous processes terminate at the dead state.

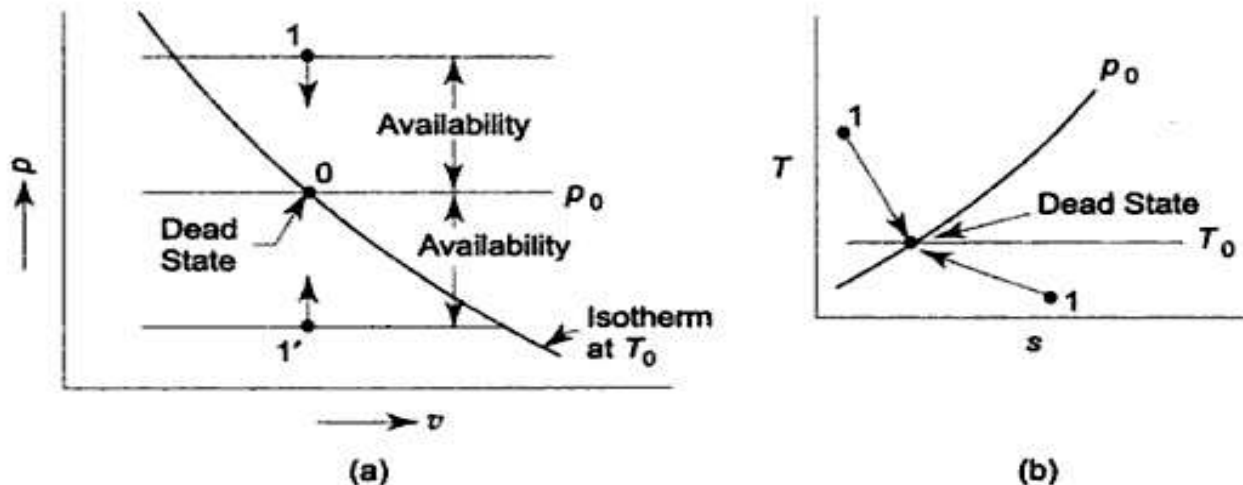


Fig. 1 Available work of a system decreases as its state approaches P_0, T_0

Availability:-

The availability (A) of a given system is defined as *the maximum useful work (total work minus pdV work) that is obtainable in a process in which the system comes to equilibrium with its surroundings*. Availability is thus a composite property depending on the state of both the system and surroundings.

Availability in a Steady flow Process:-

The reversible (maximum) work associated with a steady flow process for a single flow is given by

$$W_{\text{rev}} = \left(H_1 - T_0 S_1 + \frac{m V_1^2}{2} + m g z_1 \right) - \left(H_2 - T_0 S_2 + \frac{m V_2^2}{2} + m g z_2 \right)$$

With a given state for the mass entering the control volume, the maximum useful work obtainable (i.e., the availability) would be when this mass leaves the control volume in equilibrium with the surroundings (i.e., at the dead state). Since there is no change in volume, no work will be done on the atmosphere. Let us designate the initial state of the mass entering the C.V. with parameters having *no subscript* and the final dead state of the mass leaving the C.V. with parameters having subscript 0. The maximum work or availability, A , would be

$$A = \left(H - T_0 S + \frac{m V^2}{2} + m g z \right) - (H_0 - T_0 S_0 + m g z_0) = \psi - \psi_0$$

where ψ is called the *availability function for a steady flow system* and $V_0 = 0$. This is the availability of a system at any state as it enters a C.V. in a steady flow process. The availability per unit mass would be

$$a = \left(h - T_0 s + \frac{V^2}{2} + g z \right) - (h_0 - T_0 s_0 + g z) = \psi - \psi_0$$

If subscripts 1 and 2 denote the states of a system entering and leaving a C.V., the decrease in availability or maximum work obtainable for the given system-surroundings combination would be

$$\begin{aligned}
 W_{\max} &= a_1 - a_2 = \psi_1 - \psi_2 \\
 &= \left[\left(h_1 - T_0 s_1 + \frac{V_1^2}{2} + g z_1 \right) - (h_0 - T_0 s_0 + g z_0) \right] \\
 &\quad - \left[\left(h_2 - T_0 s_2 + \frac{V_2^2}{2} + g z_2 \right) - (h_0 - T_0 s_0 + g z_0) \right] \\
 &= (h_1 - h_2) - T_0 (s_1 - s_2) + \frac{V_1^2 - V_2^2}{2} + g(z_1 - z_2)
 \end{aligned}$$

If K.E. and P.E. changes are neglected,

$$\begin{aligned}
 W_{\max} &= (h_1 - T_0 s_1) - (h_2 - T_0 s_2) \\
 &= b_1 - b_2
 \end{aligned}$$

where b is the specific Keenan function.

