

Syllabus

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Unit – I

System and surroundings: -

A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings. The surroundings include everything other than the system. System and the surroundings together constitute the universe .

The universe = the system + the surroundings However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighborhood of the system constitutes its surroundings. The wall that separates the system from the surroundings is called boundary. This is designed to allow us to control and keep track of all movements of matter and energy in or out of the system. The wall that separates the system from the surroundings is called boundary. This is designed to allow us to control and keep track of all movements of matter and energy in or out of the system.

Types of the System :-

systems are classified according to the movements of matter and energy in or out of the system.

1. **Open System:-** In an open system, there is exchange of energy and matter between system and surroundings. The presence of reactants in an open beaker is an example of an open system.
2. **Closed System:-** In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings. The presence of reactants in a closed vessel made of conducting material e.g., copper or steel is an example of a closed system.
3. **Isolated System:-** In an isolated system, there is no exchange of energy or matter between the system and the surroundings. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

The State of the system and state variables:-

The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. We can describe the state of a gas by quoting its pressure (p), volume (V), temperature (T), amount (n) etc. Variables like P, V, T are called state variables or state functions because their values depend only on the state of the system and not on how it is reached.

The Zeroth Law

It states that if two bodies are in thermal equilibrium with some third body, then they are also in equilibrium with each other. This establishes temperature as a fundamental and measurable property of matter.

First law of thermodynamic:-

The first law of thermodynamics is a version of the law of conservation of energy, adapted for thermodynamic systems. The law of conservation of energy states that the total energy of an isolated system is constant; energy can be transformed from one form to another, but cannot be created or destroyed. The first law is often formulated by stating that the change in the internal energy of a closed system is equal to the amount of heat supplied to the system, minus the amount of work done by the system on its surroundings.

If the change in the internal energy of a system is equal to net energy added as heat to the system minus the net work done by the system, both being measured in mechanical units. Taking ΔU as a change in internal energy, one writes

$$\Delta U = Q - W$$

where Q denotes the net quantity of heat supplied to the system by its surroundings and W denotes the net work done by the system.

Reversible and irreversible process: The process in which the system and surroundings can be restored to the initial state from the final state without producing any changes in the thermodynamics properties of the universe is called a reversible process.

For the system to undergo reversible change, it should occur infinitely slowly due to infinitesimal gradient. During reversible process all the changes in state that occur in the system are in thermodynamic equilibrium with each other.

Thus there are two important conditions for the reversible process to occur. Firstly, the process should occur in infinitesimally small time and secondly all of the initial and final state of the system should be in equilibrium with each other.

The irreversible process is also called the natural process because all the processes occurring in nature are irreversible processes. The natural process occurs due to the finite gradient between the two states of the system. For instance, heat flow between two bodies occurs due to the temperature gradient between the two bodies; this is in fact the natural flow of heat. Similarly, water flows from high level to low level, current moves from high potential to low potential, etc.

Heat Engine:

A heat engine is a system that converts heat or thermal energy and chemical energy to mechanical energy, which can then be used to do mechanical work. It does this by bringing a working substance from a higher state temperature to a lower state temperature. A heat "source" generates thermal energy that brings the working substance to the high temperature state. The working substance generates work in the "working body" of the engine while transferring heat to the colder "sink" until it reaches a low temperature state. During this process some of the thermal energy is converted into work by exploiting the properties of the working substance. The working substance can be any system with a non-zero heat capacity, but it usually is a gas or liquid. During this process, a lot of heat is lost to the surroundings, i.e. it cannot be used.

The Carnot Cycle

Heat engine operates on a cycle. The efficiency of heat engine depends on how the individual processes are executed. The most efficient cycles are reversible cycles, that is, the processes that make up the cycle are all reversible processes.

Reversible cycles cannot be achieved in practice. However, they provide the upper limits on the performance of real cycles.

