Course Title:

Fundamental of Thermodynamics and Heat Transfer

Lecture 10 (Week 10):

Second Law of Thermodynamics and Entropy

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Learning Objective of Lecture:

To impart a great deal of knowledge to undergraduate students on the topics:

- ✓ Second Law of Thermodynamics
- ✓ Drawbacks of First Law and Necessity of Second Law of Thermodynamics
- ✓ Second law of Thermodynamics for an isolated system
- ✓ Reversible and irreversible processes as per Second Law of Thermodynamics
- ✓ Approximation of Irreversible Process as Reversible Process
- ✓ Entropy and Entropy relations for ideal gases and incompressible substances

5.0. Second Law of Thermodynamics

5.1. Drawbacks of First Law and Necessity of Second Law of Thermodynamics

First law of thermodynamics deals with conservation and conversion of energy. It stipulates that when a thermodynamic process is carried out, energy is neither created nor destroyed, but it transforms from one form into another so that the energy balance is maintained. However, the first law fails to state the conditions under which energy conversions are possible. It explains thermodynamic processes with the quantitative aspect of the energy and gives the only condition that any process can take place in either direction provided that the total energy remains constant. But this is not true, because some processes in nature proceed spontaneously in only one direction and cannot occur in opposite direction even though the reversal of process does not violate the first law i.e., energy conservation principle is satisfied. Hence, such directional feature of the thermodynamic process cannot be explained only with the first law of thermodynamics. This inadequacy of the first law to identify whether a process can take place is remedied by introducing another general principle, the *second law of thermodynamics*. The second law of thermodynamics deals with quality or nature of energy and defines the direction of the thermodynamic process in which the system can proceed.

As per the first law of thermodynamics all forms of energy are equivalent and for a cyclic process either heat is converted completely into work or work is converted into heat. However, any real device, even operating on a cycle, cannot convert heat supplied to it completely into output work. In this regard, the second law of thermodynamics declares that different forms of energy are not equivalent in their ability to produce useful output work and explains why any real engine cannot operate without heat loss, i.e. heat cannot be completely converted into work.

The following three more examples are presented to demonstrate the inability of the first law of thermodynamics to describe any process or system completely.

I. Let us consider an isolated container having two compartments as shown in figure 5.1(a). One of the compartments contains gas and another is evacuated which is the initial state indicated as 1. If the partition is suddenly removed or the gas pressure is sufficient to break the partition wall, gas expands and fills up the entire container which is the final state denoted as 2. If we analyze the process 1 - 2, total mass and internal energy are same for both state 1 and state 2. Hence, the first law of thermodynamics is obviously satisfied. But if we assume that process occurs in reverse direction as shown in figure 5.1(b), again the principles of conservation of mass and energy are satisfied or first law of thermodynamics is still satisfied. But from our experience the process can never proceed in this direction. The inability of the first law of thermodynamic to explain this impossibility indicates the need of another fundamental law [1].

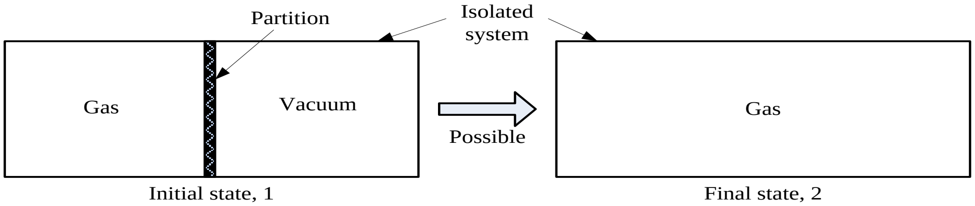


Figure 5.1(a). Possible process direction for expansion of a gas into a vacuum within an isolated system [1]

