U. P. RajarshiTandon Open University, Prayagraj.

Bachelor of Science

DCEPHS-106

THERMAL PHYSICS

U. P. Rajarshi Tandon
Open University

Bachelor of Science
DCEPHS -106
Thermal Physics

Block

1 Thermodynamics

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1.1 INTRODUCTION:

Thermodynamics is that branch of physics which is mainly concerned with the transformation of heat into mechanical work. It involves the study of the interaction of one body on another, the interaction being described in terms of the quantities heat and work. Thus, thermodynamics may be said to be an exact mathematical science that describe the inter-relationship between heat and mechanical energy. With the passage of time, however, the scope of thermodynamics has increased and now-a-days it covers all the branches of physics as well as chemistry whenever we have to deal with heat and its relationship to energy in any of its diverse forms – electrical, mechanical, chemical, magnetic etc.

Thermodynamics constitutes a very subtle study in physics, chemistry and engineering and has innumerable applications. It is based upon two general laws of nature which govern the conversion of heat into work and vice versa. The first law represents the connection between heat and mechanical work while the second law depicts the manner in which these energy changes take place.

Thermodynamics takes no account of the atomic constitution of matter. Here we only deal with macroscopic (large scale) properties

and do not go into the detailed structure. Thermodynamics is an empirical or experimental science and the laws of thermodynamics have been developed by means of observation and experiments over a long period of years. Thermodynamical formulae have necessarily the same general validity as the two laws from which they are derived.

1.2   OBJECTIVES

After studying this Unit, student should able to:

- Understand the Concept of Thermodynamic System.

- Explain Zeroth Law of Thermodynamics.

- Define the term Equation of State.

- Understand macroscopic and Microscopic Variables.

- Explain Thermodynamic Equilibrium.

1.3   THERMODYNAMIC SYSTEM

We use cars and bikes in our daily routine to travel. To keep them going, we fill in petrol or diesel as per the design of the vehicle. The petrol or diesel in the vehicle undergoes combustion inside the engine and is an ideal example of a thermodynamic system. The system which involves the processing of heat and converting it to

useful work involves thermodynamic processes. Nuclear power, electronic heat sink and rocket launch involve thermodynamics.

Thermodynamics is the branch of science that deals with heat and temperature and the inter-conversion of heat and other forms of energy. Since thermodynamics deals with the bulk system and does not deal with the molecular constitution of matter, it is known as macroscopic science.

Some examples of thermodynamic systems are washing machines, refrigerators and air-conditioners. Air-conditioner is a closed system that circulates refrigerant inside the system, altering the pressure of the refrigerant at different points to promote the transfer of heat. A refrigerator is an open system that absorbs heat from a closed space and passes it to a warmer area. In this article, let us study in detail the thermodynamic system and its types.

Types of Thermodynamic System

A system that is delimited from the surroundings by real or hypothetical boundaries is known as a thermodynamic system. A thermodynamic system refers to that part of the universe in which observations are made, and the remaining universe constitutes the

surroundings. The surroundings contain everything other than the system. The system and the surroundings together make up the universe.

The universe = The system + The surroundings

A thermodynamic system is embedded in its environment or surroundings, through which it can exchange heat with, and do work on. It exchanges the [heat](#) to its surroundings through a boundary. The boundary is the wall that separates the system and the environment. Thermodynamic systems can exchange energy or matter with the external environment and can also undergo internal transformations.

The below figure shows the thermodynamic system, surroundings and boundary concept.
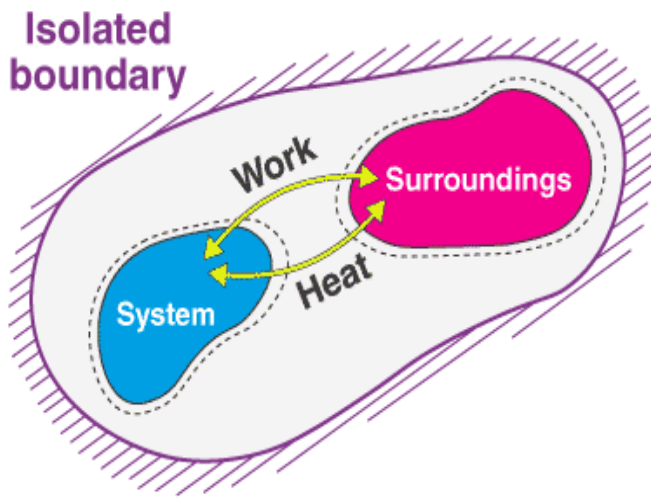
System boundary

A boundary is a closed surface surrounding a system through which energy and mass may enter or leave the system.

Surroundings

Everything that interacts with the system

System

A system is a region containing energy and/or matter that is separated from its surroundings by arbitrarily imposed walls or boundaries

Example: In a car, the engine burns gasoline inside the cylinder and is considered as a thermodynamic system; the radiator, piston, exhaust system and air outside form the environment of the system. The inner surfaces of the cylinder and piston are considered as the boundary.

Thermodynamic systems are classified as:

- Open systems

- Closed systems

- Isolated Systems

Open System

If the thermodynamic system has the capacity to exchange both matter and energy with its surroundings, it is said to be an open system.

Example: Consider a beaker in the presence of reactants in an open beaker. Here the boundary is an imaginary surface enclosing the beaker and reactants.

Example: A steam turbine, a pool filled with water, where the water can enter or leave the pool.
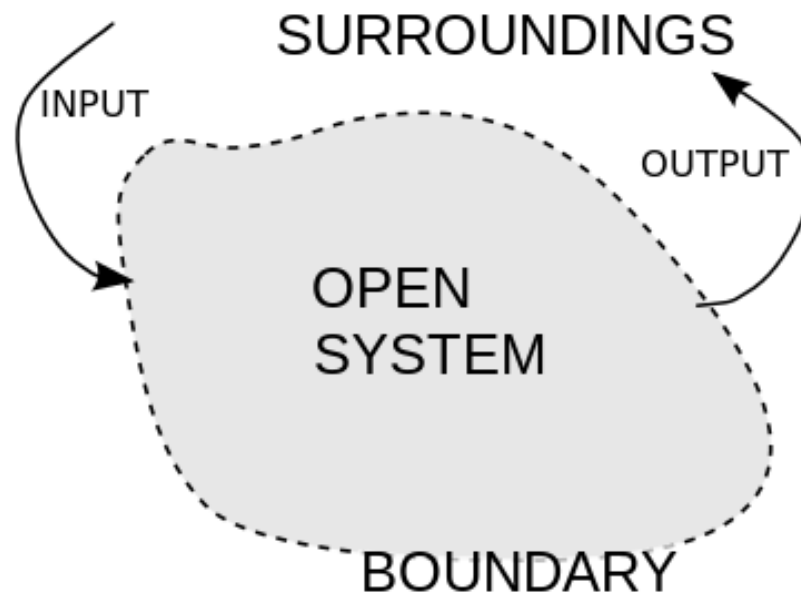
Closed System

A system which has the ability to exchange only energy with its surroundings and cannot exchange matter is known as a closed system.

Example: Reactants placed in a closed vessel made of materials like steel, copper, and silver are an ideal example of a closed system since the material of the vessel is conducting in nature.

A cylinder in which the valve is closed is an example of a closed system. When the cylinder is heated or cooled, it does not lose its mass.
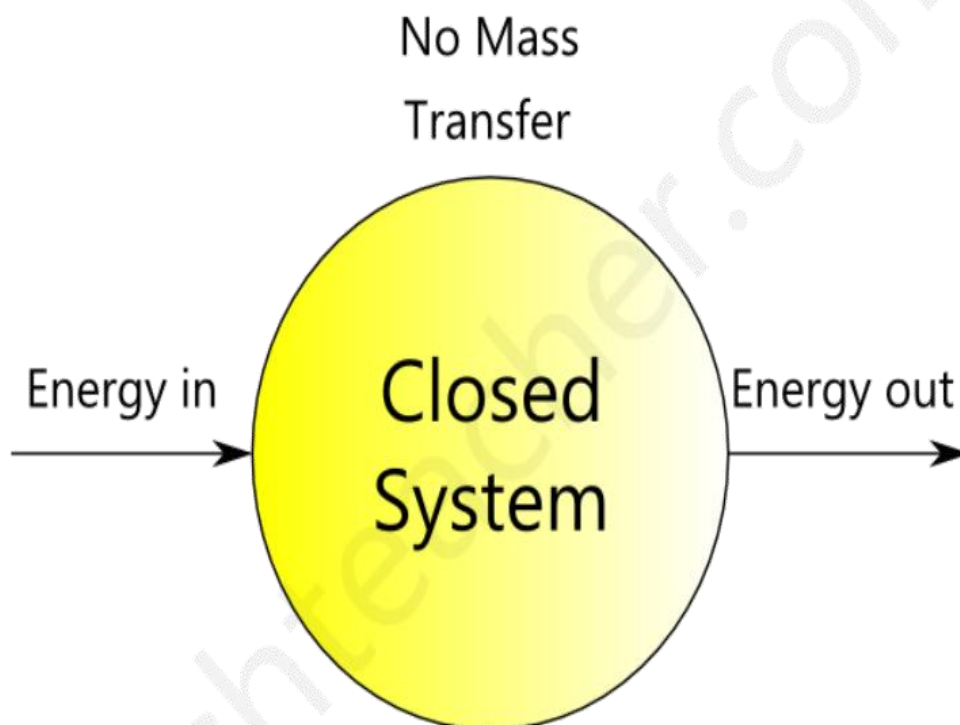
Isolated System

A system which cannot exchange matter or energy with the surroundings is known as an isolated system. The zeroth law of thermodynamics states that thermodynamic processes do not affect the total energy of the system.
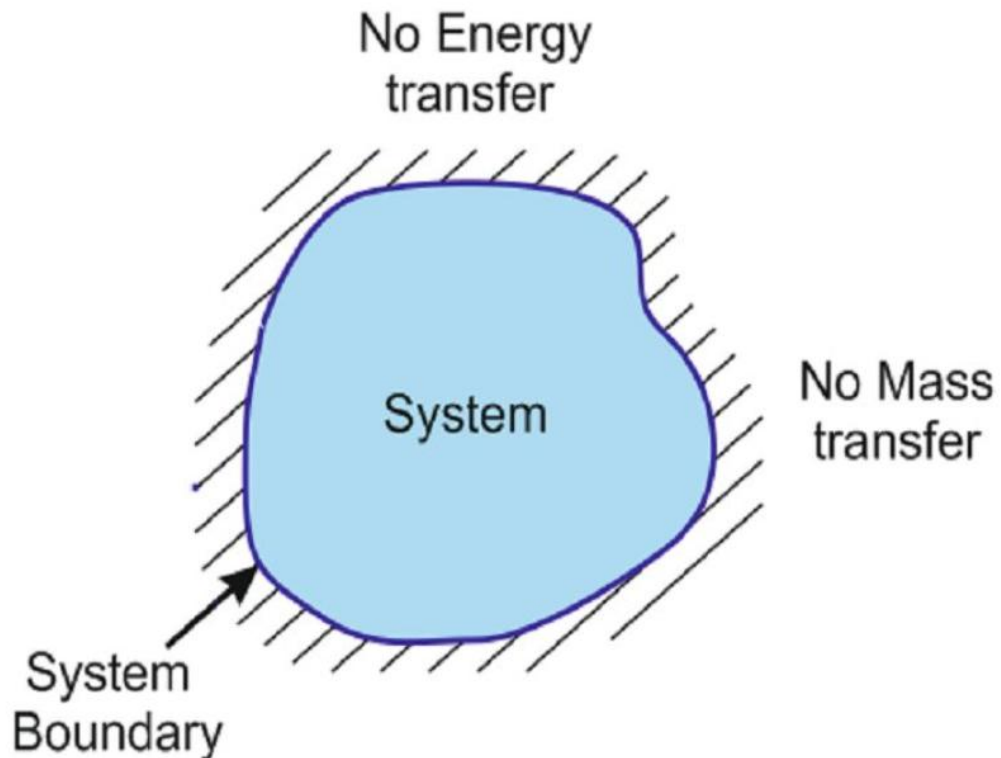
Example: Reactants are present in a thermos flask or an insulated vessel, where neither energy nor matter is exchanged with the environment.

Example: If the piston and cylinder arrangement in which the fluid like air or gas is being compressed or expanded is insulated, it becomes an isolated system.

No Energy transfer

System

No Mass transfer

System Boundary

1.4   THERMODYNAMIC VARIABLES

Thermodynamic variables (or state variables) are easily measurable macroscopic quantities used to describe the state of a thermodynamic system. These quantities are different depending on the type of system we want to describe; it is not the same to describe the behavior of a magnet, a galaxy, or a living being. To

describe each of these systems it is necessary to use a different set of quantities.

In the situations that we will discuss throughout these pages, we will assume that the system studied is in **thermodynamic equilibrium**:

It is the internal state of a system in which the thermodynamic variables that describe it do not undergo macroscopic changes.

- **Mass** (m): expressed in kilograms (kg) or in number of moles (n).

- **Volume** (V): expressed in cubic meters (m^3).

- **Pressure** (p): the one that exerts the gas on the walls of the container that contains it. Expressed in pascals (Pa).

- **Temperature** (T): Usually expressed in Kelvin (K) or in degrees Celsius (^{0}C).
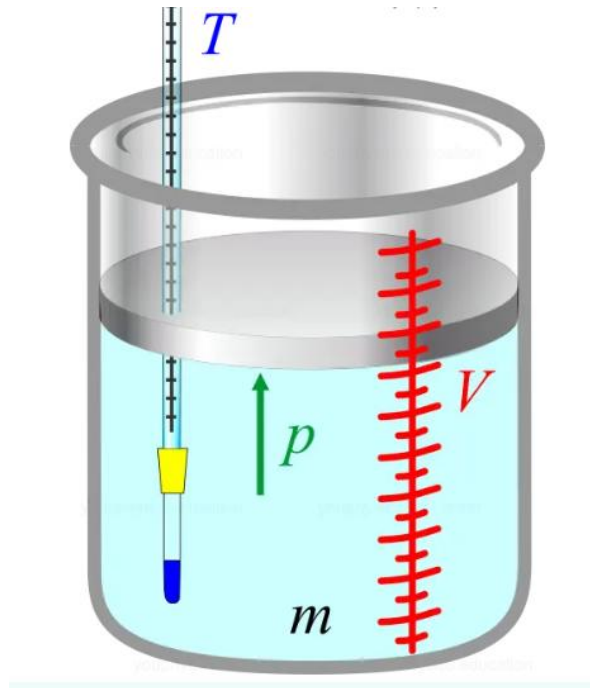
1.5   THERMODYNAMIC EQUILIBRIUM

In this segment, we will be studying Thermodynamic Equilibrium Definition and Types with example and in the end, you can download the whole document in PDF format.

So, let's dive to the topic,

The term **"Thermodynamic"** means it is a branch of physics that deals with the heat, work, and form of energy. The term **"Equilibrium"** means the state of balance of the system within itself and between the system and surrounding.

What is Thermodynamic Equilibrium?

The system is said to be thermodynamic equilibrium when there is no spontaneous change in any macroscopic property is observed, as the system is isolated from its surroundings is known as thermodynamic Equilibrium.

Types of Thermodynamic Equilibrium:

There is a total 3 thermodynamic equilibrium which are:

- **Chemical Equilibrium**

- **Mechanical Equilibrium and**

- **Thermal Equilibrium**

1.5.1 Thermal Equilibrium

A system is said to be thermal equilibrium when there is no temperature difference present and the temperature remains equal at all .