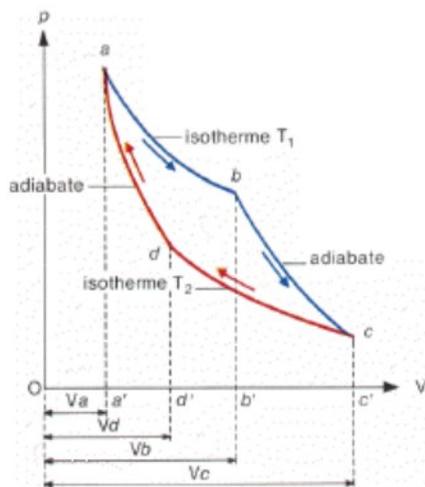
Carnot cycle is one of the best-known reversible cycles. The Carnot cycle is composed of four reversible processes. Consider an adiabatic piston-cylinder device that contains gas. The four reversible processes that make up the Carnot cycle are as follows:

Reversible Isothermal Expansion (process 1-2):
Heat transfer between the heat source and the cylinder occurs with an infinitesimal temperature difference. Hence, it is a reversible heat transfer process. Gas in the cylinder expands slowly, does work to its surroundings, and remains at a constant temperature T_H . The total amount of heat transferred to the gas during this process is Q_H .

Reversible adiabatic expansion (process 2-3):
The heat source is removed, and the gas expands in an adiabatic manner. Gas in the cylinder continues to expand slowly, do work to its surroundings till the temperature of the gas drops from T_H to T_L . Assuming the piston moves frictionless and the process to be quasi-equilibrium, the process is reversible as well as adiabatic.

Reversible isothermal compression (process 3-4):
The cylinder is brought into contact with a heat sink at temperature T_L . The piston is pushed by an external force and which does work on the gas. During the compression, the gas temperature maintains at T_L and the process is a reversible heat transfer process. The total amount of heat rejected to the heat sink from the gas during this process is Q_L .

Reversible adiabatic compression (process 4-1):
The heat sink is removed and the gas is compressed in an adiabatic manner. Gas in the cylinder continues to be compressed slowly, accepting work from its surroundings till the temperature of the gas rises from T_L to T_H . The gas returns to its initial state, which completes the cycle.



Carnot's Theorem

During one part of the cycle performed in an engine, some heat is absorbed from a hot reservoir. During another part, a smaller amount of heat is rejected to a cooler reservoir. The engine is therefore said to operate between these two reservoirs. It is a fact of experience that some heat is always rejected to the cooler reservoir. Because of this, the efficiency of an actual engine is never 100%. The first cycle we will look at is the Carnot cycle. The processes that make up this cycle are either isothermal or adiabatic.

For an ideal gas Carnot cycle, the four steps are shown below:
Isothermal expansion from V_a, P_a to V_b, P_b at T_{hot} absorbing heat Q .

Reversible adiabatic expansion from V_b, P_b to V_c, P_c as the temperature falls from T_{hot} to T_{cold}
 Isothermal contraction from V_c, P_c to V_d, P_d at T_{cold} exhausting heat Q_c .
 Reversible adiabatic contraction from V_d, P_d to V_a, P_a as the temperature rises from T_{cold} to T_{hot}

The system has returned to its initial state and an amount of work, W , has been done to the system. By the conservation of energy,

$$W = Q_h - Q_c \quad \text{Equation (1).}$$

The PV diagram for this cycle is shown in Figure (1) below.

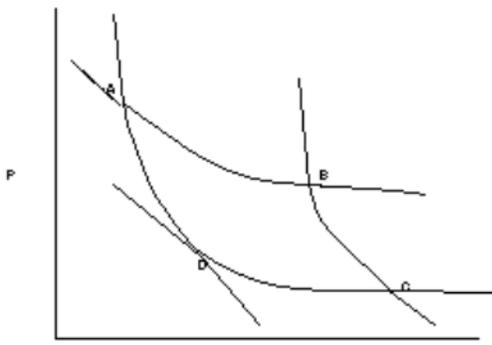


Figure (1): PV diagram showing the ideal gas Carnot cycle.