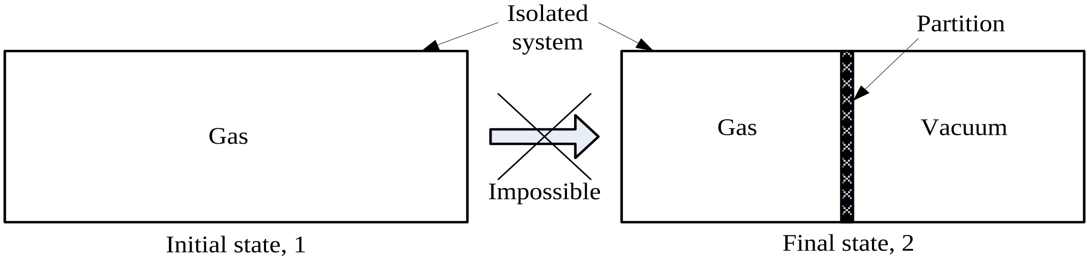


Figure 5.1(b). Impossible process direction for compression of a gas by creating a vacuum within a isolated system [1]

II. Let us consider two bodies A and B at different temperatures T_A and T_B $(T_A > T_B)$ are brought in thermal contact inside an isolated system as shown in figure 5.2(a) which is the initial state indicated by 1. Heat energy will transfer from body A to body B because of the temperature difference. This energy transfer continues till the both the bodies attain a same intermediate equilibrium temperature T which is the final state indicated by 2. If we analyze the process 1 - 2, total mass and internal energy are same for both state 1 and state 2. Thus, the process satisfies the first law of thermodynamics as well as our physical expectations. But if we assume the process occurs in reverse direction, i.e. the two bodies are initially brought together at the same temperature and the final state results when body A is at a high temperature T_A and the block B at a low temperature T_B as shown in figure 5.2(b). Again, the conservation principles of mass and energy are satisfied. This, however, is never seen to happen [1].

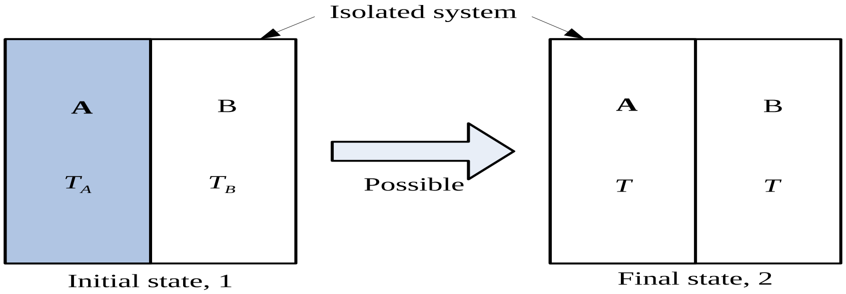


Figure 5.2(a). Possible process direction for heat transfer between two bodies having different temperatures within an isolated system [1]

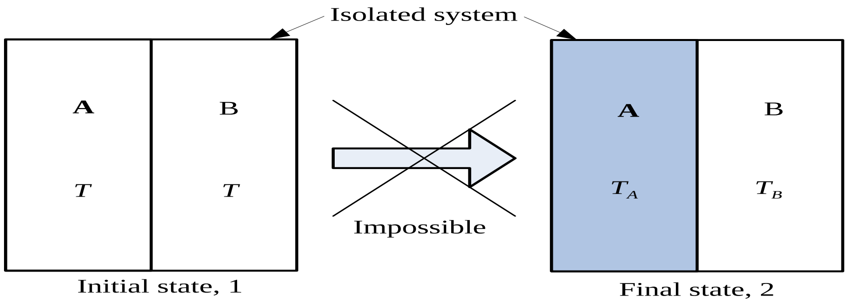


Figure 5.2(b). Impossible process direction for heat transfer between two bodies having same temperature within an isolated system [1]

III. Let us consider a running vehicle stopped by applying brakes. The process changes the kinetic energy of the vehicle into heat and the brakes get heated up. The increase in the temperature and therefore in the internal energy of the brakes is in accordance with the first law of thermodynamics. The stopping of the vehicle by friction, however, is an irreversible process. Cooling of brakes to their initial condition never puts the vehicle back into motion. Heat in the brakes cannot be converted back into mechanical work although that act would not violate the first law of thermodynamics.

These examples present the two main features of the second law of thermodynamics. First, the second law of thermodynamics prescribes the direction of the processes in which the system can proceed, i.e. a basic nature or inherent tendency of a system or process. Second, there exists a system property which is always changing in a specified direction. Hence, second law of thermodynamics defines the direction of the process with reference to a system property called *entropy*.