If more than one flow into and out of the C.V. is involved.

$$W_{\max} = \sum_i m_i \psi_i - \sum_e m_e \psi_e$$

Availability in a Non flow Process:-

Let us consider a closed system and denote its initial state by parameters without any subscript and the final dead state with subscript '0'. The availability of the system A , i.e., the maximum useful work obtainable as the system reaches the dead state, is given by

$$\begin{aligned} A &= (W_u)_{\max} = E - E_0 + p_0 (V - V_0) - T_0(S - S_0) \\ &= \left(U + \frac{mV^2}{2} + mgz \right) - (U_0 + mgz_0) + p_0(V - V_0) - T_0(S - S_0) \end{aligned}$$

If K.E. and P.E. changes are neglected and for unit mass, the availability becomes

$$\begin{aligned} a &= u - u_0 + p_0(v - v_0) - T_0 (s - s_0) \\ &= (u + p_0v - T_0s) - (u_0 - p_0v_0 - T_0s_0) \\ &= \phi - \phi_0 \end{aligned}$$

where ϕ is the availability function of the closed system.

If the system undergoes a change of state from 1 to 2, the decrease in availability will be

$$\begin{aligned} a &= (\phi_1 - \phi_0) - (\phi_2 - \phi_0) \\ &= \phi_1 - \phi_2 \\ &= (u_1 - u_2) + p_0 (v_1 - v_2) - T_0(s_1 - s_2) \end{aligned}$$

This is the maximum useful work obtainable under the given surroundings.

Engineering Thermodynamics (BME-12)
UNIT-III

Lecture-9

The lecture contains

- Irreversibility
- Second law efficiency
- Helmholtz & Gibb's function

Irreversibility:-

The actual work done by a system is always less than the idealized reversible work, and the difference between the two is called the irreversibility of the process.

$$I = W_{\max} - W$$

This is also sometimes referred to as '*degradation*' or '*dissipation*'.

For a non-flow process between the equilibrium states, when the system exchanges heat only with the environment

$$\begin{aligned} I &= [(U_1 - U_2) - T_0(S_1 - S_2)] - [(U_1 - U_2) + Q] \\ &= T_0(S_2 - S_1) - Q \\ &= T_0(\Delta S)_{\text{system}} + T_0(\Delta S)_{\text{surr}} \\ &= T_0[(\Delta S)_{\text{system}} + (\Delta S)_{\text{surr}}] \end{aligned}$$

∴

$$I \geq 0$$

Similarly, for the steady flow process

$$\begin{aligned} I &= W_{\max} - W \\ &= \left[\left(B_1 + \frac{m V_1^2}{2} + m g Z_1 \right) - \left(B_2 + \frac{m V_2^2}{2} + m g Z_2 \right) \right] \\ &\quad - \left[\left(H_1 + \frac{m V_1^2}{2} + m g Z_1 \right) - \left(H_2 + \frac{m V_2^2}{2} + m g Z_2 \right) + Q \right] \\ &= T_0(S_2 - S_1) - Q \\ &= T_0(\Delta S)_{\text{system}} + T_0(\Delta S)_{\text{surr}} \\ &= T_0(\Delta S_{\text{system}} + \Delta S_{\text{surr}}) = T_0 \Delta S_{\text{univ}} \end{aligned}$$

The same expression for irreversibility applies to both flow and non-flow processes. The quantity $T_0(\Delta S_{\text{system}} + \Delta S_{\text{surr}})$ represents an increase in unavailable energy (or anergy).

Second law efficiency:-

The second law efficiency, η_{II} , of a process is defined as the ratio of the minimum available energy (or exergy) which must be consumed to do a task divided by the actual amount of available energy (or exergy) consumed in performing the task.

$$\eta_{II} = \frac{\text{minimum exergy intake to perform the given task}}{\text{actual exergy intake to perform the same task}}$$

or

$$\eta_{II} = \frac{A_{\min}}{A}$$

where A is the availability or exergy.

Helmholtz & Gibb's function:-

For a simple compressible system of fixed chemical composition thermodynamic properties can be given from combination of first law and second law of thermodynamics as,

- $du = T \cdot ds - pdv$
- $dh = T \cdot ds + vdp$

Gibbs function (g) and Helmholtz function (f) are properties defined as below.

Gibbs function,

$g = h - T \cdot s$, on unit mass basis i.e. specific Gibb's function

also, $G = H - T \cdot S$

Helmholtz function, $f = u - T \cdot s$, on unit mass basis i.e. specific Helmholtz function

also, $F = U - T \cdot S$, In differential form Gibbs function can be given as below for an infinitesimal reversible process $dg = dh - T \cdot ds - s \cdot dT$

$$dg = vdp - sdT \text{ for a reversible isothermal process, } \int_1^2 dG = \int_1^2 vdp$$

For a “reversible isobaric and isothermal process”, $dp = 0$, $dT = 0$ $dG = 0$ i.e. $G = \text{constant}$

- ‘Gibbs function’ is also termed as ‘Gibbs free energy’. For a reversible isobaric and isothermal process Gibbs free energy remains constant or Gibbs function of the process remains constant. Such reversible thermodynamic processes may occur in the processes involving change of phase, such as sublimation, fusion, vaporization etc., in which Gibbs free energy remains constant.