The thermal efficiency, η , of a cycle operating as a heat engine is defined as

$$\eta = \frac{W}{|Q_h|} \quad \text{Equation (2).}$$

The absolute value sign was used to eliminate any confusion about which way the heat is flowing and whether Q is positive or negative. We can use conservation of energy in the form of Equation (1) to find the efficiency of the cycle in terms of the Q_c and Q_h .

$$\eta = 1 - \frac{|Q_c|}{|Q_h|} \quad \text{Equation (3).}$$

Equations (2) and (3) apply to any cycle. The Carnot cycle is useful in studying real engines and refrigerators largely because one can derive the efficiency of the ideal gas Carnot cycle in terms of the temperatures of the heat reservoirs.

Second law of Thermodynamics:

According to the second law of thermodynamics, it is impossible to construct the perpetual machine of the second kind. There are the following two statements inherent in it.

The Kelvin–Planck statement (or the heat engine statement) of the second law of thermodynamics states that it is impossible to devise a cyclically operating device, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work. This implies that it is impossible to build a heat engine that has 100% thermal efficiency.

The Clausius statement

Energy will not flow spontaneously from a low temperature object to a higher temperature object. This precludes a perfect refrigerator. The statements about refrigerators apply to air conditioners and heat pumps, which embody the same principles. This is the "second form" or Clausius statement of the second law.

Otto Engine

The Internal combustion engine (Otto Cycle)

The Otto cycle is a set of processes used by spark ignition internal combustion engines (2-stroke or 4-stroke cycles). These engines a) ingest a mixture of fuel and air, b) compress it, c) cause it to react, thus effectively adding heat through converting chemical energy into thermal energy, d) expand the combustion products, and then e) eject the combustion products and replace them with a new charge of fuel and air. The different processes are shown in Figure 1

1. Intake stroke, gasoline vapor and air drawn into engine ($5 \rightarrow 1$).
2. Compression stroke, P , T increase ($1 \rightarrow 2$).
3. Combustion (spark), short time, essentially constant volume ($2 \rightarrow 3$). Model: heat absorbed from a series of reservoirs at temperatures T_2 to T_3 .
4. Power stroke: expansion ($3 \rightarrow 4$).
5. Valve exhaust: valve opens, gas escapes.
6. ($4 \rightarrow 1$) Model: rejection of heat to series of reservoirs at temperatures T_4 to T_1 .
7. Exhaust stroke, piston pushes remaining combustion products out of chamber ($1 \rightarrow 5$).

We model the processes as all acting on a fixed mass of air contained in a piston-cylinder arrangement, as shown in Figure 2