Thermal Equilibrium
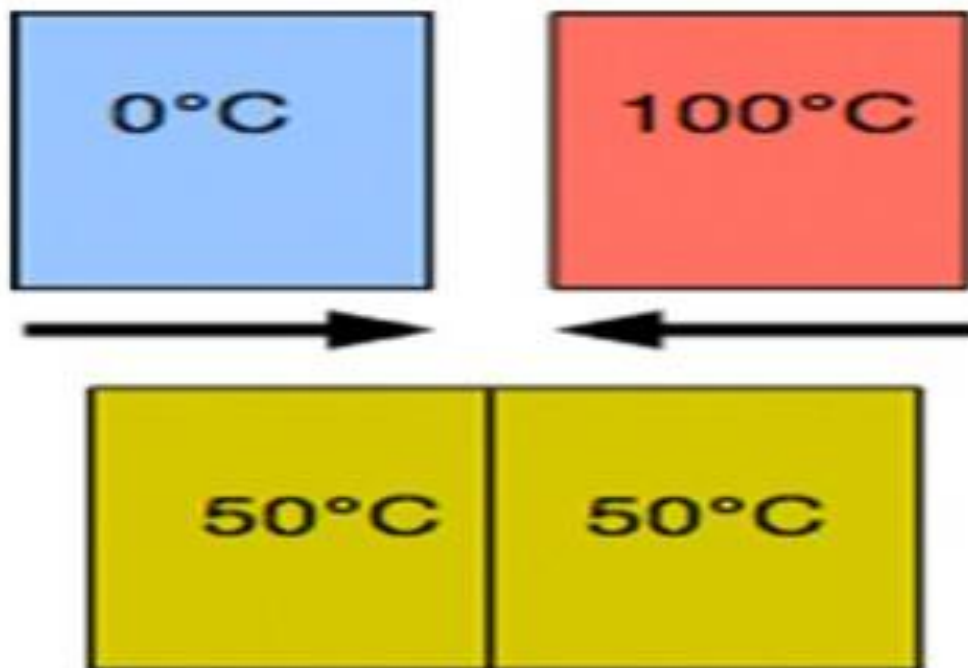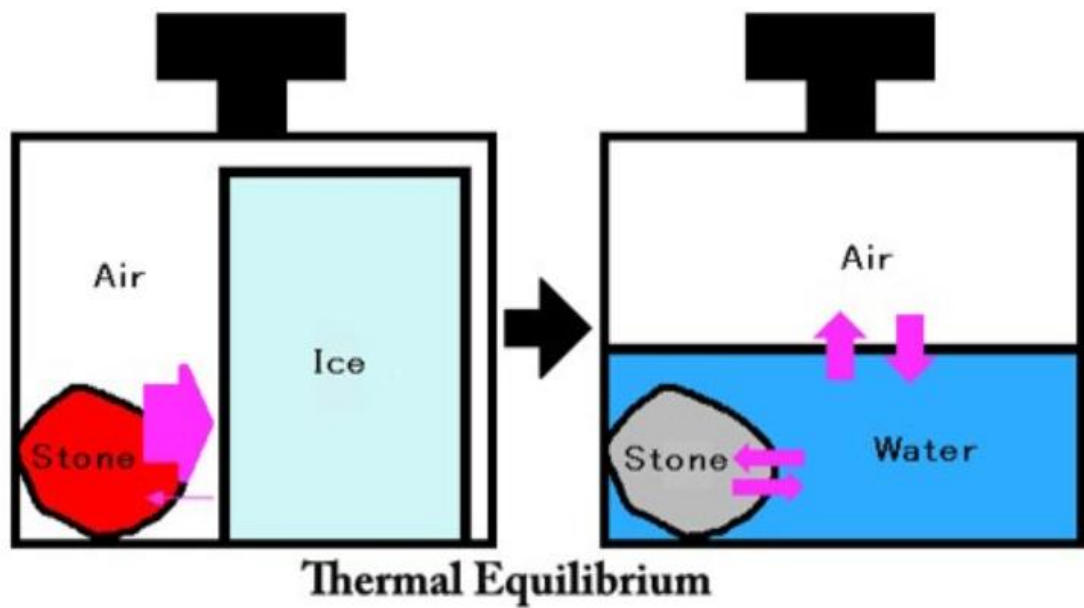
Thermal Equilibrium obeys the zeroth law of thermodynamics. A system is said to be in thermal equilibrium with itself if the temperature within the system is spatially and temporally uniform.
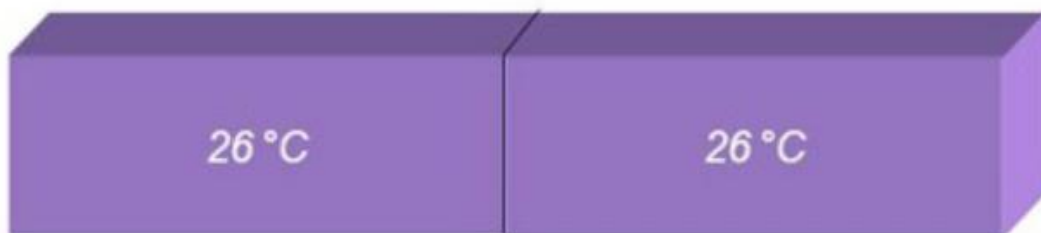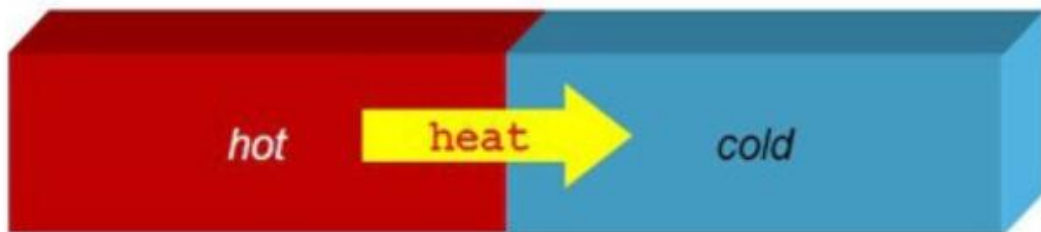
Example:

A hot cup of tea has a higher temperature as compared to surrounding so this is not in thermal equilibrium.

But when you keep this in an open environment for some duration, the temperature starts emitting by radiation process to the

environment and the surrounding temperature and a cup of tea temperature remains the same at that moment we can say this is in thermal equilibrium.

Applications of Thermal Equilibrium

Refrigerator –

- When food is put in the refrigerator, the heat from the food is transferred into the air of the refrigerator.

- This process is continued until the temperature of the food equal to the temperature of the air in the refrigerator, when thermal equilibrium is reached between the food and the refrigerator.

Oven –

- When food such as meat or cake is put in the oven, the heat of the oven is transferred into the food.

- This process will continue until the food is in thermal equilibrium with the air in the oven.

- This happen when the temperature of the food is equal to the temperature of the air in the oven.

Thermometer –

- Thermometer is placed in contact with the patient's body.

- If both the body temperature of the patient and that of the mercury (or alcohol) in the clinical thermometer have reached thermal equilibrium, then the temperature of the thermometer is the same as the body temperature, hence the reading of the thermometer shows the body temperature of the patient.

1.5.2 Mechanical Equilibrium

A system is said to be mechanical equilibrium when there is no unbalanced force within the system or between system and surroundings.

It deals with the force. The pressure in the system is the same at all points and does not change with respect to time.

Mechanical Equilibrium

- ### Mechanical equilibrium means that there is no change in pressure in the system.
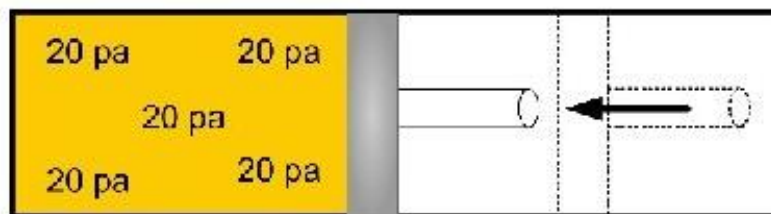
(a) Slow compression (quasi-equilibrium)

(b) fast compression (non quasi-equilibrium)

Example:

Treadmill: This is a gym instrument on which we run but we don't move forward because the force you trying to push forward the same force acting opposite to push backward. So, this is one of the best examples of mechanical equilibrium.

1.5.3 Chemical Equilibrium

A system is said to be chemical equilibrium when no chemical reaction takes place in the system or between system and surrounding. The chemical composition will be the same throughout the system and this will not vary that system in chemical equilibrium. This is a reversible reaction.

Example:

$$CaCO_3 \rightarrow CaO + CO_2$$

When we heat Calcium Carbonate ($CaCO_3$) at temperature 1073K will get CaO and CO_2

Chemical Equilibrium
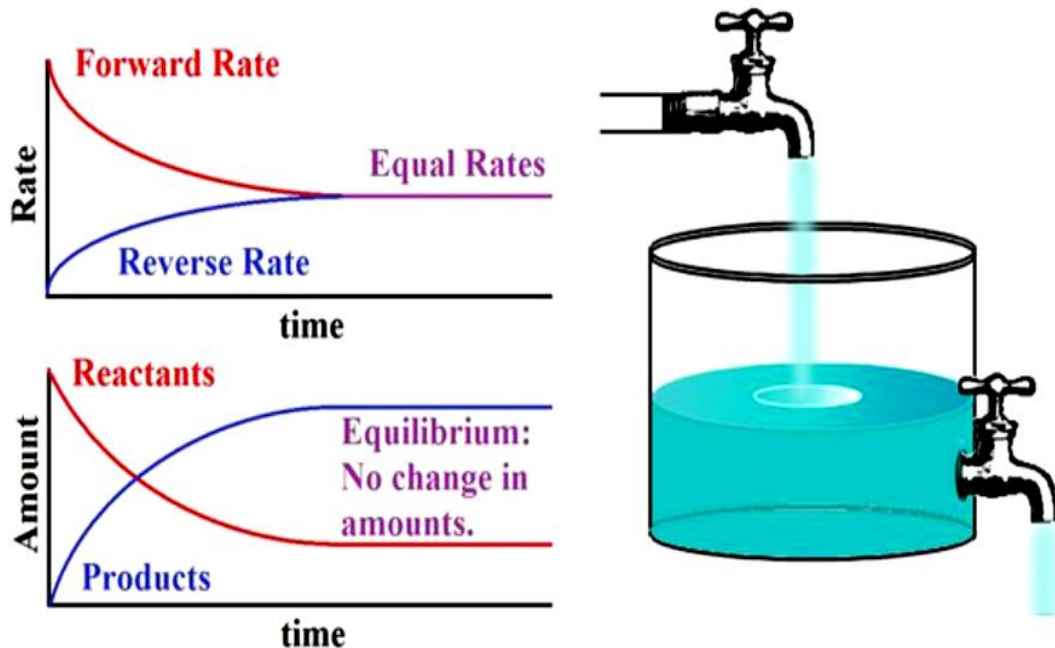
1.6   EQUATION OF STATE

In physics, chemistry, and thermodynamics, an equation of state is a thermodynamic equation relating state variables, which describe the state of matter under a given set of physical conditions, such as pressure, volume, temperature, or internal energy. Most modern equations of state are formulated in the Helmholtz free energy. Equations of state are useful in describing the properties of pure substances and mixtures in liquids, gases, and solid states as well as the state of matter in the interior of stars.

At present, there is no single equation of state that accurately predicts the properties of all substances under all conditions. An example of an equation of state correlates densities of gases and liquids to temperatures and pressures, known as the ideal gas law, which is roughly accurate for weakly polar gases at low pressures and moderate temperatures. This equation becomes increasingly inaccurate at higher pressures and lower temperatures, and fails to predict condensation from a gas to a liquid.

The general form of an equation of state may be written as

$$f(p, V, T) = 0$$

where p is the pressure, V the volume, and T the temperature of the system. Yet also other variables may be used in that form. It is directly related to Gibbs phase rule, that is, the number of independent variables depends on the number of substances and phases in the system.

1.7 THERMODYNAMIC CONSTRAINTS

Thermodynamic constraints are introduced by putting the system of interest in contact with some other virtually infinite system, the 'reservoir', with a coupling vanishingly small in the thermodynamic limit. Neither of these ' infinite' conditions can be reproduced in

molecular dynamics simulations where the time evolution of an isolated system with a finite number of degrees of freedom is numerically integrated, producing trajectories representative of the microcanonical ensemble. Several ways have been proposed to overcome this limitation. Here the case of MD simulations at constant temperature and/or pressure will be treated within the extended system framework introduced by Andersen in his 1980 seminal paper, and later generalized mainly by Nose. The N-particle physical system of interest is put in contact with external reservoirs, which are, in contrast to theoretical infinite ones, represented just by a few degrees of freedom. The equations of motion for the extended system are chosen in such a way that the dynamical trajectory in the phase space of the system of interest is representative of the desired ensemble. Moreover the coupling is non-linear yielding good ergodic properties and can be chosen to be weak enough to leave the dynamical properties of the system of interest unaltered.

1.8   ZEROTH LAW OF THERMODYMICS

Zeroth law of thermodynamics is one of the four laws of thermodynamics. The credit for formulating the law goes to Ralph H. Fowler. Interestingly, the zeroth law of thermodynamics was actually developed much later than the original three laws. However, there was some confusion regarding the nomenclature, whether it should be named the fourth law or some other name. The complication arose because the new law gave a much clearer definition of the temperature and basically replaced what the other

three laws had to state. Fowler finally came up with the name to end this conflict.

The zeroth law of <u>thermodynamics</u> frames an idea of temperature as an indicator of thermal equilibrium.

What is Zeroth Law of Thermodynamics?

When a body 'A' is in thermal equilibrium with another body 'b', and also separately in thermal equilibrium with a body 'C', then body 'B' and 'C' will also be in thermal equilibrium with each other. This statement defines the zeroth law of thermodynamics. The law is based on temperature measurement.
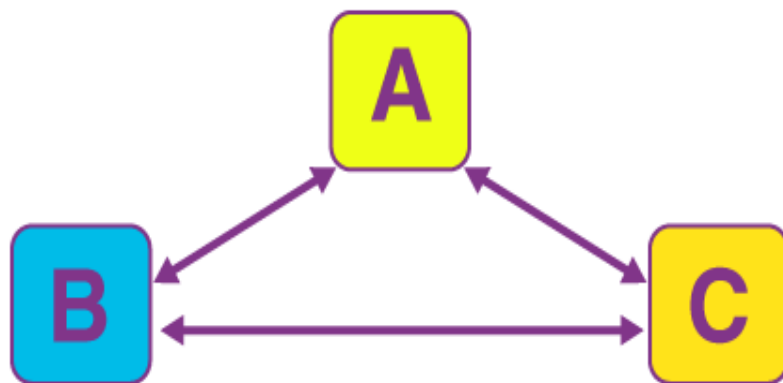
The zeroth law of thermodynamics states that if two thermodynamic systems are each in thermal equilibrium with a third one, then they are in thermal equilibrium with each other.

There are also various ways to state the zeroth law of thermodynamics. However, in simple terms, it can be said, "Systems that are in thermal equilibrium exist at the same temperature".

Zeroth law of thermodynamics takes into account that temperature is something worth measuring because it predicts whether the heat will transfer between objects or not. This is true regardless of how the objects interact. Even if two objects are not in physical contact, heat still can flow between them, by means of radiation <u>mode of heat transfer</u>. Whereas, zeroth law of thermodynamics states that, if the systems are in thermal equilibrium, no heat flow will take place.

Thermal Equilibrium

Temperature is a property that distinguishes thermodynamics from other sciences. This property can distinguish between hot and cold. When two or more bodies at different temperatures are brought into contact then after some time, they attain a common temperature and they are said to exist in thermal equilibrium.

Systems are said to be in thermal equilibrium if there is no heat transfer, even if they are in a position to transfer heat, based on other factors. For example, if we put food in the refrigerator overnight

then that food is in thermal equilibrium with the air of that refrigerator. Heat no longer flows from food to the air or from the air to the food, this state is known as thermal equilibrium.

Zeroth Law of Thermodynamics Example and Applications

The law is important for the mathematical formulation of thermodynamics or more precisely for stating the mathematical definition of temperature. This law is mostly used to compare temperatures of different objects.