Let us again consider the examples mentioned above to understand the system property "entropy" clearly. If we analyze the system shown in figure 5.1, the state of the gas is changed by rearranging the positions of the molecules of the gas. Because more positions are available for a given molecule after the expansion in large volume than before it (in small volume), the uncertainty as to the position of a given molecule is greater due to the expansion. Thus, this example indicates that the organized state of a system in initial state 1 tends to proceed to a more random state of a gas molecule in final state 2.

Similarly, if the system shown in figure 5.2 is analyzed, the state of the system is changed by allowing heat transfer between high temperature body A and low temperature body B. According to statistical mechanics, the microscopic disorder of a body depends on the temperature. The heat transfer process between the two bodies increases uncertainty about the molecular disorder in the two bodies compared with the disorder before the process. Thus, this example demonstrates that the organized state of a separate high temperature body and low temperature body in initial state

1 tends to proceed towards a more disorganized state of a single homogeneous temperature in final state 2.

In both examples the reverse process is not possible (see fig 5.1(b) and 5.2(b)). Thus, there is a specific direction to the process. The direction appears to be related to the disorder, randomness, or uncertainty of the microscopic scale of the system. Hence, the second law needs to describe the direction for the processes in terms of a system property that characterizes the system's randomness, disorganization or uncertainty.

Thus, the disorder of the system can be changed in at least two ways namely geometric rearrangement and heat transfer.

As described in third example, we can also compare the basic nature of work and heat energy. Work is produced due to the relative displacement at the system boundary. Hence, during the work transfer process all molecules or particles have uniform orientation, i.e. all particles have same velocity, whereas when heat is supplied to the system, its molecular randomness increases. In this regard, work is called high grade of energy and heat is called low grade of energy.

From the above discussion, we can conclude that:

- System itself tends to undergo a process from less uncertain or less random state to more uncertain or more random state. But the reverse direction is not possible.
- High grade of energy (work) itself get converted into low grade of energy (heat) and the reverse direction is not possible without using any device.

The property of a system which gives a measure of molecular randomness, disorganization, disorder or uncertainty existing in a system is called *entropy*. Larger values of entropy imply the greater disorder or uncertainty and lower values imply more microscopically organized states. It is an extensive property and is denoted by S. The unit of entropy is J/K.

5.2. Second Law of Thermodynamics for an Isolated System

The previous examples of the isolated system as explained earlier indicate that any isolated system can only proceed to a direction in which its randomness, disorder, disorganization or uncertainty, i.e. entropy increases. This feature of an isolated system can be stated as second law of thermodynamics as:

The change in entropy of an isolated system is greater than or equal to zero.

OR

Entropy of an isolated system always increases or may remain constant in an ideal process [2].

This statement is expressed mathematically as

$$(dS)_{isolated} \geq 0 \qquad \text{……… (5.1)}$$

or, $$S_{final} - S_{initial} \geq 0$$

$$\therefore \quad S_{final} \geq S_{initial} \qquad \text{……… (5.2)}$$

Like other thermodynamic properties entropy is defined only at equilibrium states or for quasi-static processes. The property entropy is used to specify a state of the system. In other words, it can be used as independent property combined with another property to specify all other properties of a state according to the state postulate. Equations (5.1) and (5.2) show that entropy of an isolated system at the final state in any real process is always greater than that at the initial state. This is possible only when there is production or generation of entropy during any process within the system as the system is isolated from its surroundings, i.e. it does no interactions with the surroundings. So, the difference between entropies at the final state and the initial state during any process is called *entropy production or entropy generation* and is denoted by δS_{gen}. Now, equation (5.1) can be expressed in equivalent form to eliminate inequality sign as

$$\left(dS - \delta S_{gen}\right)_{isolated} = 0 \qquad \text{……… (5.3)}$$

where,

$$\delta S_{gen} = dS \geq 0 \qquad \text{……… (5.4)}$$

is the entropy generated during a process within the isolated system and it is always positive or zero. It represents the amount of inequality.