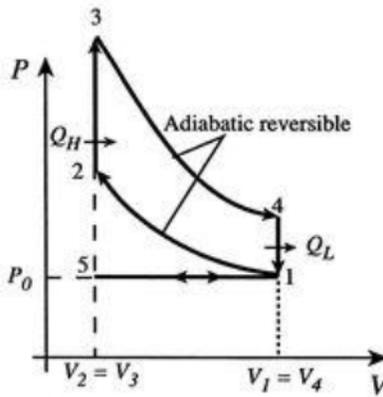


Figure 1 The ideal Otto cycle

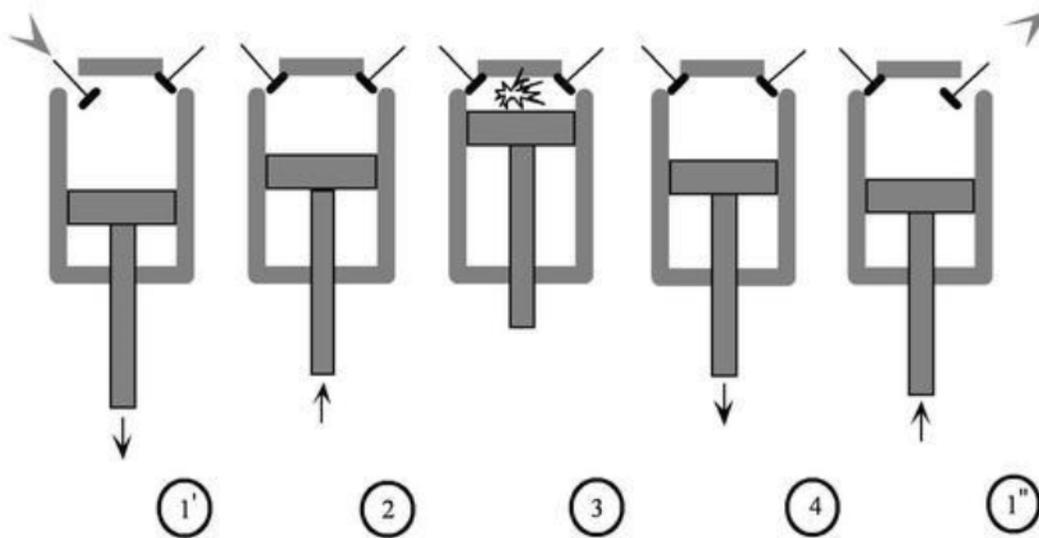


Figure 2: Piston and valves in a four-stroke internal combustion engine

Efficiency of an ideal Otto cycle

The starting point is the general expression for the thermal efficiency of a cycle:

$$\eta = \frac{\text{work}}{\text{heat input}} = \frac{Q_H + Q_L}{Q_H} = 1 + \frac{Q_L}{Q_H}$$

The convention, as previously, is that heat exchange is positive if heat is flowing into the system

or engine, so Q_L is negative. The heat absorbed occurs during combustion when the spark occurs, roughly at constant volume. The heat absorbed can be related to the temperature change from state 2 to state 3 as:

$$Q_H = Q_{23} = \Delta U_{23} \quad (W_{23} = 0)$$

$$= \int_{T_2}^{T_3} C_v dT = C_v(T_3 - T_2).$$

The heat rejected is given by (for a perfect gas with constant specific heats)

$$Q_L = Q_{41} = \Delta U_{41} = C_v(T_1 - T_4).$$

Substituting the expressions for the heat absorbed and rejected in the expression for thermal efficiency yields

$$\eta = 1 - \frac{T_4 - T_1}{T_3 - T_2}.$$

We can simplify the above expression using the fact that the processes from 1 to 2 and from 3 to 4 are isentropic:

$$T_4 V_1^{\gamma-1} = T_3 V_2^{\gamma-1}, \quad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$(T_4 - T_1) V_1^{\gamma-1} = (T_3 - T_2) V_2^{\gamma-1}$$

$$\frac{T_4 - T_1}{T_3 - T_2} = \left(\frac{V_2}{V_1} \right)^{\gamma-1}.$$

$$V_1/V_2 = r$$

The quantity r is called the compression ratio. In terms of compression ratio, the efficiency of an ideal Otto cycle is:

$$\eta_{\text{Otto}} = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}} = 1 - \frac{1}{r^{\gamma-1}}.$$