If we want to measure the accurate temperature, a reference body is required and a certain characteristic of that body which changes with temperature. The change in that characteristic may be taken as an indication of a change of temperature. That selected characteristic is known as thermodynamic property.

Nonetheless, the most common application of the zeroth law of thermodynamics can be seen in thermometers. We can observe the zeroth law in action by taking a very common thermometer having mercury in a tube. As the temperature is increased this mercury expands since the area of the tube is constant. Due to this expansion, the height is increased. Now, the increase in the height of the

mercury label shows the changes in temperature and basically helps us to measure it.

There are different kinds of thermometers that can be used depending on their thermometric property. They are as follows.

Thermometer	Thermometric Property
Constant volume gas thermometer	Pressure
Constant pressure gas thermometer	Volume
Electrical resistance thermometer	Resistant
Thermocouple	Thermal e.m.f
Mercury -in -glass thermometer	Length

Similarly, another example of the zeroth law of thermodynamics is when you have two glasses of water. One glass will have hot water and the other will contain cold water. Now if we leave them in the table for a few hours they will attain thermal equilibrium with the temperature of the room.

1.8.1 Concept of Temperature

Temperature is the degree of hotness or coolness of a body. The hotter the body is higher is its temperature.

1. Unit of Temperature

The SI unit of temperature is *kelvin* **(K)**. For day-to-day applications, *Celsius* (˚C) is used. Temperature is measured with a thermometer.

2. Temperature scales

There are three scales of temperature.

i. Fahrenheit scale

ii. Celsius or Centigrade scale

iii. Kelvin or Absolute scale

Temperature Scales

Fahrenheit — Celsius — Kelvin

212°F	100°C	373.15 K	Boiling Point of Water
32°F	0°C	273.15 K	Freezing Point of Water
0°F	-18°C	255 K	
-460°F	-273°C	0 K	Absolute Zero
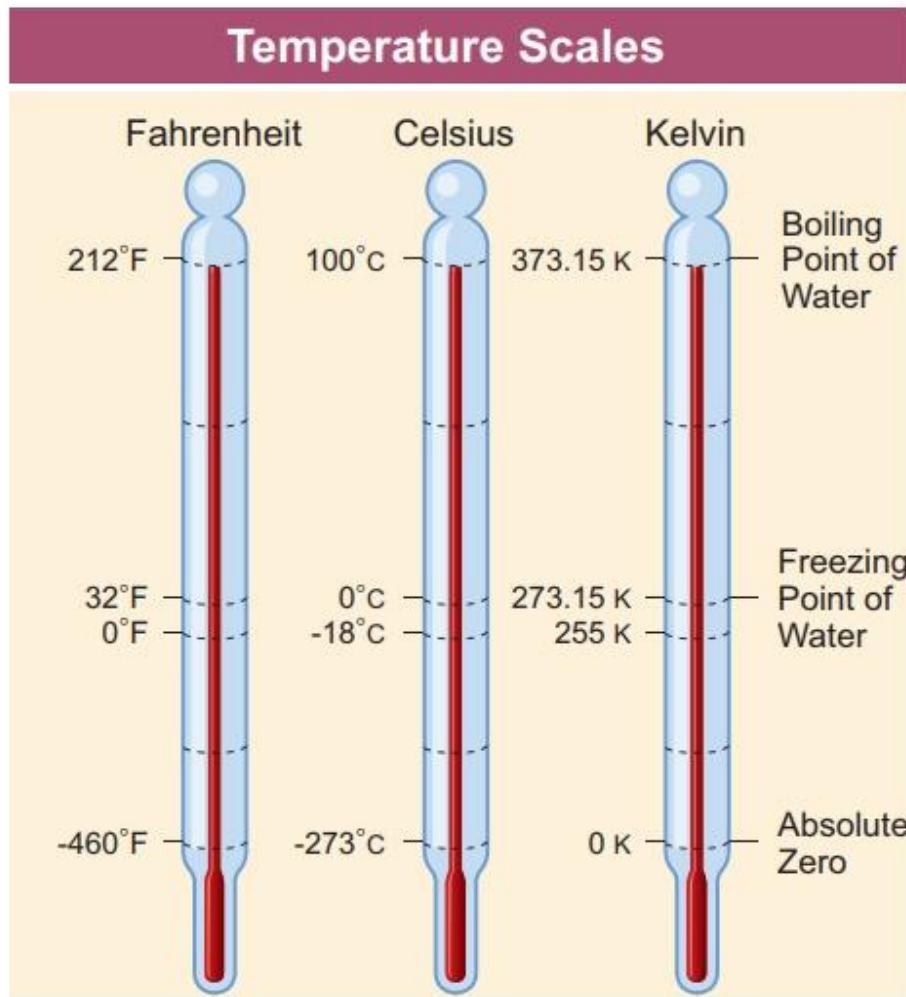
i. Fahrenheit scale

In Fahrenheit scale, 32 °F and 212 °F are the freezing point and boiling points respectively. Interval has been divided into 180 parts.

ii. Celsius temperature scale

In Celsius scale, also called centigrade scale, 0°C and 100 °C are the freezing point and boiling respectively. Interval has been divided into 100 parts. The formula for converting a Celsius scale to Fahrenheit scale is:

$$F = \frac{9}{5}C + 32$$

The formula for converting a Fahrenheit scale to Celsius scale is:

$$C = \frac{5}{9}(F\text{-}32)$$

iii. Kelvin scale (Absolute scale)

Kelvin scale is known as the absolute scale. On the Kelvin scale 0 K represents absolute zero, the temperature at which the molecules of a substance have their lowest possible energy. The solid, liquid, gaseous phases of water can coexist in equilibrium at 273.16 K.

Kelvin is defined as 1/273.16 of the triple point temperature.

The formula for converting a Celsius scale to Kelvin scale is:

K = C + 273.15

The formula for converting a Kelvin scale to Celsius scale is:

C = K - 273.15

1.9   MACROSCOPIC AND MICROSCOPIC VARIABLES

Microscopic Variable: A variable pertaining to the individual atoms and molecules making up the system. Examples include the x component of a particle's velocity, the orientation of the axis of a diatomic molecule, the quantum number for a particular vibrational mode of a molecule, and the magnetic moment vector of a paramagnetic ion.

Macroscopic Variable: A measurable quantity used to describe the gross state of the system. It depends collectively on the behavior of all the atoms and molecules. These are also referred to as thermodynamic variables.
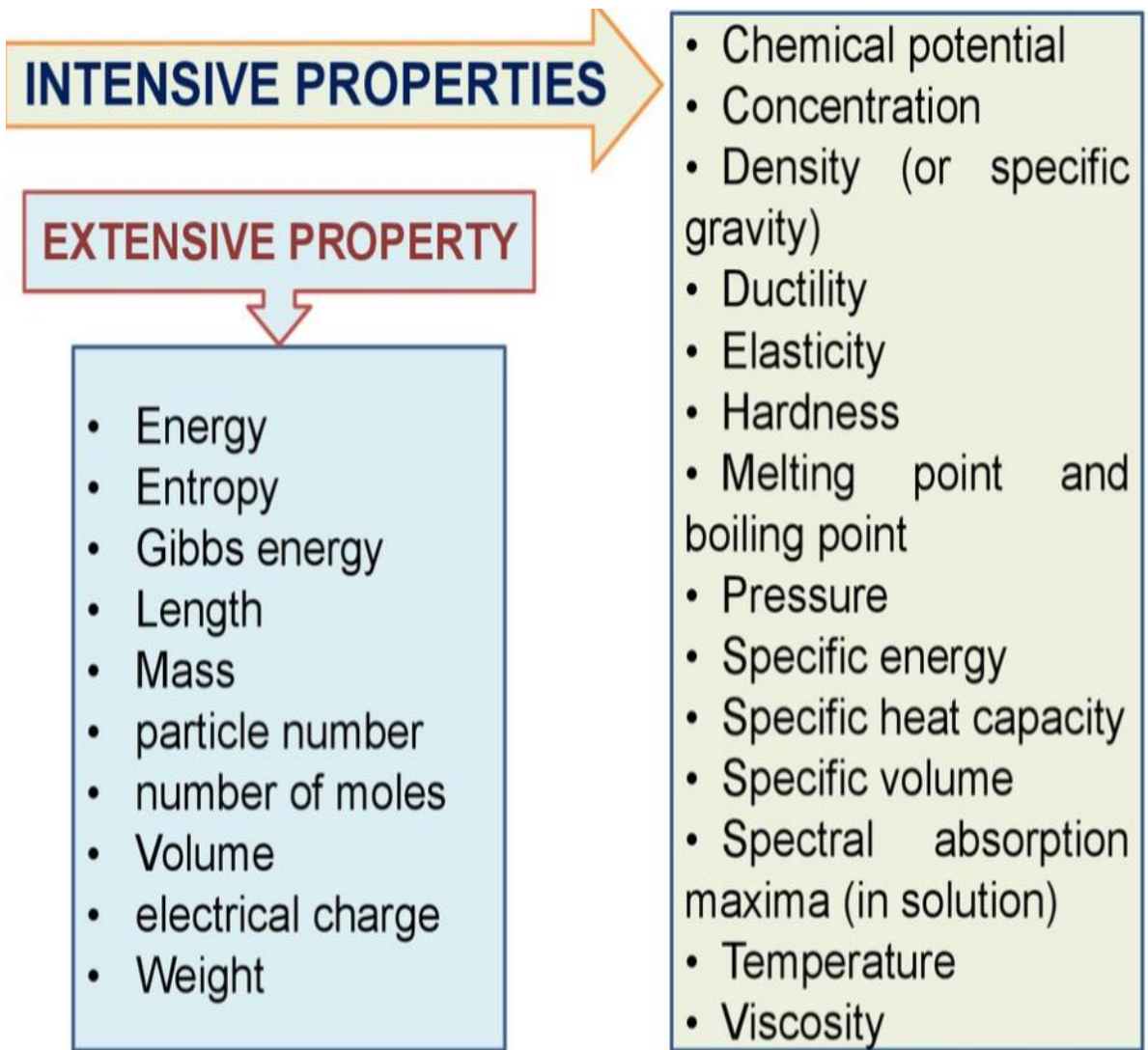
1.10 EXTENSIVE AND INTENSIVE VARIABLE

Extensive variable depends on the size or mass of the system.

Examples: Volume, total entropy, internal energy, heat capacity, etc.

Intensive variable does not depend on the size or mass of the system.

Examples: Temperature, pressure, specific heat capacity, density, etc.

INTENSIVE PROPERTIES

- Chemical potential
- Concentration
- Density (or specific gravity)
- Ductility
- Elasticity
- Hardness
- Melting point and boiling point
- Pressure
- Specific energy
- Specific heat capacity
- Specific volume
- Spectral absorption maxima (in solution)
- Temperature
- Viscosity

EXTENSIVE PROPERTY

- Energy
- Entropy
- Gibbs energy
- Length
- Mass
- particle number
- number of moles
- Volume
- electrical charge
- Weight

1.11 QUASI-STATIC AND NON-QUASI-STATIC PROCESS

In thermodynamics, a quasi-static process is referred to as a slow process. It is **a process that happens at an infinitesimally slow rate**. A quasi-static process has all of its states in equilibrium. A quasi-static process is one in which the system is in thermodynamic equilibrium with its surroundings at all times.

NON-QUASI-STATIC PROCESS

If a process is carried out in such a way that at every instant the system departs finitely from thermodynamic equilibrium state, such a process is called non-quasi-static process. Example: Fast compression process is an example for non-quasi-static process

Figure:

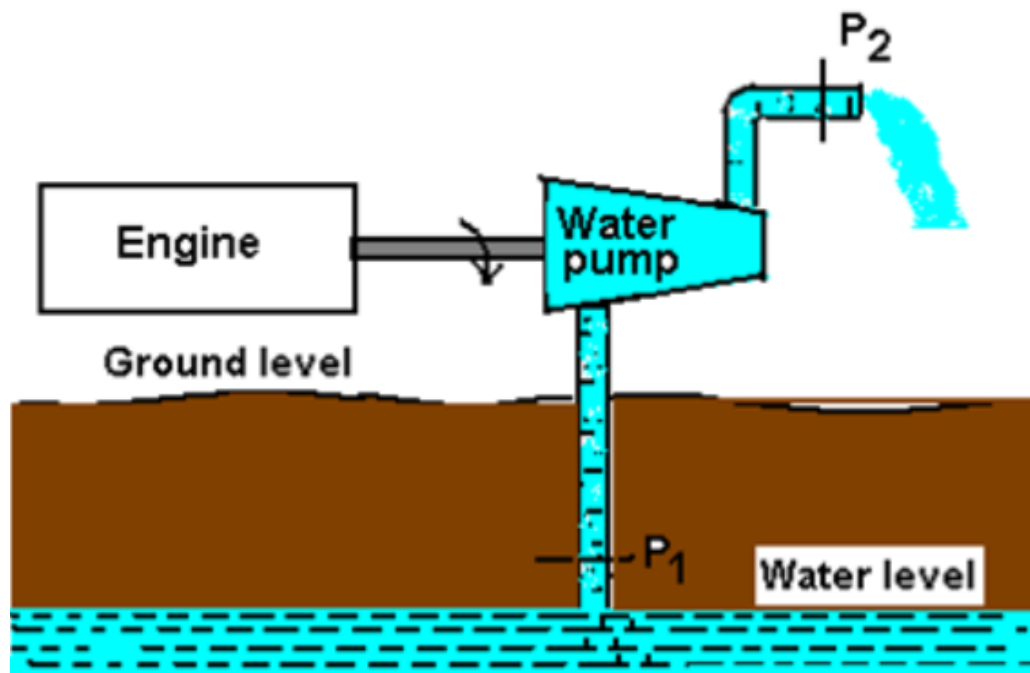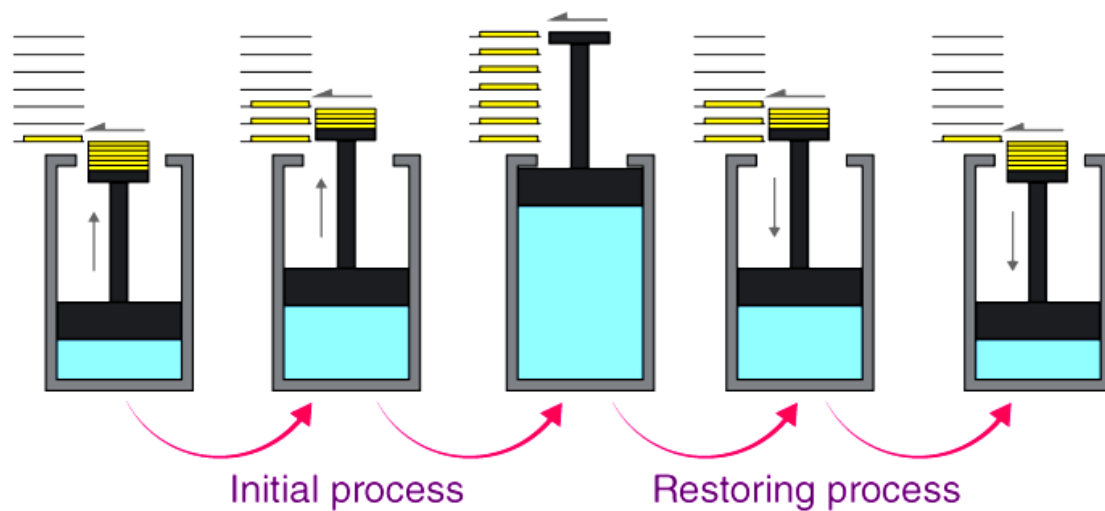## 1.12 REVERSIBLE AND IRREVERSIBLE PROCESSES

We see so many changes happening around us every day, such as boiling water, rusting of iron, melting ice, burning of paper, etc. In all these processes, we observe that the system in consideration goes from an initial state to a final state where some amount of heat is absorbed from the surroundings and some amount of work W is

done by the system on the surrounding. Now, for how many such systems can the system and the surrounding be brought back to their initial state? With common examples such as rusting and fermentation, we can say that it is not possible in most cases. In this section, we shall learn about reversible and irreversible processes.