Equations (5.1) and (5.3) can also be expressed on a rate basis by considering the time interval *dt* as

$$\left(\frac{dS}{dt}\right)_{isolated} \geq 0 \qquad \text{……… (5.5)}$$

and

$$\left(\frac{dS}{dt}\right)_{isolated} - \dot{S}_{gen} = 0 \qquad \text{……… (5.6)}$$

where,

$$\dot{S}_{gen} = \left(\frac{dS}{dt}\right)_{isolated} \geq 0 \qquad \text{........(5.7)}$$

is the rate of entropy generation or production within the isolated system and it is always positive or zero.

5.2.1. Reversible and Irreversible Processes as per Second Law of Thermodynamics

The concepts of reversible and irreversible processes play a fundamental role in thermodynamics. A goal of many thermodynamic analyses is the reduction of irreversibility (or entropy generation). A reversible and irreversible process can be differentiated with respect to the nature of intermediate states of any process as already discussed in chapter 1. The system property entropy is another yardstick to distinguish the reversible and irreversible process completely. To better understand these concepts, let us take any previous example of the isolated system. According to second law of thermodynamics for an isolated system, the change in entropy of the isolated system during any real process is always greater than or equal to zero, i.e. for any process between initial state and final state,

$$S_{final} \geq S_{initial} \qquad \text{......... (5.8)}$$

where $S_{initial}$ and S_{final} are the entropies at the initial and final states of any process respectively.

If the entropy at initial state is equal to that of final state ($S_{initial} = S_{final}$) during any process, the reverse process is also possible because entropy is same for both forward and reverse directions as there is no generation of entropy in the system. Such a process is termed as reversible. But if the entropy at the final state is greater than that of the initial state ($S_{final} > S_{initial}$) during any process, entropy increases in forward direction due to the entropy generation in the system, and then the reverse direction is not possible. Because any real process of the isolated system cannot proceed to a direction where there is decrease in entropy. Such a process is termed as irreversible. Thus, as per second law of thermodynamics a reversible and irreversible process can be defined as followings:

A process is said to be a *totally reversible process* if the initial conditions of both the system and surroundings can be restored by the reverse action such that the change in entropy is zero for both forward and reverse processes, i.e. entropy generation (S_{gen}) is zero.

A process is said to be a *totally irreversible process,* if the initial conditions of both the system and surroundings cannot be restored, but certain effects are left either on the system or on the surroundings by the reverse action. In this case entropy of the system increases in the forward process and the process in the reverse direction is not possible, i.e. entropy generation (S_{gen}) is finite and positive.

If an isolated system is composed of number of subsystems and a particular subsystem is considered as the system whereas remaining subsystems act as the surroundings, then the concepts of internally reversible or irreversible and externally reversible or irreversible are needed.

Internally and Externally Reversible Processes

A process is said to be an *internally reversible* if the initial condition of only the system is restored, but certain effects are left on the surroundings when the system is taken through reverse direction. However, the irreversibility can occur outside the system on the surroundings. A quasi-static or quasi-equilibrium process is an example of an internally reversible process.

Similarly, a process is said to be an *externally reversible* if the initial condition of only the surroundings is restored, but certain effects are left on the system when the system is taken through the reverse direction. However, the irreversibility can occur within the system. For example, heat transfer process to a system from surroundings with infinitely small temperature difference would be an externally reversible process.

Therefore, for a process to be a *totally reversible process*, it should be internally as well as externally reversible.

Let us again consider the previous examples II and III (see section 5.1) regarding the heat transfer and friction to explain how irreversibility arises in real processes. The example II clearly highlights the fact that the cause of irreversibility in any real process is heat transfer because heat always increases the randomness of the system. As described in the example III, another cause of irreversibility is the friction during work transfer because most of the real processes involving work transfer are irreversible due to the friction.

Mechanical Irreversibility and Thermal Irreversibility

Thus, the major factors causing irreversibility in any process are the friction and the heat transfer. Hence, as per the nature of the causes, irreversibility in any process is classified as mechanical irreversibility and thermal irreversibility. *Mechanical irreversibility* is associated with the friction between the system and the surroundings as well as within the system. *Thermal* *irreversibility* is associated with the heat transfer between the system and the surroundings as well as within the system.