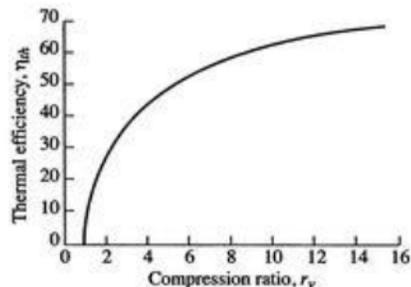


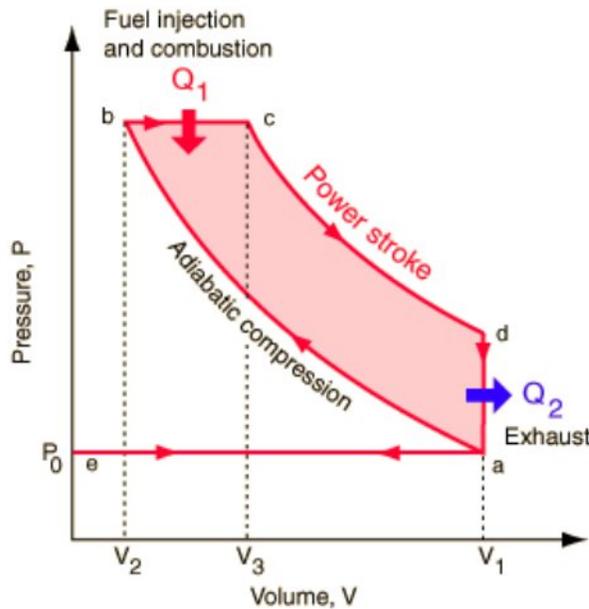
Figure 3: Ideal Otto cycle thermal efficiency

Diesel Engine

The diesel internal combustion engine differs from the gasoline powered Otto cycle by using a higher compression of the fuel to ignite the fuel rather than using a spark plug ("compression ignition" rather than "spark ignition").

In the diesel engine, air is compressed adiabatically with a compression ratio typically between 15 and 20. This compression raises the temperature to the ignition temperature of the fuel mixture which is formed by injecting fuel once the air is compressed.

The ideal air-standard cycle is modeled as a reversible adiabatic compression followed by a constant pressure combustion process, then an adiabatic expansion as a power stroke and isovolumetric exhaust. A new air charge is taken in at the end of the exhaust, as indicated by the



processes a-e-a on

Diesel Engine Theoretical Efficiency

Since the compression and power strokes of this idealized cycle are adiabatic, the efficiency can be calculated from the constant pressure and constant volume processes. The input and output energies and the efficiency can be calculated from the temperatures and specific heats:

$$Q_1 = C_p(T_c - T_b)$$

$$Q_2 = C_v(T_a - T_d)$$

$$\text{Efficiency} = \eta = \frac{Q_1 + Q_2}{Q_1}$$

It is convenient to express this efficiency in terms of the compression ratio $r_C = V_1/V_2$ and the expansion ratio $r_E = V_1/V_3$.

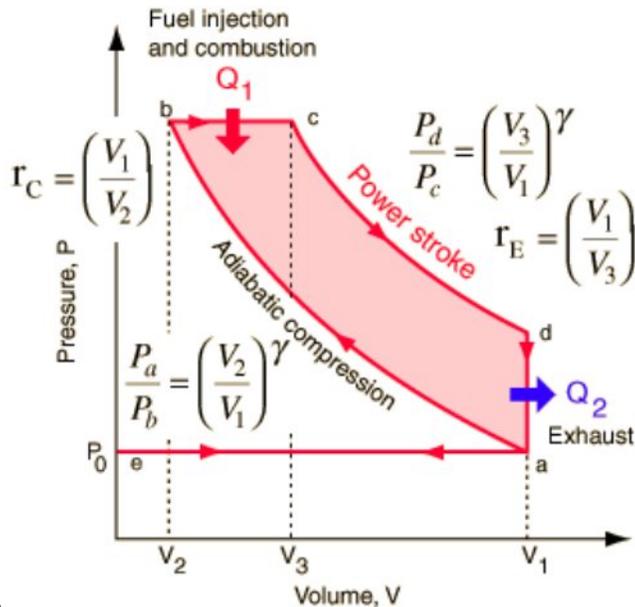
The efficiency can be expressed in terms of the specific heats and temperatures.

$$\eta = 1 + \frac{C_V(T_a - T_d)}{C_P(T_c - T_b)}$$

Now using the ideal gas law $PV=nRT$ and $\gamma = C_P/C_V$, this can be written

$$\eta = 1 + \frac{1}{\gamma} \frac{P_a V_a - P_d V_d}{P_c V_c - P_b V_b}$$

Now using the fact that $V_a = V_d = V_1$ and $P_c = P_b$ from the



diagram

$$\eta = 1 + \frac{1}{\gamma} \frac{V_1(P_a - P_d)}{P_c(V_3 - V_2)}$$

Dividing the numerator and denominator by $V_1 P_c$

$$\eta = 1 + \frac{1}{\gamma} \frac{\frac{P_a}{P_c} - \frac{P_d}{P_c}}{r_E^{-1} - r_C^{-1}}$$