Initial process   Restoring process

What are Reversible Processes?

A thermodynamic process (state i → state f) is said to be reversible if the process can be turned back to such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe. As we know, in reality, no such processes as reversible processes can exist. Thus, the reversible processes can easily be defined as idealizations or models of real processes on which the limits of the system or device are to be defined. They help us in incurring the maximum efficiency a system

can provide in ideal working conditions and thus the target design that can be set.

Examples of Reversible Processes

Here, we have listed a few examples of Reversible Processes:

- extension of springs

- slow adiabatic compression or expansion of gases

- electrolysis (with no resistance in the electrolyte)

- the frictionless motion of solids

- slow isothermal compression or expansion of gases

What are Irreversible Processes?

An irreversible process can be defined as a process in which the system and the surroundings do not return to their original condition once the process is initiated. Take an example of an automobile engine that has travelled a distance with the aid of fuel equal to an amount 'x'. During the process, the fuel burns to provide energy to the engine, converting itself into smoke and heat energy. We cannot retrieve the energy lost by the fuel and cannot get back the original

form. There are many factors due to which the irreversibility of a process occurs, namely:

1. The friction that converts the energy of the fuel to heat energy

2. The unrestrained expansion of the fluid prevents from regaining the original form of the fuel Heat transfer through a finite temperature, the reverse of which is not possible as the forward process, in this case, is spontaneous

3. Mixing of two different substances that cannot be separated as the intermixing process is again spontaneous in nature, the reverse of which is not feasible.

Thus, some processes are reversible while others are irreversible in nature depending upon their ability to return to their original state from their final state.

Examples of Irreversible Processes

A few examples of Irreversible Processes are:

- Relative motion with friction

- Throttling

- Heat transfer

- Diffusion

- Electricity flow through a resistance

1.13 CONDITION FOR REVERSIBILITY

(i)   The process should proceed at an extremely slow rate.

(ii)   The system should remain in mechanical thermal and chemical equilibrium state at all the time with the surrounding during the process.

(iii) No dissipative forces such as friction viscosity electrical resistance should be present.

1.14. SUMMARY:

Every science has its own unique vocabulary associated with it. Precise definition of basic concepts forms a sound foundation for development of a science and prevents possible misunderstandings. Careful study of these concepts is essential for a good understanding of topics in thermodynamics.

Thermodynamics, science of   the   relationship between heat, work, temperature,   and energy. In broad terms, thermodynamics deals with the transfer of energy from one place to

another and from one form to another. The key <u>concept</u> is that heat is a form of energy corresponding to a definite amount of mechanical work.

Heat was not formally recognized as a form of energy until about 1798, when Count Rumford (<u>Sir Benjamin Thompson</u>), a British military engineer, noticed that limitless amounts of heat could be generated in the boring of cannon barrels and that the amount of heat generated is proportional to the work done in turning a blunt boring tool. Rumford's observation of the proportionality between heat generated and work done lies at the foundation of thermodynamics. Another pioneer was the French military engineer <u>Sadi Carnot</u>, who introduced the concept of the heat-engine cycle and the principle of <u>reversibility</u> in 1824. Carnot's work concerned the limitations on the maximum amount of work that can be obtained from a <u>steam engine</u> operating with a high-temperature <u>heat transfer</u> as its driving force. Later that century, these ideas were developed by <u>Rudolf Clausius</u>, a German mathematician and physicist, into the first and second laws of thermodynamics, respectively.

The most important laws of thermodynamics are:

- *The zeroth law of thermodynamics.* When two systems are each in <u>thermal equilibrium</u> with a third system, the first two systems are in thermal <u>equilibrium</u> with each other. This property makes it meaningful to use thermometers as the "third system" and to define a temperature scale.

1.15 TERMINAL QUESTIONS:

1. What is thermodynamic system.

2. State the Zeroth law of thermodynamics.

3. Distinguish between chemical, mechanical and thermal equilibrium.

4. Explain the concept of temperature on the basis of Zeroth law of thermodynamics.

5. Explain reversible and irreversible processes.

6. What is an equation of state? Give its limitation.

1.16 ANSWER AND SOLUTIONS OF TERMINAL QUESTION

1. Section 1.3

2. Section 1.8

3. Section 1.5.1, 1.5.2, 1.5.3

4. Section 1.8, 1.8.1

5. Section 1.12

6. Section 1.6

1.17 SUGGESTED READINGS

1. Thermal Physics : with Kinetic Theory, Thermodynamics : SC Garg.

2. Thermal Physics : R. Murugeshan, Er. Kiruthiga Siva Prasath.

3. Thermal Physics : C.B.P. Finn.

4. Heat Thermodynamics and Statistical Physics : Brij lal, Dr. N. Subrahmanyam, P.S. Hemne.

UNIT- 2   FIRST LAW OF THERMODYMICS

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2.3   Types of Work Done

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2.1 INTRODUCTION:

Thermodynamics is a branch of physics which deals with the energy and work of a system. Thermodynamics deals only with the large scale response of a system which we can observe and measure in experiments. Small scale gas interactions are described by the kinetic theory of gases. There are three principal laws of thermodynamics which are described on separate slides. Each law leads to the definition of thermodynamic properties which help us to understand and predict the operation of a physical system. We will present some simple examples of these laws and properties for a variety of physical systems, although we are most interested in the thermodynamics of propulsion systems and high speed flows. Fortunately, many of the classical examples of thermodynamics involve gas dynamics.

In our observations of the work done on, or by a gas, we have found that the amount of work depends not only on the initial and final states of the gas but also on the process, or path which produces the final state. Similarly, the amount

of <u>heat</u> transferred into, or from a gas also depends on the initial and final states and the process which produces the final state. Many observations of real gases have shown that the difference of the heat flow into the gas and the work done by the gas depends only on the initial and final states of the gas and does not depend on the process or path which produces the final state. This suggests the existence of an additional variable, called the internal energy of the gas, which depends only on the state of the gas and not on any process. The internal energy is a state variable, just like the temperature or the pressure. The first law of thermodynamics defines the internal energy (E) as equal to the difference of the heat transfer (Q) into a system and the work (W) done by the system.

$$E_2 - E_1 = Q - W$$

We have emphasized the words "into" and "by" in the definition. Heat removed from a system would be assigned a negative sign in the equation. Similarly work done on the system is assigned a negative sign.

The internal energy is just a form of energy like the potential energy of an object at some height above the earth, or the kinetic energy of an object in motion. In the same way that potential energy can be converted to kinetic energy while conserving the total energy of the system, the internal energy of a thermodynamic system can be converted to either kinetic or potential energy. Like potential energy, the internal energy can be stored in the system. *Notice, however, that heat and work cannot be stored or conserved independently since they depend on the process.* The first law of thermodynamics allows for many possible states of a system to exist, but only certain states are found to exist in nature. The <u>second law</u> of thermodynamics helps to explain this observation.

If a system is fully insulated from the outside environment, it is possible to have a change of state in which no heat is transferred into the system. Scientists refer to a process which does not involve heat transfer as an adiabatic process. The <u>implementation </u>of the first law of thermodynamics for

gases introduces another useful state variable called the <u>enthalpy</u> which is described on a separate page.

2.2 OBJECTIVES

After studying this Unit, student should able to

- Understand the concept of Enthalpy.

- Explain first law of Thermodynamics.

- Define Point and Path function.

- Understand the term degree of freedom.

- Compute the Mayer's relation.

- What is P-V indicator diagram.

2.3 TYPES OF WORK DONE

There are two types of work done

(i)   Closed system work

(ii)   Open system work

(i)   Closed System Work

- It is also called Non flow work.
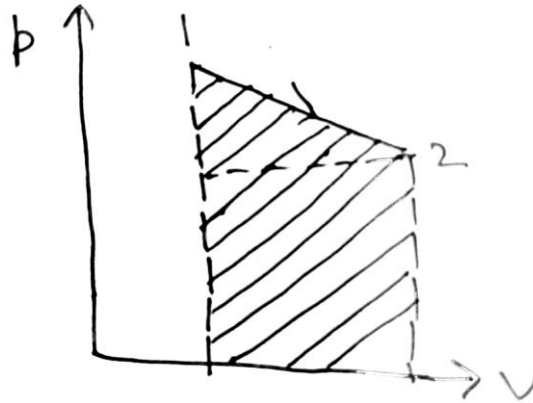
- Mathematically, If is written as

$$W = \int p\,dv$$

Figure : 1

(ii) Open System Work

- It is also collected flow work.

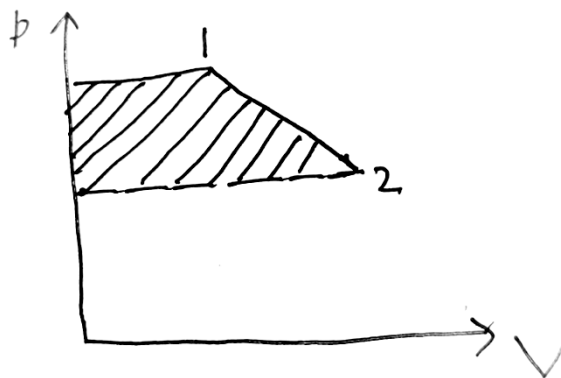- Mathematically, if is written as

$$W = -\int v\,dp$$

Figure : 2

2.4 POINT FUNCTION

Point function or State function

The property of a system which does not depends on Path of Process, but depends on states (two end condition of process), this property is called point function.

- Thermodynamics properties are point function, for given state, there is a definite value for each property.

- The thermodynamics properties of system change with change of state, it is independent of the path of the system.

- It depends only on the initial and final states of the system.

- Examples: Pressure, temperature, volume etc.

- The differential of Point Function are exact or perfect differentials and the integration is simply

$$\int_{V_1}^{V_2} dV = V_2 - V_1 \qquad (an\ exact\ differential)$$

- The change in Volume is depends only on the initial and final states of the system, not depends on the Path of the System follows
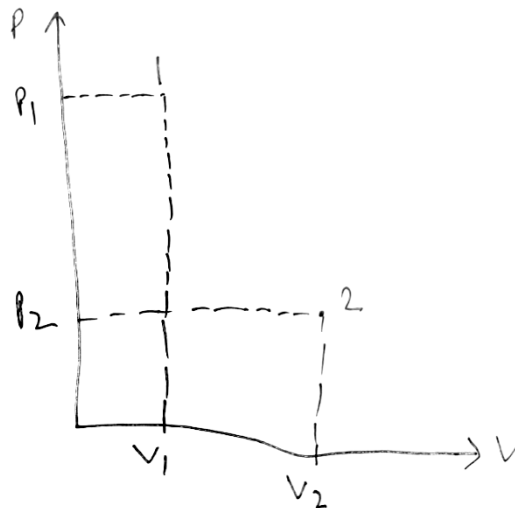
Figure : 3

2.5 PATH FUNCTION

There are certain quantities which cannot be located on a graph by a point but are represented by the area on that graph.

Those quantities are dependent on the path of the process and are called path function.

Examples: Work, heat, etc.

Heat and work are in exact differentials their change cannot be written as difference between, their initial and final (end) states.

$$\int_1^2 \delta Q \neq Q_2 - Q_1 \quad and \; is \; shown \; as \; Q_{12} \; and$$

$$\int_1^2 \delta W \neq W_2 - W_1 \quad and\ is\ shown\ as\ W_{12}$$

The operator (δ) is used to denote inexact differential operator (d) is used to denote exact differentials.
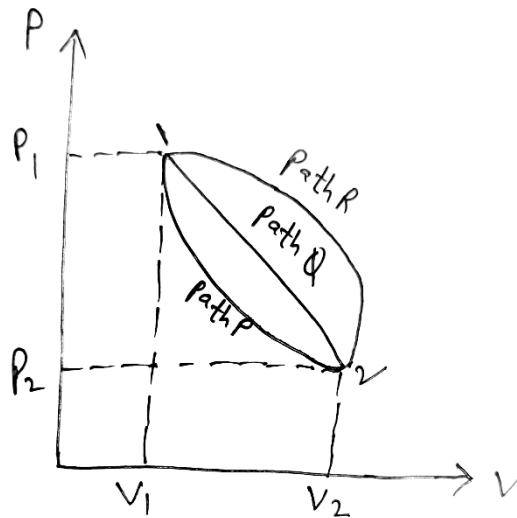

Figure : 4

2.6 INTERNAL ENERGY

An energy form inherent in every system is the internal energy, which arises from the molecular state of motion of matter. The symbol U is used for the internal energy and the unit of measurement is the joules (J).

Internal energy increases with rising temperature and with [changes of state](#) or phase from solid to liquid and liquid to gas. Planetary bodies can be thought of as combinations of heat reservoirs and heat engines. The heat reservoirs store internal energy E, and the heat engines convert some of this thermal energy into various types of mechanical, electrical and chemical energies.

Internal Energy Explanation

Internal energy U of a system or a body with well-defined boundaries is the total of the kinetic energy due to the motion of molecules and the potential energy associated with the vibrational motion and electric energy of atoms within molecules. Internal energy also includes the energy in all the CHEMICAL BONDS From a microscopic point of view, the internal energy may be found in many different forms. For any material or repulsion between the individual molecules.

Internal energy is a state function of a system and is an extensive quantity. One can have a corresponding intensive

thermodynamic property called specific internal energy, commonly symbolized by the lowercase letter u, which is internal energy per mass of the substance in question. As such the SI unit of specific internal energy would be the J/g. If the internal energy is expressed on an amount of substance basis, then it could be referred to as molar internal energy and the unit would be the J/mol.

Internal Energy of a Closed System

For a closed system the internal energy is essentially defined by

$$\Delta U = q + W$$

Where

- U is the change in internal energy of a system during a process

- q is the heat

- W is the mechanical work.

If an energy exchange occurs because of temperature difference between a system and its surroundings, this energy appears as

heat otherwise it appears as work. When a force acts on a system through a distance the energy is transferred as work. The above equation shows that energy is conserved.

The different components of internal energy of a system is given below.

Thermal energy	Sensible heat	Energy change of a system associated with: • Molecular translation, rotation, vibration. • Electron translation and spin. • Nuclear spin of molecules.
	Latent heat	Energy required or released for phase change, change from liquid to vapour phase requires heat of vaporization.
Chemical energy	Energy associated with the chemical bonds in a molecule.	

Nuclear energy	The large amount of energy associated with the bonds within the nucleus of the atom.

The physical and chemical processes that can change the internal energy of a system is given below.

Transferring energy across the system boundary by	Heat transfer	Energy transfer from a high temperature to low temperature state.
	Work transfer	Energy transfer driven by changes in macroscopic physical properties of a system such as compression or expansion work.
	Mass transfer	Energy transfer by mass flowing across a system boundary.
Change through internal processes	Mixing	Heat releases upon components mixing that may lead to lower

		internal energy.
	Chemical reaction	Heat required or released during a chemical reaction that changes chemical energy.
	Nuclear reaction	Heat released during a nuclear reaction that changes nuclear energy.

Internal Energy Change

Every substance possesses a fixed quantity of energy which depends upon its chemical nature and its state of existence. This is known as intrinsic energy. Every substance has a definite value of internal energy and is equal to the energies possessed by all its constituents namely atoms, ions or molecules.

The change in internal energy of a reaction may be considered as the difference between the internal energies of the two states.

Let E_A and E_b are the initial energies in states A and B respectively. Then the difference between the initial energies in the two states will be

$$\Delta U = E_B - E_A$$

The difference in internal energies has a fixed value and will be independent of the path taken between two states A and B. For the chemical reaction, the change in internal energy may be considered as the difference between the internal energies of the products and that of the reactants.

$$\Delta U = E_{products} - E_{reactants}$$

Thus, the internal energy, ΔU is a state function. This means that ΔU depends only on the initial and final states and is independent of the path. In other words, ΔU will be the same even if the change is brought about differently.