Internal Irreversibility and External Irreversibility

According to the location of the causes irreversibility in any process can also be classified as internal irreversibility and external irreversibility. *Internal irreversibility* is associated with the friction as well as the heat transfer within the system. *External irreversibility* is associated with the friction as well as the heat transfer between the system and the surroundings.

5.2.2. Approximation of Irreversible Process as Reversible Process

Most of the real processes in nature are irreversible and those processes can be modeled as reversible process with certain simplifying assumptions. To explain how real irreversible processes can be approximated as reversible processes few examples are presented here below.

(a) Process involving Friction

Let us consider a piston cylinder device containing a gas as shown in figure 5.3. During a certain process in the system piston can move and gas can undergo either compression or expansion. Such types of processes are usually irreversible because of the friction between the piston and the cylinder wall as shown in figure 5.3(a). But most of the time such processes occurring in a piston cylinder device can be considered as a reversible process assuming the surface between the piston and cylinder wall to be frictionless as shown in figure 5.3(b).

(a) Irreversible process (b) Reversible process

Figure 5.3. Process with friction and without friction [2]

(b) Process involving Nonlinear or Inelastic Spring

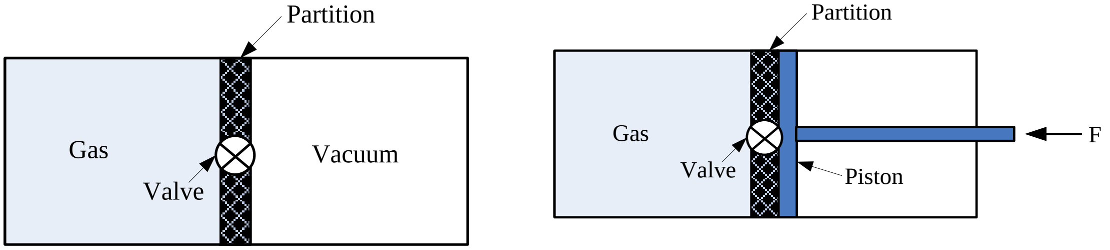
If the piston cylinder device is restrained by a spring, the process will be irreversible if spring characteristic is nonlinear or inelastic as shown in figure 5.4(a) and will be reversible if spring characteristic is linear or elastic as shown in figure 5.4(b). Similarly, if certain part of the system undergoes inelastic deformation during the process, the process will be irreversible because system cannot regain its original position even after the removal of the load. Process in which deformations are within the elastic range can be assumed as a reversible process.

(a) Irreversible process (b) Reversible process

Figure 5.4. Process involving nonlinear or inelastic spring and process involving linear and elastic spring [2]

(c) Free Expansion Process

Let us consider an isolated system (an insulated closed rigid container) having two compartments consisting of a gas and a vacuum separated by a wall connected with a valve as shown in figure 5.5 (a). When the valve is open, then gas expands spontaneously and it cannot be reversed back from any intermediate state. Hence, free expansion or unrestricted expansion is an irreversible process. However, expansion of a gas can be assumed as a reversible process if it is restrained by some external forces as shown in figure 5.5 (b). During any process in this system, if the valve is open, gas molecules exert force on the piston surface but gas cannot undergo spontaneous expansion because of restraining force F on the piston. When the restraining force F is reduced, then the gas undergoes an expansion and when F is increased, then the gas undergoes a compression. Hence, such a controlled and slow expansion against a restraining force so called a restricted expansion can be assumed as a reversible process.



(a) Irreversible process (b) Reversible process

Figure 5.5. Free expansion and restricted expansion of a gas [2]

(d) Heat Transfer with Finite Temperature Difference

If any system having a temperature T_B is brought in contact with a source having a higher temperature T_A $(T_A > T_B)$, then heat Q flows from the source to the system as shown in figure 5.6(a). During the heat transfer there will be temperature gradient within the system and it passes through a series of non-equilibrium states and the process becomes irreversible. The process can be made approximately reversible (or less irreversible) by reducing the temperature gradient within the system. For this first the system with the lower temperature T_B is brought in contact with the source having a slightly higher temperature $T_A = T_B + dT$, as shown in figure 5.6(b). Due to the temperature difference heat is transferred from the source to the system and after some time the temperature of the system reaches an intermediate temperature between T_B and $T_B + dT$. Again, the system is brought in contact with a source having a temperature $T_A = T_B + 2dT$, such that a very small temperature difference (e.g. dT) exists during every interval. Thus, heat transfer with infinitesimally small temperature difference can be approximated as a reversible heat transfer process.