‘Helmholtz function’ is also called ‘Helmholtz free energy’. For any infinitesimal reversible process Helmholtz function can be given in differential form as,

$$df = du - T \cdot ds - sdT$$

$$\text{or, } df = -pdv - sdT$$

$$\text{or, } dF = -pdV - SdT$$

Example 1 In a steam boiler, hot gases from a fire transfer heat to water which vaporizes at constant temperature. In a certain case, the gases are cooled from 1100°C to 550°C while the water evaporates at 220°C . The specific heat of gases is 1.005kJ/kgK , and the latent heat of water at 220°C , is 1858.5 kJ/kg . All the heat transferred from the gases goes to the water. How much does the total entropy of the combined system of gas and water increase as a result of the irreversible heat transfer? Obtain the result on the basis of 1 kg of water evaporated.

If the temperature of the surroundings is 30°C , find the increase in unavailable energy due to irreversible heat transfer.

Solution Gas (m_g) is cooled from state 1 to state 2 (Fig. Ex. 1). For reversible heat transfer, the working fluid (w.f.) in the heat engine having the same c_p would have been heated along 2-1, so that at any instant, the temperature difference between gas and the working fluid is zero. Then 1-b would have been the expansion of the working fluid down to the lowest possible temperature T_0 , and the amount of heat rejection would have been given by the area $abcd$.

$$\begin{aligned}\Delta S_{\text{gas}} &= \int_{T_{g1}}^{T_{g2}} \frac{dQ}{T} = \int_{T_{g1}}^{T_{g2}} \dot{m}_g c_{p_g} \frac{dT}{T} \\ &= \dot{m}_g c_{p_g} \ln \frac{T_{g2}}{T_{g1}} = 3.38 \ln \frac{823}{1373} \\ &= -3.38 \times 0.51 \\ &= -1.725 \text{ kJ/K}\end{aligned}$$

$$\begin{aligned}\therefore \Delta S_{\text{total}} &= (\Delta S)_{\text{water}} + (\Delta S)_{\text{gas}} \\ &= 3.77 - 1.725 = 2.045 \text{ kJ/K}\end{aligned}$$

*Ans.***Increase in unavailale energy**

$$\begin{aligned}&= T_0 (\Delta S)_{\text{total}} = 303 \times 2.045 \\ &= 620 \text{ kJ}\end{aligned}$$

Ans.

Example 2 Calculate the decrease in available energy when 25 kg of water at 95°C mix with 35 kg of water at 35°C, the pressure being taken as constant and the temperature of the surroundings being 15°C (c_p of water = 4.2 kJ/kg K).

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

$$\text{A.E.} = mc_p \int_{T_0}^T \left(1 - \frac{T_0}{T}\right) dT$$

∴

(A.E.)₂₅ = Available energy of 25 kg of water at 95°C

$$= 25 \times 4.2 \int_{273+15}^{273+95} \left(1 - \frac{288}{T}\right) dT$$

$$= 105 \left[(368 - 288) - 288 \ln \frac{368}{288} \right]$$

$$= 987.49 \text{ kJ}$$

(A.E.)₃₅ = Available energy of 35 kg of water at 35°C

$$= 147 \left[(308 - 288) - 288 \ln \frac{308}{288} \right]$$

$$= 97.59 \text{ kJ}$$

Total available energy

$$(\text{A.E.})_{\text{total}} = (\text{A.E.})_{25} + (\text{A.E.})_{35}$$

$$= 987.49 + 97.59$$

$$= 1085.08 \text{ kJ}$$

After mixing, if t is the final temperature

$$25 \times 4.2 (95 - t) = 35 \times 4.2(t - 35)$$

$$\therefore t = \frac{25 \times 95 \times 35 \times 35}{25 + 35}$$

$$= 60^\circ\text{C}$$

Total mass after mixing = $25 + 35 = 60$ kg

(A.E.)₆₀ = Available energy of 60 kg of water at 60°C

$$= 4.2 \times 60 \left[(333 - 288) - 288 \ln \frac{333}{288} \right]$$

$$= 803.27 \text{ kJ}$$

\therefore Decrease in available energy due to mixing

$$= \text{Total available energy before mixing}$$

$$- \text{Total available energy after mixing}$$

$$= 1085.08 - 803.27$$

$$= 281.81 \text{ kJ}$$

Ans.