2.6.1 Enthalpy

Enthalpy is significant because it tells us how much heat is there in a system (energy). Heat is essential because it allows us to produce useful work. In this article, let's study Enthalpy.

The heat absorbed or released during a process at constant pressure is equal to the change in enthalpy.

Sometimes referred to as "heat content," enthalpy is a fascinating and uncommon word that most people prefer to use.

According to its Etymology, the words "entropy" and "enthalpy" are derivations of the Greek words for "turning" and "warming," respectively.

In terms of pronunciation, the first syllable of entropy is commonly stressed, whereas the later syllable of enthalpy is generally emphasised.

Enthalpy(H) is the sum of the internal energy(U) and the product of pressure(P) and volume(V).

Enthalpy H can be written as,

H = U + pV

Where, H = Enthalpy of the system

U = Internal energy of the system

p = Pressure of the system

V = Volume of the system

The heat added or lost by the system is measured as the change in enthalpy (ΔH), not the actual amount of heat. It is totally reliant on T, p, and U, the state functions. Enthalpy can also be written as:

- ΔH = ΔU + ΔPV

At constant temperature, the heat flow(q) for the process is equal to the change in enthalpy, which is expressed as

- Where ΔH = q (Heat Flow)

Enthalpy Units

Dimensions can be used to represent any physical quantity. Units are the arbitrary magnitudes assigned to the dimensions.

Dimensions are classified into two types: primary or fundamental dimensions and secondary or derived dimensions.

- **Primary dimensions:**

  - Example: Mass (m); length(l); time(t); temperature(T)

- **Secondary dimensions:**

  - Those which can be deduced from primary dimensions.

  - Example: Velocity(m/s^2), Pressure (Pa = kg/m.s^2).

- The Enthalpy is written as,

  - H = Energy/Mass

- The secondary physical quantity is enthalpy

  - SI Unit of Enthalpy: Joule

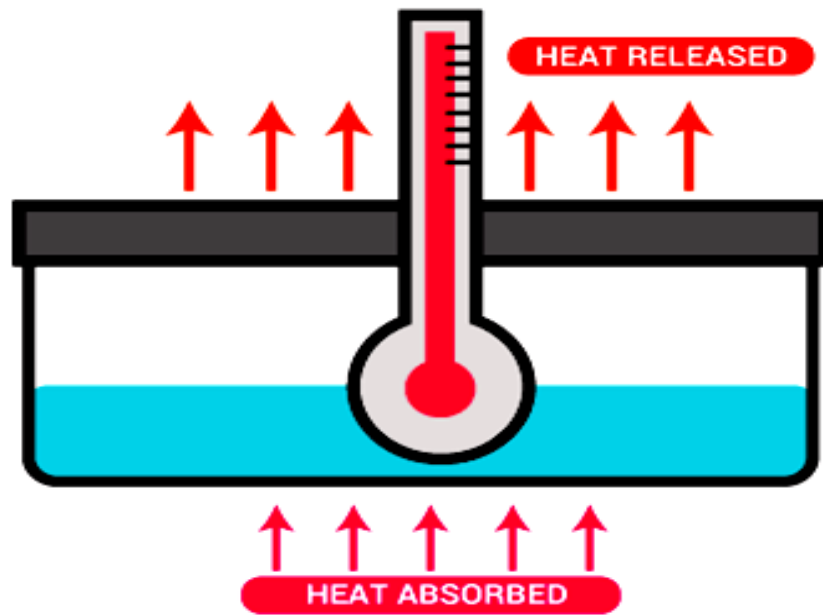 - Dimensional Formula: $[ML^2T^{-2}]$

Figure : 5

2.6.2 Internal Energy as a State or Point Function

We know that the thermodynamic properties which do not depend upon the path followed by the thermodynamic process are known as state properties. State property depends only upon the initial and final state of the system. The properties which depend upon the amount of matter are known as extensive properties.

As we know, the thermodynamic system can be described by a number of thermodynamic parameters such as pressure, volume, temperature, internal energy, enthalpy etc. These can be divided

into state functions and path functions. A state function is a property of a system whose value depends upon the initial and final states of the system. It is also known as point function. These types of functions describe an equilibrium state of a function and does not depend on how the system arrived in that state. For example, Internal energy is considered as a state function and is independent of the path followed to change the state of the system.

It is the total energy of a system. This is made up of a number of components such as translational kinetic energy of molecules, bond energy, electronic energy, intermolecular interaction energy of the constituents' particles of the system etc. Internal energy is a function of pressure, volume, temperature etc. These all variables are state functions. Other examples of state function include mass, volume, pressure, temperature, density, entropy etc. There are some variables that depend upon the amount of matter present. These are known as Extensive properties. Examples include mass, volume etc. Some other variables are independent of the amount of matter known as intensive

properties. Examples: density. Property of the system which depends upon only the state of the system and not on the path by which it is achieved is called state function. Internal energy does not depend on the path used to go from initial state to final state, but it depends on state. Internal energy of a system is an extensive   property.

Note:

Remember that the thermodynamic properties which depend upon the path followed by the thermodynamic process are known as path properties. Internal energy only depends upon the initial and final state of the system, not on the path followed. So, the internal energy is a state function.

2.6.3 Concept of Heat

Heat may be defined as the energy in transit. If flows from one point to another. If the flow of heat stops, we can not use the word heat i.e., the word heat may be used only when there is transfer of energy between two or more thermodynamic systems. When two bodies of different temperatures are placed in contact with each other, the two temperatures approach each

other and after some time become equal. This phenomenon is described by saying that energy has flown from one body to another. Thermodynamically this flow of energy from one body to another on account of difference of temperature between them is called heat. Thus the flow of heat is a non-mechanical energy transfer brought about by a temperature difference between two bodies. For example, if a system loses energy by conduction or radiation, we may say that it is giving up heat as the process of conduction or radiation depends upon the temperature difference between the system and its surroundings. But if a system loses energy by other methods, generally by working against external mechanical forces, it is said to do work. Thus work is the transfer of energy without a temperature difference. Hence, heat must e carefully distinguished from work.

Regarding heat, it is worth noting that :

(i)   Heat ΔQ is path dependent.

(ii) It is taken positive if the system absorbs heat and negative if releases it.

(iii) In case of solids and liquids

$\Delta Q = mL \rightarrow$ when temperature of state

$\Delta Q = mC . \Delta T \rightarrow$ when temperature changes by ΔT

(iv) For gases when heat is absorbed and temperature changes, for μ gm mole of gas

$(\Delta Q_V = \mu C_V . \Delta T \rightarrow$ when volume is constant

$(\Delta Q)_P = \mu C_P . \Delta T \rightarrow$ when pressure is constant

2.7 FIRST LAW OF THERMODYNAMICS

Before we get into the first law of thermodynamics we need to understand the relation between heat and work and the concept of internal energy. Just like mass, energy is always conserved i.e. it can neither be created nor destroyed but it can be transformed from one form to another. Internal energy is a thermodynamic property of the system that refers to the energy

associated with the molecules of the system which includes kinetic energy and potential energy.

Whenever a system goes through any change due to interaction of heat, work and internal energy, it is followed by numerous energy transfer and conversions. However, during these transfers, there is no net change in the total energy.

Similarly, if we look at the first law of thermodynamics it affirms that heat is a form of energy. What it means is that the thermodynamic processes are governed by the principle of conservation of energy. The first law of thermodynamics is also sometimes referred to as the Law of Conservation of Energy.
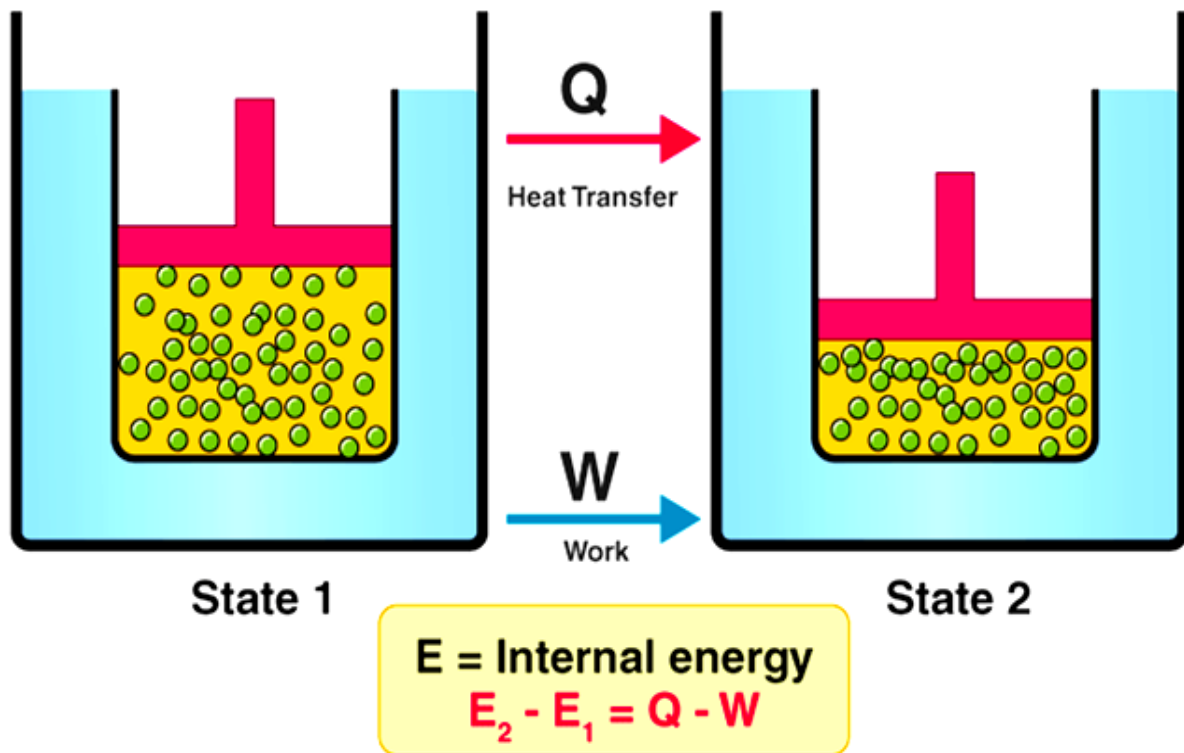
Figure : 6

A thermodynamic system in an equilibrium state possesses a state variable known as the internal energy(E). Between two systems the change in the internal energy is equal to the difference of the heat transfer into the system and the work done by the system.

2.7.1 Statement

The first law of thermodynamics states that the energy of the universe remains the same. Though it may be exchanged

between the system and the surroundings, it can't be created or destroyed. The law basically relates to the changes in energy states due to work and heat transfer. It redefines the conservation of energy concept.

The First Law of Thermodynamics states that heat is a form of energy, and thermodynamic processes are therefore subject to the principle of conservation of energy. This means that heat energy cannot be created or destroyed. It can, however, be transferred from one location to another and converted to and from other forms of energy.

To help you understand the meaning of the First Law, we can take the common example of a <u>heat engine</u>. In a Heat engine, the thermal energy is converted into mechanical energy and the process also is vice versa. Heat engines are mostly categorized as an open system. The basic working principle of a heat engine is that it makes use of the different relationships between heat, pressure and volume of a working fluid which is usually a gas. Sometimes phase changes might also occur involving a gas to liquid and back to gas.

2.7.2 Derivation

The internal energy of a system can be increased in two ways

(i)   By applying heat to the system

(ii)   By doing some work on the system

Suppose initially the internal energy of the system $= U_1$. It absorbs heat (q), its energy will become $= U_1 + q$ further, W is the work done on the system, then the internal energy further increased and becomes $= U_1 + q + w$.

Let the final internal energy $= U_2$

$$U_2 = U_1 + q + w$$

$$U_2 - U_1 = q + w$$

$$\boxed{\Delta U = q + w} \qquad \qquad \ldots\ldots\ldots (1)$$

Equation (1) is called mathematical formulation of first law of thermodynamics.

Here, we consider work of expansion,

Work done by the system   (w) = -PΔV   ……. (2)

Where, P → External Pressure

Putting Equation (2) in Equ. (1), we get

ΔU = q - PΔV

Now, $\boxed{q = \Delta U + P\Delta V}$ ……………….. (3)

Equation (1) can be rewritten as

$$\boxed{dU = \delta q + \delta w}$$

Where, dU – very-very small change in internal energy. It is represented by (d) because (d) is a state function and it is an exact differential, whereas q and w are path function and they are in exact differential equation, small changes denoted by (δ) Equation (3) can be rewritten as

$$\boxed{\delta q = dU + PdV}$$

Here, Volume is a state function.

If differential will be exact.

2.7.3 Limitation

1. The first law of thermodynamics does note state anything about the heat flow direction.

2. The process is not reversible.

3. It is difficult to distinguish whether the process is spontaneous or not.

2.7.4 Application

(1) **Isothermal Process :** In isothermal process, temperature of the system remains constant. Since, internal energy of a system depends on temperature, it will not change in isothermal process, i.e., $dU = 0$. Therefore, applying first law of thermodynamics

$$dQ = dU + dW \quad 0 - dW$$

or $\qquad dQ = dW$

∎ Heat received by the system = External mechanical work done

(2) **Adiabatic Process :** In adiabatic process, no heat flows into or out of the system, i.e., $dQ = 0$. Therefore, from first law

$$O = dU + dW$$

or $\qquad\qquad dU = -dW$

∎ Change in internal energy = negative of the work done

Thus if work is done by the system

$$dU = -dW \qquad \text{(positive work)}$$

And if work is done on the system

$$dU = (-dW) = dW \qquad \text{(negative work)}$$

i.e., internal energy of the system will increase.

Thus if a gas is adiabatically compressed (work done on the system, negative work), $dU = dW$, i.e., internal energy

and hence the temperature of the gas increases. If, on the other hand, gas expands asdiabatically (work done by the system, positive work), then $dU = -dW$ and hence temperature of the gas will fall, i.e., external work is done by the gas at the cost of its internal energy.

(3) **Isobaric Process :** Pressure of the system remains constant in isobaric process. Boiling of water into steam and freezing of water into ice are the examples of isobaric process. These process are isothermal as well.

Suppose m mass of water is changed into steam at constant pressure. Then heat absorbed by water in the process

$$dQ = mL$$

If V is the volume of water in liquid state and V_v in the vapour state, then work done by the system

$$dW = P.dV = P(V_v - V)$$

Applying first law to the process

$$dQ = dU + dW$$

$$dW = dQ - dW = mL - P(V_v - V)$$

Similarly, the change in internal energy in the process of freezing

$$dU = dQ - dW = -mL - P(V_{ice} - V)$$

because during freezing heat is given by the water (dQ is negative).

(4) **Isochoric Process :** Volume of the system remains constant in isochoric process. Hence

$$dW = P.dV = 0$$

Therefore, from first law

$$dQ = dU + 0 = dU$$

Thus, entire heat taken by the system, increases its internal energy and hence the temperature of the system increases.

(5) **Cyclic Process :** In cyclic process, the system returns to its initial state after a series of changes. Thus in the process, there is no change in the internal energy of the system i.e., $dU = 0$.

Hence, from first law of thermodynamics,

$$dQ = dU + dW = 0 + dW$$

In the differential form, we may write

$$\oint dQ = \oint dW$$

Thus for a closed system undergoing a cyclic process, the entire heat entering the system is used up in doing external work.

(6) **Free Expansion :** In free expansion, no heat enters or leaves the system (adiabatic process) and also no work is done by or on the system. Thus in the expansion.

$$dQ = 0, \ dW = 0$$

Therefore, from first law

$$dQ = dU + dW$$

$$0 = dU + 0$$

$$\square \qquad\qquad U_i = U_f$$

Thus, in free expansion, initial and final internal energies are equal. Consider a system made of rigid walls, and covered by asbestos. If it is divided into two parts one containing gas and another vacuum and the partition is suddenly broken, then it will be the free expansion of the gas.

2.7.5 Significance

Significances that the first law of thermodynamics has are as follows :

- The relation between heat and work is established by the first law of thermodynamics.