(a) Irreversible process

(b) Reversible process

Figure 5.6. Heat transfer with finite temperature difference and with infinitely small temperature difference [2]

In each of the above cases the main features of irreversible processes are that there are dissipative effects which are not directly useful and that the processes can proceed through non-equilibrium states. These both tend to increase the molecular disorder or entropy of the systems. Both contributions make processes irreversible. Hence, the causes of irreversibility may be

- Friction
- Inelastic deformation
- Free expansion
- Heat transfer across a finite temperature difference
- Mixing

However, the reversible processes progress through equilibrium states and there are no dissipative effects.

5.3. Entropy - a Property of a System and its Relations

Entropy is a thermodynamic property which is specified for every equilibrium state of a system. It represents the disorder, randomness or uncertainty of the microscopic scale within the system.

As per the state postulate two independent thermodynamic properties are necessary to specify a state of the system. Therefore, entropy is an additional property that can be used with any other independent property to completely specify the state of a system. Applying the state postulate, the internal energy of a state of a system can be determined if any two independent properties e.g. entropy and volume are known, i.e.

$$U = U(S, V) \qquad \text{……….} (5.9)$$

The change in internal energy during any process is an exact differential and can be written as the function of two partial derivatives as

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \qquad \text{……….} (5.10)$$

The two partial derivatives in the equation (5.10) are intensive properties since the ratio of two extensive properties is an intensive property. The first partial derivative is defined as the temperature in classical thermodynamics [1], i.e.

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad \dots\dots\dots\dots\dots..(5.11)$$

Similarly, the second partial derivative is defined as the negative of the pressure[1], i.e.

$$P = -\left(\frac{\partial U}{\partial V}\right)_S \qquad \dots.\dots\dots..(5.12)$$

Putting these equations (5.11) and (5.12) in equation (5.10) to yield

$$dU = TdS - PdV \qquad \text{……….} (5.13)$$

This is an extremely important relation in thermodynamics and is commonly known as *Gibb's equation*. It is applied generally to a control mass. Rearranging Gibbs equation, the expression for the change in entropy can be derived as

$$dS = \frac{dU}{T} + \frac{P}{T} dV \qquad \text{……….} (5.14)$$

Entropy equation can also be expressed in terms of enthalpy. For this let us start with the definition of enthalpy as

$$H = U + PV \qquad \text{……….} (5.15)$$

The change in enthalpy during any process is then given as

$$dH = dU + PdV + VdP \qquad \text{………. (5.16)}$$

Substituting equation (5.13) in equation (5.16), we get

$$dH = TdS + VdP \qquad \text{………. (5.17)}$$

Rearranging the equation (5.16), the expression for the change in entropy can be derived as

$$dS = \frac{dH}{T} - \frac{V}{T}dP \qquad \text{………. (5.18)}$$

Equations (5.13) and (5.17) can also be expressed on an intensive basis or a specific form by dividing both sides by mass as

$$du = Tds - Pdv \qquad \text{………..(5.19)}$$

$$dh = Tds + Vdp \qquad \text{………..(5.20)}$$

Similarly, the changes in specific entropy are obtained from equations (5.14) and (5.18) as

$$ds = \frac{du}{T} + \frac{P}{T}dv \qquad \text{... ... ... (5.21)}$$

$$ds = \frac{dh}{T} - \frac{v}{T}dP \qquad \text{... ... ... (5.22)}$$

5.3.1. Entropy Relations for an Ideal Gas

For an ideal gas, the state properties P, V and T are related by the equation of state as