Now making use of the adiabatic condition $PV^\gamma = \text{constant}$,

$$\frac{P_a}{P_c} = \left(\frac{V_2}{V_1}\right)^\gamma \quad \frac{P_d}{P_c} = \left(\frac{V_3}{V_1}\right)^\gamma$$

the efficiency can be written

$$\eta = 1 - \frac{1}{\gamma} \frac{r_E^{-\gamma} - r_C^{-\gamma}}{r_E^{-1} - r_C^{-1}}$$

UNIT-II

ENTROPY:

Entropy, the measure of a system's thermal energy per unit temperature that is unavailable for doing useful work. Because work is obtained from ordered molecular motion, the amount of entropy is also a measure of the molecular disorder, or randomness, of a system. The concept of entropy provides deep insight into the direction of spontaneous change for many everyday phenomena. Its introduction by the German physicist Rudolf Clausius in 1850 is a highlight of 19th-century physics.

Clausius introduced the concept of entropy as a precise way of expressing the second law of thermodynamics. The Clausius form of the second law states that spontaneous change for an irreversible process in an isolated system (that is, one that does not exchange heat or work with its surroundings) always proceeds in the direction of increasing entropy. For example, the block of ice and the stove constitute two parts of an isolated system for which total entropy increases as the ice melts.

By the Clausius definition, if an amount of heat Q flows into a large heat reservoir at temperature T above absolute zero, then the entropy increase is $\Delta S = Q/T$. This equation effectively gives an alternate definition of temperature that agrees with the usual definition. Assume that there are two heat reservoirs R_1 and R_2 at temperatures T_1 and T_2 (such as the stove and the block of ice). If an amount of heat Q flows from R_1 to R_2 , then the net entropy change

for the two reservoirs is

$$\Delta S = Q \left(\frac{1}{T_2} - \frac{1}{T_1} \right),$$

which is positive provided that $T_1 > T_2$. Thus, the observation that heat never flows spontaneously from cold to hot is equivalent to requiring the net entropy change to be positive for a spontaneous flow of heat. If $T_1 = T_2$, then the reservoirs are in equilibrium, no heat flows, and $\Delta S = 0$.

Definition of entropy

1: a measure of the unavailable energy in a closed thermodynamic system that is also usually considered to be a measure of the system's disorder, that is a property of the system's state, and that varies directly with any reversible change in heat in the system and inversely with the temperature of the system; broadly : the degree of disorder or uncertainty in a system

2a : the degradation of the matter and energy in the universe to an ultimate state of inert uniformity

b : a process of degradation or running down or a trend to disorder

The entropy of a system depends on its internal energy and its external parameters, such as its volume. In the thermodynamic limit, this fact leads to an equation relating the change in the internal energy U to changes in the entropy and the external parameters. This relation is known as the fundamental thermodynamic relation. If external pressure P bears on the volume V as the only external parameter, this relation is: $dU = TdS - PdV$

Change of Entropy in a Reversible process

Let us consider a complete reversible process – a Carnots Cycle ABCD as shown in figure. In the isothermal expansion from A to B, the working substance absorbs an amount of heat Q_1 at a constant temperature T_1 of the source. When heat is absorbed by the system, Q_1 is positive, and hence entropy change is positive because T is positive. Hence

gain in entropy from A-to-B = Q_1/T_1 . ----- (1)

Ie, source loses this heat Q_1 at temperature T_1 : so its entropy decreases by Q_1/T_1 .

During the adiabatic expansion from B-to-C, there is no change in entropy (since heat is neither taken nor given out).