- Both work and Heat are equivalent to each other.

- The exact equivalent amount of energy of the surrounding will be lost or gained, if any system gains or loses energy.

Applied heat is always equal to the sum of work done and change in internal energy. The energy is constant for an isolated system.

2.8   DEGREE OF FREEDOM

The number of independent ways in which a molecule of gas can move is called the degree of freedom.

It is an independent physical parameter in the formal description of the state of a physical system. The degrees of freedom refers to the number of ways a molecule in the gas phase may move, rotate, or vibrate in space. The number of degrees of freedom a molecule possesses plays a role in estimating the values of various thermodynamic variables using the equipartition theorem.

There are three types of degrees of freedom, such as translational, rotational, and vibrational. The number of degrees of freedom of each type possessed by a molecule depends on both the number of atoms in the molecule and the geometry of the molecule, with geometry referring to the way in which the atoms are arranged in space.

Types of degree of freedom

A gaseous molecule has a certain number of degrees of freedom, such as the ability to translate (the motion of its centre of mass

through space), rotate around its centre of mass, or vibrate (as its bond lengths and angles change). Many physical and chemical properties depend on the energy associated with each of these modes of motion. If a molecule has N number of independent particles, then total degree of freedom in three dimensions of the molecule is determined by: **F= 3N**

(a) Translational degree of freedom

Translational degrees of freedom arise from the ability of gas molecules to move freely in space. A molecule may move in the *x*, *y,* and *z* directions of a Cartesian coordinate system. When the centre of mass of a particle moves from its initial position to a new position, we say that the particle is having a translational motion along the x-axis, y-axis and z-axis. So, the translational motion of the molecule of gas has three degrees of freedom associated with it. This is applicable for all gas molecules, whether they are monatomic, diatomic, or polyatomic, as any molecule may move freely in all directions in three-dimensional space.
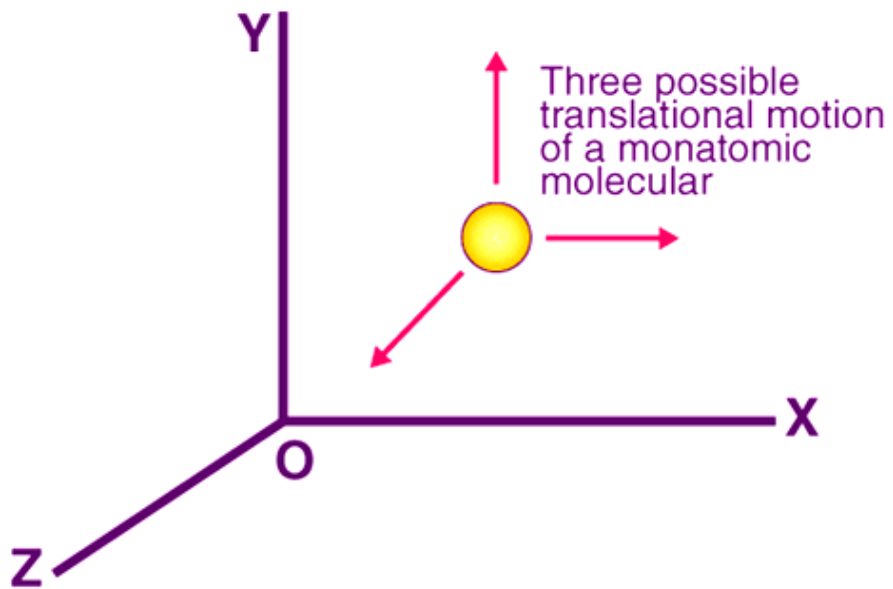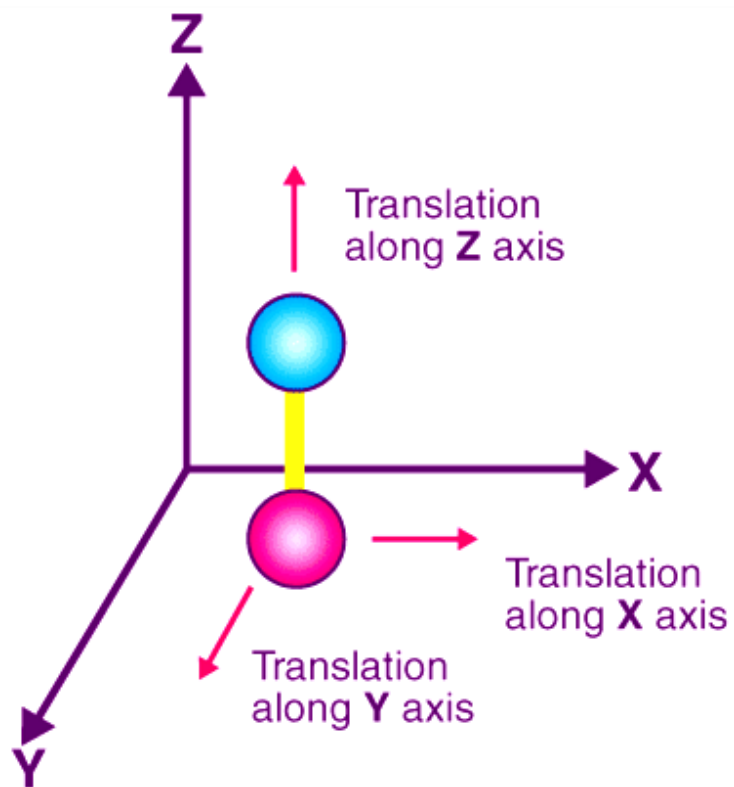
Figure : 7

Figure : 8

(b) Rotational degree of freedom

A molecule's rotational degrees of freedom represent the number of unique ways the molecule may rotate in space about its center of mass with a change in the molecule's orientation. A monatomic gaseous molecule such as a noble gas possesses no rotational degrees of freedom, as the center of mass sits directly on the atom and no rotation which creates change is possible. In the below image a diatomic molecule lying along the Y-axis can undergo rotation about the mutually perpendicular X-axis and Z-axis passing through its centre of gravity, This shows that the linear molecule has **two** rotational degrees of freedom. However, non-linear molecules have **three** rotational degrees of freedom.
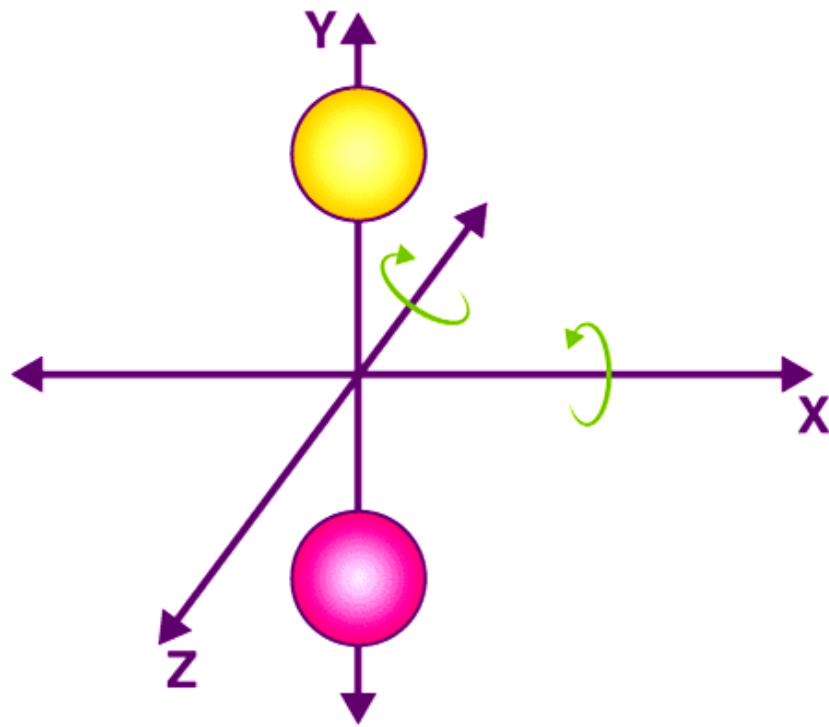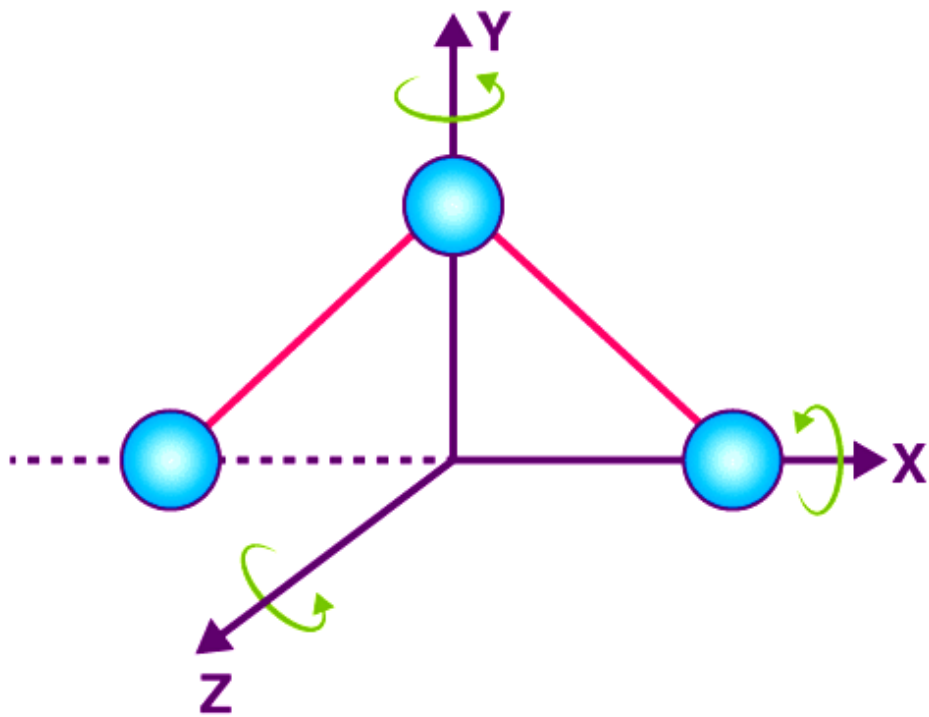
Figure : 9

Figure : 10

(c) Vibrational degree of freedom

The atoms of a molecule can also vibrate and these vibrations of the atoms of a molecule slightly change the internuclear distances between the atoms of the molecule. The number of vibrational degrees of freedom (or vibrational modes) of a molecule is determined by examining the number of unique ways the atoms within the molecule may move relative to one another, such as in bond stretches or bends.

As already mentioned, atoms possess only a translational degree of freedom. A diatomic molecule has only one vibrational degree of freedom During the vibrational motion the bonds of the molecules behave like a spring and the molecule exhibits simple harmonic motion.

A polyatomic molecule containing N atoms has 3N degrees of freedom. If we subtract the translational and rotational degree of freedom from the total degree of freedom please find the total number of vibrational degrees of freedom of linear and nonlinear molecules.
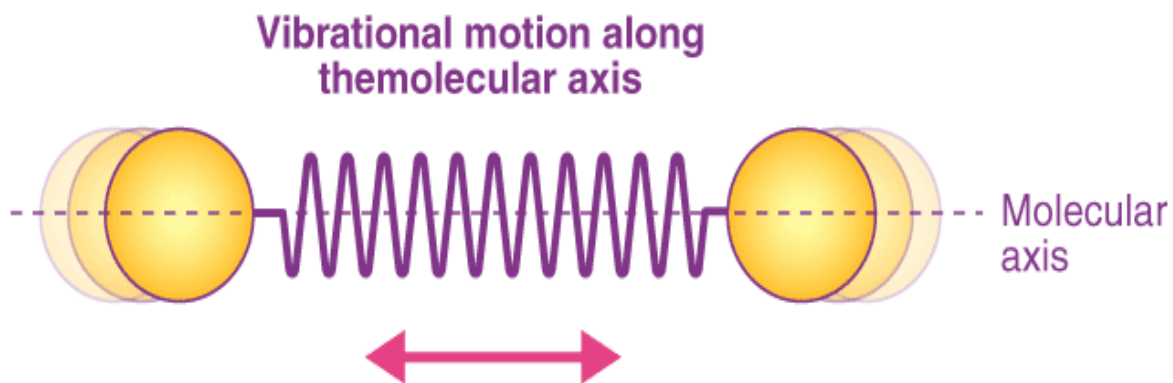
Figure : 11

Degree of freedom	Monatomic	Linear molecules	Non-linear molecules
Translational	3	3	3
Rotational	0	2	3
Vibrational	0	$3N - 5$	$3N - 6$
Total	3	$3N$	$3N$

Equipartition law of energy

For a system in equilibrium, there is an average energy of ½ kT or

½ RT per molecule associated with each degree of freedom. (where

k = Boltzmann constant and T is the temperature of the system). This energy associated with each degree of freedom is in the form of kinetic energy and potential energy.

- One translational degree of freedom = ½ kT or ½ RT

- One rotational degree of freedom= ½ kT or ½ RT

- One vibrational degree of freedom= kT or RT

Note: As regards the vibrational motion, two atoms oscillate against each other therefore both potential and kinetic energy the energy of vibration involve two degrees of freedom, so that vibrational motion in a molecule is associated with energy= 2 x ½ kT = kT

Total energy E= E_{tr} + E_{rot} + E_{vib} + E_{elc}

Points to be noted:

- At room temperatures, the degrees of freedom need **not include** the **vibrational modes**. For molecules to vibrate in their normal modes they require much higher energies which is not possible at room temperature.

Energy contribution for linear molecules

Degree of freedom	Translational	Rotational	Vibrational
Linear molecule	3	2	3N-5
Energy contribution At room temperature	3 x ½ kT	2 x ½ kT	Inactive (no contribution)
Energy contribution At high temperature	3 x ½ kT	2 x ½ kT	(3N-5) x kT

Energy contribution for non-linear molecules

Degree of freedom	Translational	Rotational	Vibrational
non-linear	3	3	3N-6

molecule			
Energy contribution At room temperature	3 x ½ kT	3 x ½ kT	Inactive (no contribution)
Energy contribution At high temperature	3 x ½ kT	3 x ½ kT	(3N-6) x kT

Degree of freedom of monoatomic gas

- Since a monatomic molecule consists of only a single atom of point mass it has three degrees of freedom of translatory motion along the three coordinate axes x, y and z.

- Examples: Molecules of Inert gases like helium(He), Neon(Ne), Argon(Ar), etc.

Degree of freedom of diatomic molecule

- The diatomic molecule can rotate about any axis at right angles to its own axis. Hence it has **two** rotational degrees of freedom, in addition, it has **three** translational degrees of freedom along the three axes. A diatomic molecule shows **one** vibrational degree of freedom. So, a diatomic molecule has a total of **six** degrees of freedom at high temperatures.

- At room temperature the total degree of freedom of a diatomic molecule is **five** because vibrational motion is not contributed. Examples: molecules of O_2, N_2, CO, Cl_2, etc.

Degree of freedom of triatomic molecule

- In the case of a triatomic molecule of linear type, the centre of mass lies at the central atom.

- It, therefore, behaves like a diatomic molecule with **three** degrees of freedom of translation and **two** degrees of freedom of rotation, it has **five** degrees of freedom as shown at room temperature.

- At high temperatures, It shows four vibrational degrees of freedom. Hence, it shows a total of **nine** degrees of freedom. Examples: molecules of CO_2, CS_2, etc.

- At room temperature a triatomic **nonlinear molecule** possesses **three** degrees of freedom of rotation in addition to **three** degrees of freedom of translation. Hence it has **six** degrees of freedom.