$$PV = mRT$$

$$\therefore \qquad \frac{P}{T} = \frac{mR}{V} \qquad \text{………. (5.23)}$$

As we know the change in internal energy of an ideal gas is given by

$$dU = mc_V dT \qquad \text{………. (5.24)}$$

Substituting above equations (5.23) and (5.24) in equation (5.14), we get

$$dS = mc_V \frac{dT}{T} + mR\frac{dV}{V} \qquad \text{……… (5.25)}$$

To evaluate the equation (5.25) accurately, the functional form of the specific heat variation with temperature is required. However, the specific heats are often approximated by a single average value. Hence, for an ideal assuming specific heat at constant volume c_V and gas constant R as constants, the expression for the change in entropy for an ideal gas during any process between state 1 and state 2 can be derived in terms of temperature and volume ratios by integrating the equation (5.25), as

$$S_2 - S_1 = mc_V ln\left(\frac{T_2}{T_1}\right) + mRln\left(\frac{V_2}{V_1}\right) \qquad \text{……… (5.26)}$$

Similarly, equation of state for an ideal gas can also be rearranged as

$$\frac{V}{T} = \frac{mR}{P} \qquad \text{……… (5.27)}$$

As we know the change in enthalpy of an ideal gas is given by

$$dH = mc_P dT \qquad \text{……… (5.28)}$$

Substituting above equations (5.27) and (5.28) in equation (5.18), we get

$$dS = mc_P \frac{dT}{T} - mR\frac{dP}{P} \qquad \text{……… (5.29)}$$

With the same reason explained above assuming specific heat at constant pressure c_P and gas constant R as constants, the expression for the change in entropy for an ideal gas during any process between state 1 and state 2 can be derived in terms of temperature and pressure ratios by integrating the equation (5.29), as

$$S_2 - S_1 = mc_P ln\left(\frac{T_2}{T_1}\right) - mRln\left(\frac{P_2}{P_1}\right) \qquad \text{……… (5.30)}$$

Similarly, the expressions for the change in specific entropy for an ideal gas can be obtained by dividing both sides of the equations (5.26) and (5.30) by mass as

$$s_2 - s_1 = c_V ln\left(\frac{T_2}{T_1}\right) + Rln\left(\frac{v_2}{v_1}\right) \qquad \dots\dots\dots(5.31)$$

$$s_2 - s_1 = c_P ln\left(\frac{T_2}{T_1}\right) - Rln\left(\frac{P_2}{P_1}\right) \qquad \dots\dots\dots(5.32)$$

5.3.2. Entropy Relation for an Incompressible Substance

Solid and liquid substances are assumed as incompressible substances because their volumes do not change appreciably with the pressure or temperature. Hence, the equation of state for an incompressible substance is $V = constant$. Then the change in internal energy of an incompressible substance is given as

$$dU = mc_V dT = mcdT \qquad \dots\dots\dots.(5.33)$$

where c is the specific heat of the incompressible substance.
Putting this equation (5.33) in equation (5.14) and with $dV = 0$ the change in entropy for an incompressible substance can be written as

$$dS = \frac{dU}{T} = \frac{m\ c\ dT}{T} \qquad \dots\dots\dots (5.34)$$

Now, the change in entropy for an incompressible substance during any process between state 1 and state 2 can be obtained by integrating the equation (5.34) assuming the specific heat is approximated by a constant as

$$S_2 - S_1 = m\ c\ ln\left(\frac{T_2}{T_1}\right) \qquad \dots\dots\dots (5.35)$$

Then, the expression for the change in specific entropy for an incompressible substance can be obtained by dividing both sides of the equations (5.35) by mass as

$$s_2 - s_1 = c\ ln\left(\frac{T_2}{T_1}\right) \qquad \dots\dots\dots\ (5.36)$$

Lecture Highlights

- ➢ *Drawbacks of first law of thermodynamics which lead to necessity of second law of thermodynamics are*:
  - It deals with the quantitative aspect of the energy and gives only the condition that any process is possible provided that the total energy remains constant. But some processes in