During the isothermal compression from C-to-D, the working substance gives out a quantity of heat Q_2 at a constant temperature T_2 of sink and so the loss in entropy from C-to-D = Q_2/T_2 ----- (2)

ie, the sink gains this heat Q_2 at T_2 , so its entropy increases by Q_2/T_2 .

Again during the adiabatic compression from D-to-A there is no change in entropy.

It means that the total change in entropy of the working substance in a complete cycle of a reversible process is zero. Similarly the change in entropy of the combined system of source and sink is also zero. Thus in a cycle of reversible process, the entropy of the system remains unchanged or the change in entropy of the system is zero.

Change of entropy in an irreversible process

Consider an irreversible process such as conduction or radiation of heat. Let a system consist of two bodies at temperatures T_1 and T_2 . Since heat always flows from higher to lower temperature, both by conduction and radiation, let Q be the quantity of heat thus transmitted.

- Decrease in entropy of hotter body
- Increase in entropy of colder body
- Net change in entropy of the system

Which is a positive quantity since $T_1 > T_2$. we may, therefore, generalize the result and say that the entropy of the system increases in all irreversible processes.

Note: Since a reversible process represents a limiting ideal case, all actual processes are inherently irreversible. It means, ie., cycle after cycle of operation is performed, the entropy of the system increases and tends to a maximum value. This is the principle of increase of entropy and may be stated as “the entropy of an isolated system either remains constant or increases according as the processes it undergoes are irreversible or reversible”. Analytically it may be expressed as $dS \geq 0$.

Principle of increase of entropy

Let a system change from state 1 to state 2 by a reversible process A and return to state 1 by another reversible process B. Then 1A2B1 is a reversible cycle. Therefore, the Clausius inequality gives:

$$\int_{1A2B1} dQ/T = \int_{1A2} dQ/T + \int_{2B1} dQ/t = 0$$

If the system is restored to the initial state from 1 to state 2 by an irreversible process C, then 1A2C1 is an irreversible cycle. Then the Clausius inequality gives:

$$\int_{1A2C1} dQ/T = \int_{1A2} dQ/T + \int_{2C1} dQ/T = 0$$

Subtracting the above equation from the first one,

$$\int_{2B1} dQ/T > \int_{2C1} dQ/T$$

Since the process 2B1 is reversible,

$$\int_{2B1} dQ/T = \int_1^2 dQ/T$$

$$\text{or, } \int_1^2 dS > \int_{2C1} dQ/T$$

Where the In general, equality sign holds good for a reversible process and the inequality sign $dS \geq dQ/T$ holds good for an irreversible process.

Now let us apply the above result to evaluate the entropy change of the universe when a system interacts with its surroundings and exchanges energy as heat with the surroundings.

Let T_{sur} and T_{sys} be the temperatures of the surroundings and the system such that $T_{sur} > T_{sys}$. Let dQ represent the energy transfer as heat from the surroundings to the system during the given irreversible process.

$$dS_{sys} = dQ/T_{sys}$$

$$dS_{sur} = -dQ/T_{sur}$$

$$dS_{uni} = dS_{sys} + dS_{sur} = (dQ/T)_{sys} - (dQ/T)_{sur} > 0$$

$$dS_{uni} > 0 \text{ (since } T_{sur} > T_{sys} \text{)}$$

If the system is isolated, there is no change in the entropy of the surroundings and

$$dS \geq 0, \text{ for an isolated system}$$

Therefore the entropy of an isolated system either increases or, in the limit, remains constant.

The equality sign holds good when the process undergone by the system is reversible, the inequality sign holds good if there is any irreversibility present in the process. This statement is usually called the principle of entropy increase.

Temperature - Entropy Diagram

A temperature entropy diagram, or T-s diagram, is used in thermodynamics to visualize changes to temperature and specific entropy during a thermodynamic process or cycle. It is a useful and common tool, particularly because it helps to visualize the heat transfer during a process. For reversible (ideal) processes, the area under the T-s curve of a process is the heat transferred to the system during that process. An isentropic process is depicted as a vertical line on a T-s diagram, whereas an isothermal process is a horizontal line.