- At high temperatures, it shows a total of **nine** degrees of freedom. Examples : molecules of H_2O, SO_2, etc

2.9 HEAT CAPACITY RATIO

In thermal physics and thermodynamics, the **heat capacity ratio**, also known as the **adiabatic index**, the **ratio of specific heats**, or **Laplace's coefficient**, is the ratio of the heat capacity at constant pressure (C_P) to heat capacity at constant volume (C_V). It is sometimes also known as the *isentropic expansion factor* and is denoted by γ (gamma) for an ideal gas or κ (kappa), the isentropic exponent for a real gas. The symbol γ is used by aerospace and chemical engineers.

$$\gamma = \frac{C_P}{C_V} = \frac{\bar{C}_P}{\bar{C}_V} = \frac{c_P}{c_V},$$

where C is the heat capacity, $\bar{C}$ the molar heat capacity (heat capacity per mole), and c the specific heat capacity (heat capacity per unit mass) of a gas. The suffixes P and V refer to constant-pressure and constant-volume conditions respectively.

The heat capacity ratio is important for its applications in thermodynamical reversible processes, especially involving ideal gases; the speed of sound depends on this factor.

2.10 MAYER'S RELATION

When a gas is heated at constant pressure it expands. Therefore, heat supplied at constant pressure is partly used in doing work and partly in raising temperature of the gas. On the other hand, when gas is heated at constant volume no work is done (dW=P. dV=0) and hence whole of the heat supplied is used to raise the temperature of the gas. Thus more heat is required for increasing the temperature of the gas through 1°C at constant pressure than at constant volume. Hence specific heat of a gas at constant

pressure is greater than the specific heat at constant volume, i.e., $c_P > c_V$.

In order to bring out clearly the application of the first law of thermodynamics, let us find a relation expressing the difference between two specific heats of a gas. For it, consider two isothermals AB and CD drawn for 1 mole of an ideal gas at close temperatures T and $(T + \Delta T)$. Let the initial state of the gas be represented by point M on lower isothermal at T. Let it now be heated at constant volume until its temperature rises to $T + \Delta T$ and its new pressure corresponds to point L on the upper isothermal CD. As the volume of the gas is kept constant no external work has been done by the gas and hence the change in internal energy in the process $M \rightarrow L$ is given by first law to be

$$U_L - U_M = \Delta Q - \Delta W = c_V \, \Delta T \qquad (\Delta W = 0) \qquad \text{...... (i)}$$

Again starting from the same initial condition of the gas represented by M, let it now be heated at constant pressure until its temperature rises to $(T + \Delta T)$ and its now volume $(V + \Delta V)$

corresponds to point N on upper isothermal CD. Hence the change in internal energy in the process $M \rightarrow N$ is

$$U_N - U_M = \Delta Q - \Delta W = c_P \Delta T - P\Delta V$$

…….. (ii)

because in the case $\Delta Q = c_P \Delta T$ and work performed by the gas $\Delta W = P. \Delta V$.

Since the gas is supposed to be a perfect one, the perfect gas equation $(PV = RT)$ holds good. In the initial position at M, the pressure volume and temperature of the gas were respectively P, V and T while at N volume becomes $(V + \Delta V)$ and temperature $(T + \Delta T)$. Hence according to gas equation at M and N respectively, we have

$$PV = RT \qquad\qquad\qquad ……. \text{(iii)}$$

and $\qquad P(V + \Delta V) = R(T + \Delta T)$

……. (iv)

Subtracting eq. (iii) from (iv), we have

P. $\Delta V = R. \Delta T$

Putting this value of P. ΔV in eqn. (ii), we get

$U_N - U_M = c_P. \Delta T - R. \Delta T$

$\qquad$ …….. (v)

As the internal energy of a gas depends only upon its temperature the same change in internal will take place in both the processes M → L and M → N because temperature changes from T to T + ΔT in both the processes. Thus

$U_L - U_M = U_N - U_M$

or $\quad$ $c_V \Delta T = c_P \Delta T - R. \Delta T$ $\qquad$ [using eqns. (i) and (v)]

or $\quad$ Dividing throughout by ΔT, we have

$c_V = c_P - R$

or $\quad$ $c_P - c_V = R$ $\qquad$ …….. (vi)

This formula is known as Mayer's formula. All these quantities c_P, c_V and R in this equation should be expressed in the same units either in Joule/mole^{o}C or in cal/mol^{o}C.

2.11 THERMODYNAMIC PROCESSES

We know that if we have to take a thermodynamic system from the initial to the final state, we have several paths that can be taken. In this article, we will be discussing those thermodynamic processes. Before that, we will see what a quasi-static process is. It has been discussed that state variables are defined only when the thermodynamic system is in equilibrium with the surrounding. So a process in which the system is in thermodynamic equilibrium with the surrounding is known as a quasi-static process at each moment.

2.11.1 Cyclic

It is a process in which the final state of the system is equal to the initial state. As we know, change in internal energy is a state function, so, in this case, $\Delta U = 0$.

2.11.2 Isobaric

The pressure remains constant during this process. So,

$$W = P(V_f - V_i)$$

So if volume increases, work done is positive, else negative.

Key Points

- Pressure = Constant during this process

- W = PΔV

  - So if volume increases, work done is positive, else negative.

- According to thermodynamic 1st law lof thermodynamics

  - Q = W + dU

  - Q = PΔV + dU

2.113 Isochoric

In isochoric process the change in volume of thermodynamic system is zero. A volume change is zero, so the work done is zero.

- Volume of the system = Constant

- Change in volume = 0

- If, change in volume = 0, then work done is zero.

- According to the 1st law of thermodynamic law

  - $Q = W + dU$

  - If $W = 0$

  - $Q = dU$

2.11.4 Isothermal

It is a thermodynamic process in which temperature remains constant.

We know,
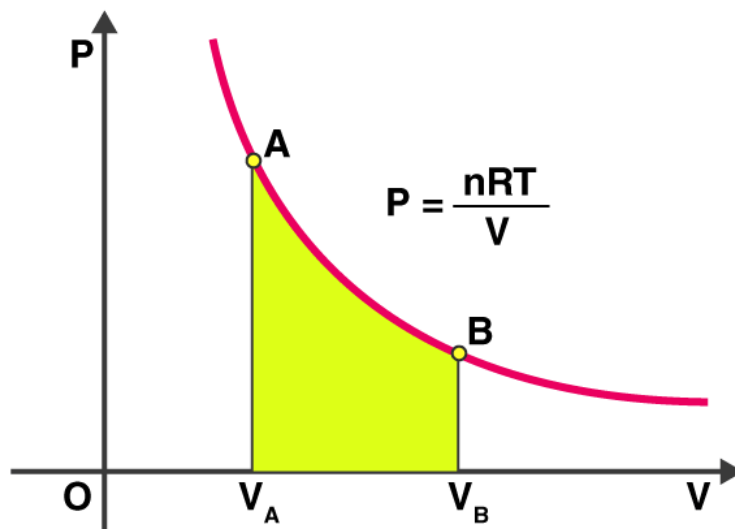
$$P = \frac{nRT}{V}$$

Figure : 12

$W = \int P dV$

According to Gas law,

$PV = nRT$

$P = \frac{nRT}{v}$

Using this value of P in work done, we get,

$W = nRT \int_{V_A}^{V_B} \frac{dV}{V}$

$W = nRT \ln \frac{V_B}{V_A}$

Key Points

- $W = +ve$ (VB > VA)

- $W = -ve$ (VA > VB)

- dU = 0

  ○ Internal energy only depends on temperature

  ○ If temperature = Constant

  ○ Internal Energy = Constant.

- From <u>first law of thermodynamics,</u>

  - $Q = W + dU$

  - $Q = W$ (dU = 0)

2.11.5 Adiabatic

It is a thermodynamic process in which no heat is exchanged between the system and the surrounding. So, Q = 0. Mathematically this process is represented as

$$PV^\gamma = K(constant)$$
$$W = \int PdV$$

Substituting P, we get,

$$W = K \int_{V_i}^{V_f} \frac{dV}{V^\gamma}$$

$$W = K \frac{(V_f^{1-\gamma} - V_i^{1-\gamma})}{1-\gamma}$$

For adiabatic process,

$$\Delta U = -W$$

Key Points

- According to the 1st law of thermodynamic process

- $Q = W + dU$

- If $Q = 0$

- $dU = -W$

So if <u>work done</u> is negative internal energy increases and vice versa.

2.12 P-V INDICATOR DIAGRAM

It is just a graph between pressure and volume of a system undergoing an operation. It is used to find out indicated horse power of an engine and provides us a mean to represent the working of an engine and to calculate the work obtained from it.

Suppose a given mass of a working substance, say a gas, is contained in a cylinder fitted with a movable and frictionless piston. Let P and V be the pressure and volume of the gas and A the area of cross-section of the piston. Suppose now, the gas expands very slowly pushing the piston out through an

infinitesimal distance dx. The external work done during expansion by the gas

dW = Force exerted on the piston × displacement

= (P × A) × dx = P × (A × dx)

= P dV

Where dV = (A × dx) is the increase in volume of the gas.

If the gas expands from an initial state (P_1, V_1) to a final state (P_2, V_2), then total work done by the gas during the process

$$W = \int_{V_1}^{V_2} P \, dV$$

Let us now represent the initial state (P_1, V_1) of the gas by the point A and its final state (P_2, V_2) by the point B on a pressure volume diagram (Fig. 2). The intermediate changes of the process are represented by different points on the line AB which, therefore, represents the whole operation.

At any point such as E during this change, let the pressure of the gas be P and let its volume increases by an infinitesimal close

dV to reach point F which is infinitestimally close to E. The shaded strip EFGH may be regarded as a rectangle of area P.dV. But P.dV is the amount of work done by the gas during the small expansion dV. Thus the work done by the gas P.dV is represented by the area of the shaded strip.

The total work done by the gas in moving from A to B is clearly equal to the sum of areas of all such strip i.e., equal to the area ABCD bounded between the curve AB and the volume axis from V_1 to V_2.

Hence $$W = \int_{V_1}^{V_2} P \,. dV = Area\ of\ ABCDA$$

Thus on an indicator diagram the area between the P-V curve, the volume axis and the two ordinates at the extremities of the P-V diagram gives directly the work done during the operation.

2.13 WORK DONE DURING AN ADIABATIC PROCESS

Let us consider one gm mole of a perfect gas enclosed in a cylinder having perfectly insulated walls. Lets if expand adiabatically from an initial volume V_1 to a final volume V_2. Then work done by the gas during this expansion is given by

$$W = \int_{V_1}^{V_2} P \, . \, dV$$

Where P is the instantaneous pressure of the gas while suffering an infinitesimal expansion dV.

Now during an adiabatic process

$$PV^y = K \text{ constant}$$

$$P = \frac{K}{V^\gamma}$$

Therefore, $W = \int_{V_1}^{V_2} K \frac{dV}{V^\gamma} = K \int_{V_1}^{V_2} V^{-\gamma} \, dV$

or $\quad W = K \left[\frac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_1}^{V_2} = \frac{K}{1+\gamma} \left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right]$

.... (i)

But in adiabatic process

$$P_1 V_1^\gamma = P_2 V_2^\gamma = K$$

$\square \qquad W = \frac{1}{1-\gamma} \left[\frac{P_2 V_2^\gamma}{V_2^{\gamma-1}} - \frac{P_1 V_1^\gamma}{V_1^{\gamma-1}} \right]$

$\qquad = \frac{1}{1-\gamma} [P_2 V_2 - P_1 V_1] \qquad \qquad .... \text{(ii)}$

$$= \frac{1}{1-\gamma}[RT_2 - RT_1]$$

Thus $\qquad W = \frac{R}{\gamma-1}[T_1 - T_2] \qquad$ ………………

(iii)

Hence the work done in adiabatic process depends only upon the initial and final temperatures T_1 and T_2. Thus the work done along any adiabatic between two isothermals is independent of the particular adiabatic. Also

Work done in adiabatic Process = Decrease in internal energy of the gas.

2.14 WORK DONE DURING AN ISOTHERMAL PROCESS

Work is done by a gas when it is allowed to expand isothermally.

Let the initial and final volumes of 1 gm. mole of an ideal gas be V_1 and V_2 respectively. Then the work done for a very small change in volume dV.

$$dW = P.dV$$

When the gas expends from volume V_1 to V_2, at constant temperature T, then work done

$$W = \int_{V_1}^{V_2} P \ dV$$

Since expansion is isothermal,

$$PV = RT \qquad or \qquad P = \frac{RT}{V}$$

☐ $\qquad W = RT \int_{V_1}^{V_2} \frac{dV}{V} = RT \ log_e \frac{V_2}{V_1}$

Thus $\qquad\qquad W = 2.3026 \ RT \ log_{10} \frac{V_2}{V_1}$

2.15. WORK DONE DURING AN ISOBARIC PROCESS

Let the initial and final volumes of one gm. mole of a perfect gas enclosed in an expanding chamber in which the pressure is kept constant be V_1 and V_2. The work done for a very small change in volume dV

$$dW = P.dV$$

When the gas expands from V_1 to V_2.

Work done $\qquad W = \int_{V_1}^{V_2} P.\,dV$

or $\qquad W = P(V_2 - V_1)$

because the pressure is kept constant in an isobaric process.

2.16 ADIABATIC EQUATION OF A PERFECT GAS

Let us consider one gm. molecule of a perfect gas thermally insulated from its surroundings. Let it suffer a very small adiabatic expansion doing external work at the cost of its own internal energy. The temperature of the gas, therefore, falls.

If the volume of the gas increases by an infinitesimal amount dV against an external pressure P, the external work done by the gas in its expansion will be

dW = P .dV

……….. (i)

Since in a perfect gas, the molecules do not attract one another, the internal energy depends only on its temperature. Hence the decrease in internal energy of the gas, suffering a fall dT in its temperature, is equal to the heat drawn from it i.e.,

$$dU = 1 \times C_V \times dT \qquad\qquad\qquad\qquad \text{……….. (ii)}$$

where C_V is the specific heat for one gm. mole of the gas at constant volume.

Applying now the first law of thermodynamics

$$dQ = dU + dW$$

or $\qquad\qquad\qquad\qquad dQ = C_V\ dT + P\ .dV$

where dQ, $C_V\ dT$ and $P\ .dV$ are all measured in the same units i.e., either Joules or in calories.

Since in an adiabatic change, no heat is supplied from outside.

Hence $\qquad\qquad\qquad\qquad dQ = 0.$

Therefore, we have

$$C_V\ dT + P\ .dV = 0 \qquad\qquad \text{…………….. (iii)}$$

Also for one gm. molecule of a perfect gas we have the relation

$$PV = RT \qquad \text{(R being gas constant)}$$

Which on differentiation yields

P .dV + V .dP = R dT

or $\qquad dT = \dfrac{P\,.dV + V\,.dP}{R}.$

Putting this value in equation (iii),

$$C_V = \left(\frac{P\,.dV + V\,.dP}{R}\right) + P\,.dV = 0$$

or $\quad$ C$_V$ (P .dV + V .dP) + R(P .dV) = 0

But from Mayer's relation

$$C_P - C_V = R$$

$\square \quad C_V = (P.dV + V.dP) + (C_P - C_V)\,P.dV = 0$

or $\quad$ C$_V$ .V .dP + C$_P$. P .dV = 0

Dividing by C$_V$ P$_V$,

$$\frac{dP}{P} + \frac{C_P}{C_V}\frac{dV}{V} = 0$$

But $\dfrac{C_P}{C_V} = \gamma$, the ratio of the principal specific heats of the gas.

Hence $\qquad \dfrac{dP}{P} + \gamma\dfrac{dV}{V} = 0.$

Integrating, $\log P + \gamma \log V = $ constant

or $\quad \log PV^\gamma = constant$

or $\quad \boxed{PV^\gamma = constant}$ .... (iv)

This is the equation connecting pressure and volume during adiabatic process and is known as Poisson's law.

There are two other forms of the above relation.