  nature cannot occur although the total energy is conserved, because most of the processes in nature proceed in only one direction. Hence, it does not focus any restriction towards the direction of energy flow.
  - It states that for a closed system undergoing a cyclic process the net heat supplied to the system is equal to the net work output of the system. However, any device even operating on a cycle cannot convert heat supplied to it completely into work. Hence, it also does not focus any restriction towards what portion of heat supplied is converted into mechanical work.
- ➢ *Second law of thermodynamics* deals with quality or nature of energy and defines the direction of the process in which the system can proceed. It defines the direction of the process with reference to the system property called entropy. Hence, it focus towards the direction of flow of energy and is also named as directional law.
- ➢ *According to the second law of thermodynamics*, only a portion of heat input to an engine can be converted into work and remaining portion is rejected to a sink at lower temperature. Thus, energy gets degraded during conversion of heat into work and therefore it is also known as law of degradation of energy.
- ➢ *Entropy:* It is a measure of molecular disorder, randomness, disorganization or uncertainty existing in a system. It is an extensive property.
- ➢ *Reversible process:* It is the process in which the initial conditions of both system and surroundings can be restored by the reverse action such that net change in entropy is zero for both forward and reverse processes.
- ➢ *Irreversible process:* It is the process in which the initial conditions of both the system and surroundings cannot be restored by the reverse action. During this process, entropy of the system increases in forward direction and the reverse direction is not possible.
- ➢ *Internally reversible process:* In this process the initial condition of only the system is restored when the system is taken through reverse direction.
- ➢ *Externally reversible process:* In this process the initial condition of only the surroundings is restored when the system is taken through the reverse direction.
- ➢ *Completely reversible process:* A process is said to be a completely reversible, if it is internally as well as externally reversible.
- ➢ *Mechanical irreversibility:* It is due to friction within the system as well as between the system and surroundings.
- ➢ *Thermal irreversibility:* It is due to heat transfer within the system as well as between the system and surroundings.
- ➢ *Internal irreversibility:* It is due to friction as well as heat transfer within the system.
- ➢ *External irreversibility:* It is due to friction as well as heat transfer between the system and surroundings.
- ➢ *The major factors causing irreversibility in any process are*:
  - Process involving friction.
  - Process involving non-linear or inelastic spring.

  - Free expansion process.
  - Heat transfer with finite temperature difference
  - Mixing of fluids

- *Gibb's equation* is given by *dU = TdS – PdV.*
- *Change in entropy relations for any substance are given by*

  $$dS = \frac{dU}{T} + \frac{P}{T}dV \quad \text{and} \quad dS = \frac{dH}{T} - \frac{V}{T}dP$$

- *Entropy relations for an ideal gas:*

  $$S_2 - S_1 = mc_v \ln(T_2/T_1) + mR\ln(V_2/V_1)$$

  $$S_2 - S_1 = mc_P \ln(T_2/T_1) - mR\ln(P_2/P_1)$$

- *Entropy relation for an incompressible substance is*

  $S_2 - S_1 = mc\ln(T_2/T_1)$ where c is specific heat of incompressible substance.

- *Second law of thermodynamics for an isolated system*: "Entropy of an isolated system always increases or may remain constant for an ideal process". Mathematically, $(dS)_{isolated} \geq 0$.
- Entropy of an isolated system at final state is always greater than that of initial state during any process.
- The difference between the entropy at the final state and initial state during any process is called *entropy generation* or *entropy production (* S_{gen}). It can be expressed as:

  $(dS - \delta S_{gen})_{isolated} = 0$ where $\delta S_{gen} \geq 0$.

  In terms of rate basis,

  $$\left(\frac{dS}{dt}\right)_{isolated} \geq 0 \quad \text{or,} \quad \left(\frac{dS}{dt}\right)_{isolated} - \dot{S}_{gen} = 0 \quad \text{where } \dot{S}_{gen} \geq 0$$

- For any process between state 1 and state 2, it reveals $S_2 \geq S_1$.

  If $S_1 = S_2$, the process is *reversible* and

  If $S_2 > S_1$, the process is *irreversible*.

References

[1] *Fundamentals of Engineering Thermodynamics*: Howell J. R. and Buckius R. O., McGraw-Hill, New York, 1992.

[2] *Fundamentals of Thermodynamics & Heat Transfer*: Luintel M.C., Heritage Publishers & Distributors Pvt. Ltd., Kathmandu, Nepal, 2016.