Relation between temperature and volume : Putting $P = \dfrac{RT}{V}$ in eq. (iv), we get

$$\frac{RT}{V} V^\gamma = constant$$

or $\quad \boxed{TV^{\gamma-1} = constant}$ .... (v)

2.17 SUMMARY

The first law of thermodynamics is the application of the conservation of energy principle to heat and thermodynamic processes:

The change in internal energy of a system is equal to the heat added to the system minus the work done by the system.

$$\Delta U = Q - W$$

Change in internal energy

Heat added to the system

Work done by the system

The first law makes use of the key concepts of <u>internal energy</u>, <u>heat</u>, and <u>system work</u>. It is used extensively in the discussion of <u>heat engines</u>. The standard unit for all these quantities would be the joule, although they are sometimes expressed in <u>calories or BTUs</u>.

It is typical for chemistry texts to write the first law as $\Delta U = Q + W$. It is the same law, of course - the thermodynamic expression of the conservation of energy principle. It is just that W is defined as the work done on the system instead of work done by the system. In the context of physics, the common scenario is one of adding heat to a volume of gas and using the expansion of that gas to do work, as in the pushing down of a piston in an internal combustion engine. In the context of chemical reactions and processes, it may be more common to

deal with situations where work is done on the system rather than by it.

2.18 TERMINAL QUESTIONS:

1. State and Explain First law of Thermodynamics.

2. Difference between Point and Path function.

3. Explain briefly P-V indicators diagrams.

4. What is degree of freedom.

5. What is Enthalpy.

6. Define the term Internal Energy.

7. Prove that C_P-C_V = R for Ideal gas.

8. Explain isothermal, adiabatic, isobaric and isochoric processes.

9. Derive an expression for the work done during an isothermal process.

10. What is the physical significance of first law of thermodynamics.

11. Write short notes on the following :

    (a)   First law of thermodynamics

    (b)   Internal Energy

    (c)   Enthalpy

    (d)   Isobaric and Isochoric Process

12. Which of the following processes is reversible

    (a)   Heat conduction

    (b)   Change of state

    (c)   Diffusion

    (d)   Radiation

13. Zeroth law of thermodynamics is related to

    (a)   Temperature

    (b)   Heat

    (c)   Internal energy

    (d)   Work

14. Which of the following function is path independent

    (a) Work

    (b) Heat

    (c) Temperature

    (d) Internal energy

15. In which process no heat is required

    (a) Isothermal

    (b) Isobaric

    (c) Isochoric

    (d) Free expansion

16. In which process net work done is zero

    (a) Cyclic

    (b) Free expansion

    (c) Isothermal

    (d) Adiabatic

17. In which process there is a change in internal energy of the system

     (a) Isothermal

     (b) Adiabatic

     (c) Free expansion

     (d) Cyclic

18. An adiabatic process occurs at constant

     (a) temperature

     (b) pressure

     (c) heat

     (d) none of above

19. The internal energy of a real gas depends upon :

     (a) temperature

     (b) pressure

     (c) volume

(d)   temperature and volume both

20.   The first law of thermodynamics is a special case of

(a)   Newton's law

(b)   Charle's law

(c)   law of heat exchange

(d)   law of conservation of energy

2.19 ANSWER AND SOLUTIONS OF TERMINAL QUESTION

1.   Section 2.7

2.   Section 2.4 & 2.5

3.   Section 2.12

4.   Section 2.8

5.   Section 2.6.1

6.   Section 2.6

7.   Section 2.10

8.   Section 2.11

9. Section 2.14

10. Section 2.7.5

11. (a) Section 2.7

    (b) Section 2.6

    (c) Section 2.6.1

    (d) Section 2.11.2, 2.11.3

12. (b) 13. (a) 14. (d) 15. (d) 16. (b)

17. (b) 18. (c) 19. (d) 20. (d)

2.20 SUGGESTED READINGS

1. Thermal Physics: with Kinetic Theory, Thermodynamics: SC Garg.

2. Thermal Physics: R. Murugeshan, Er. Kiruthiga Siva Prasath.

3. Thermal Physics: C.B.P. Finn.

4. Heat Thermodynamics and Statistical Physics: Brij lal, Dr. N. Subrahmanyam, P.S. Hemne.

UNIT - 3   SECOND LAW OF THERMODYMICS

3.1   Introduction

3.2   Objectives

3.3   Need of Second Law

3.4   Carnot Cycle

    3.4.1 P-V diagram

    3.4.2 T-S diagram

3.5   Carnot Heat Engine and Refrigerator

3.6   Thermal Efficiency

3.7   Coefficient of Performance

3.8   Carnot Theorems

    3.8.1 Statement

    3.8.2 Proof

    3.8.3 Applications of Carnot's Theorem

3.9   Classics and Kelvin Statement of Second Law

3.1 INTRODUCTION

The first law of thermodynamics states the equivalence of heat and energy. It simply tells that whenever work is obtained, an equivalent amount of heat is used up, or vice versa. It does not say anything either about the limitation in the conversion of heat into work or about the condition necessary for such a conversion. Thus for example, the first law does not tell us, whether water can flow against gravity of itself. It has no answer to the query, can a metallic rod at one uniform temperature become warmer at one end and cooler at the other of itself. In its reply it can only say that if this process occurred, the heat energy lost by one end will be exactly equal to that gained by the other end. The first law can account for the stopping of a revolving wheel as being due to conversion of its kinetic energy into heat produced in overcoming the friction at the bearings but it does not explain why the heat produced at the bearing cannot be converted into kinetic energy of wheel making it to revolve once again.

It was the quest for replies of several such questions which led to the formulation of second law of thermodynamics. This law is a generalization of certain experiences and observation and is concerned with the direction in which energy transfer take place. The law has been stated in a number of ways, but all the statements, through differently worded, are logically equivalent to one another.

3.2   OBJECTIVES

After studying this Unit, Student should able to :

- Define Carnot cycle.

- Understand the concept of Carnot Theorems.

- Explain Clausius and Kelvin statement of Second law.

- Understand the concept of Absolute Scale of Temperature.

- Define the term Thermal efficiency.

3.3   NEED OF SECOND LAW

Thermodynamics first law tells that there is an exact equivalence between various forms of energy and that heat gained is equal to heat loss. Practically it is not possible to

convert the heat energy into an equivalent amount of work. To explain this, another law is needed which is known as second law of thermodynamics. The second law of thermodynamics helps us to predict whether the reaction is feasible or not and also tell the direction of the flow of heat. It also tells that energy cannot be completely converted into equivalent work.

3.4   CARNOT CYCLE

A Carnot cycle is defined as an ideal reversible closed thermodynamic cycle. Four successive operations are involved: isothermal expansion, adiabatic expansion, isothermal compression, and adiabatic compression. During these operations, the expansion and compression of the substance can be done up to the desired point and back to the initial state.

| Isotherml expansion at T_h | Adiabatic expansion from T_h to T_l | Isotherml compression at T_l | Adiabatic compression from T_l to T_h |

(A) q_{in} (B)   (C) q_{out} (D)
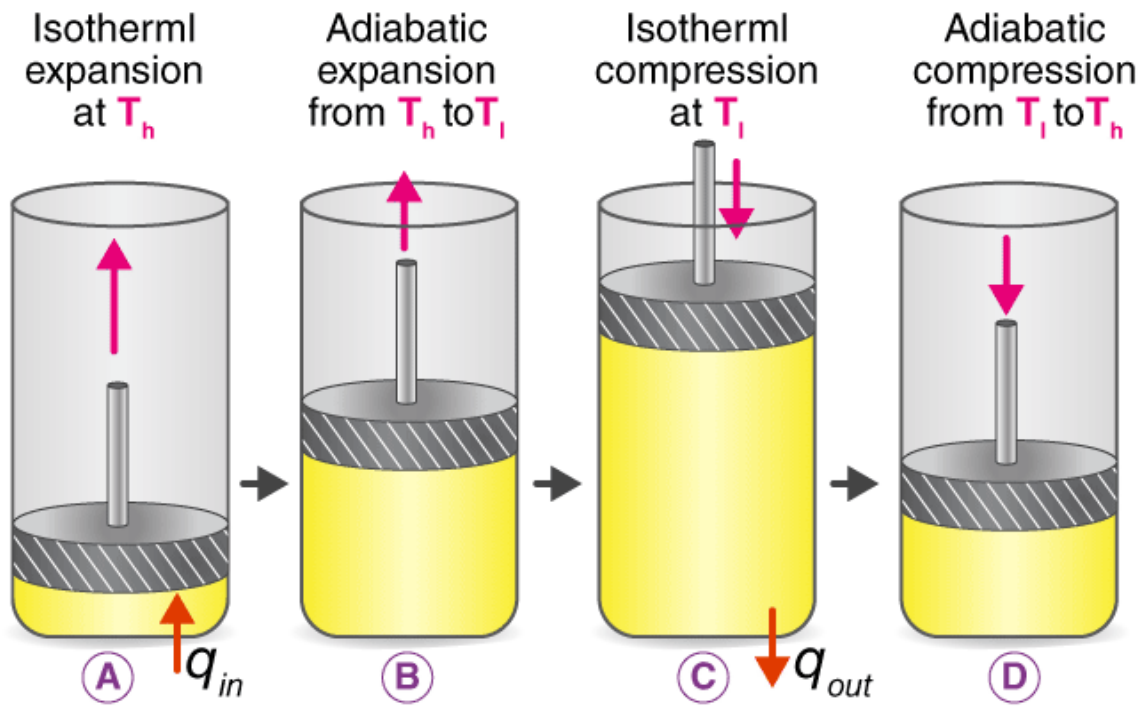
Figure : 1

Following are the four processes of the Carnot cycle:

- In (a), the process is reversible isothermal gas expansion. In this process, the amount of heat absorbed by the ideal gas is q_{in} from the heat source at a temperature of T_h. The gas expands and does work on the surroundings.

- In (b), the process is reversible adiabatic gas expansion. Here, the system is thermally insulated, and the gas continues to

expand and work is done on the surroundings. Now the temperature is lower, T_l.

- In (c), the process is a reversible isothermal gas compression process. Here, the heat loss q_{out} occurs when the surroundings do the work at temperature T_l.

- In (d), the process is reversible adiabatic gas compression. Again the system is thermally insulated. The temperature again rises back to T_h as the surrounding continue to do their work on the gas.

3.4.1 P-V diagram

The Carnot cycle is often plotted on a **pressure- volume diagram** (**pV diagram**) and on a **temperature-entropy diagram** (**Ts diagram**).

When plotted on a **pressure-volume diagram**, the isothermal processes follow the isotherm lines for the gas, adiabatic processes move between isotherms and the area bounded by the complete cycle path represents the total work that can be done during one cycle.
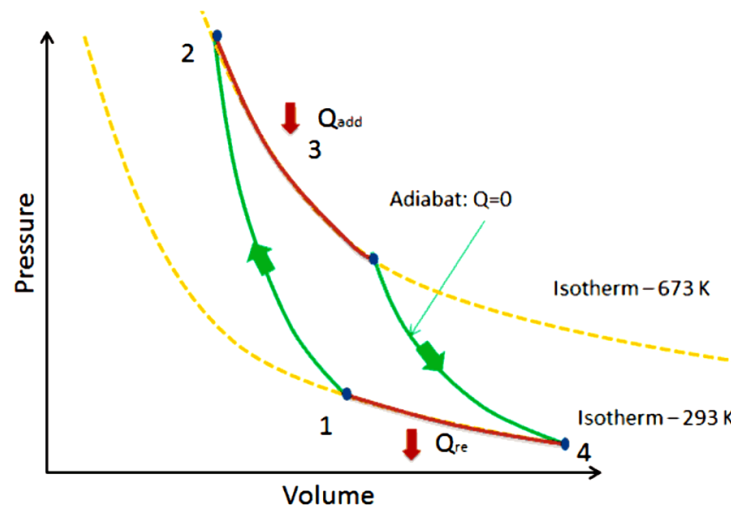
Figure : 2

3.4.2 T-S diagram

The **temperature-entropy diagram** (Ts diagram) in which the thermodynamic state is specified by a point on a graph with specific entropy (s) as the horizontal axis and absolute temperature (T) as the vertical axis, is the best diagram to describe behaviour of a **Carnot 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.
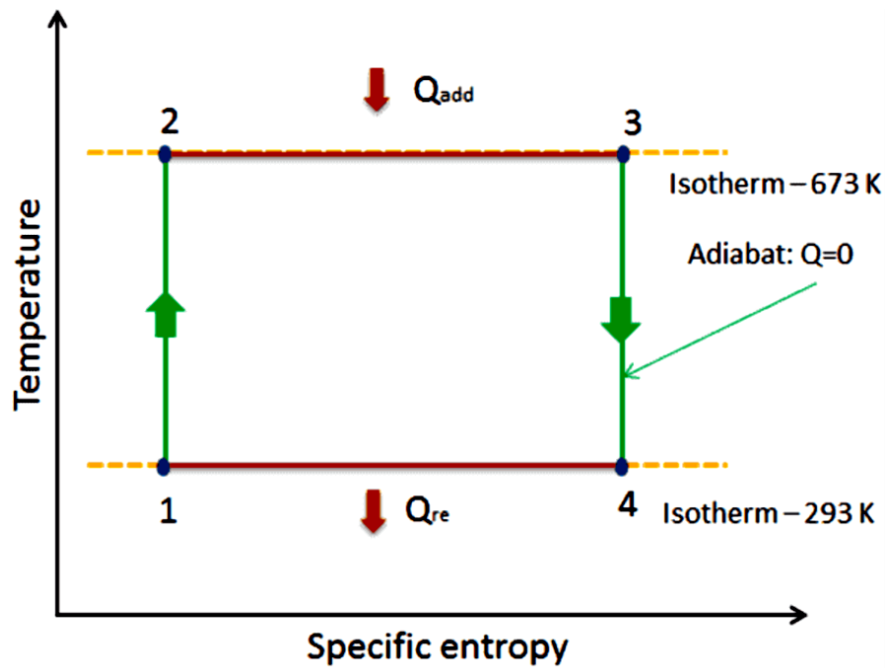
Figure : 3

3.5   CARNOT HEAT ENGINE AND REFRIGERATOR

Carnot <u>Heat engine</u> (based on Carnot Cycle) was a concept developed by Nicolas Leonard Sadi Carnot (1796-1832, a French Military Engineer and Physicist) so that one can visualize a reversible heat engine in practice.

Carnot engine is a reversible heat engine which works on Carnot cycle.
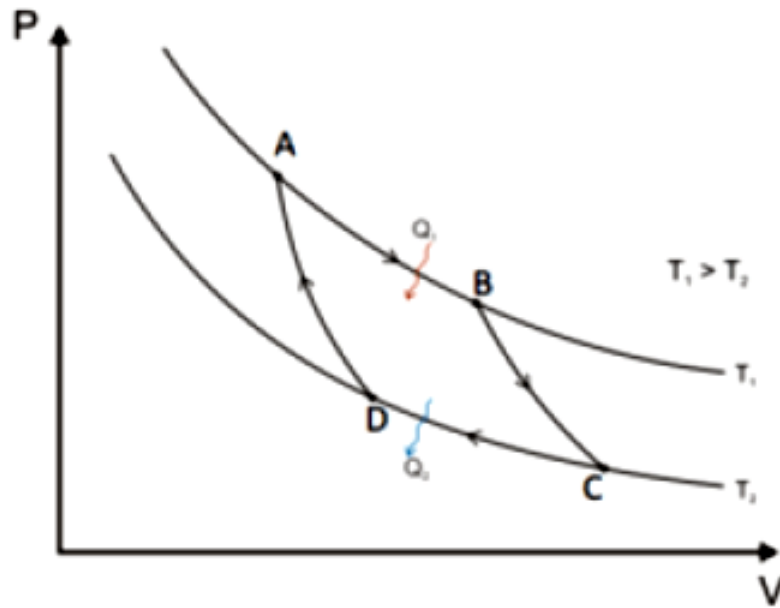
P-V Diagram

Figure : 5

Carnot cycle comprises of four <u>processes</u>.

1. Reversible isothermal process of heat addition (Process A-B)

2. Reversible adiabatic process of expansion (Process B-C)

3. Reversible isothermal process of heat rejection (Process C-D)

4. Reversible adiabatic process of compression (Process D-A)
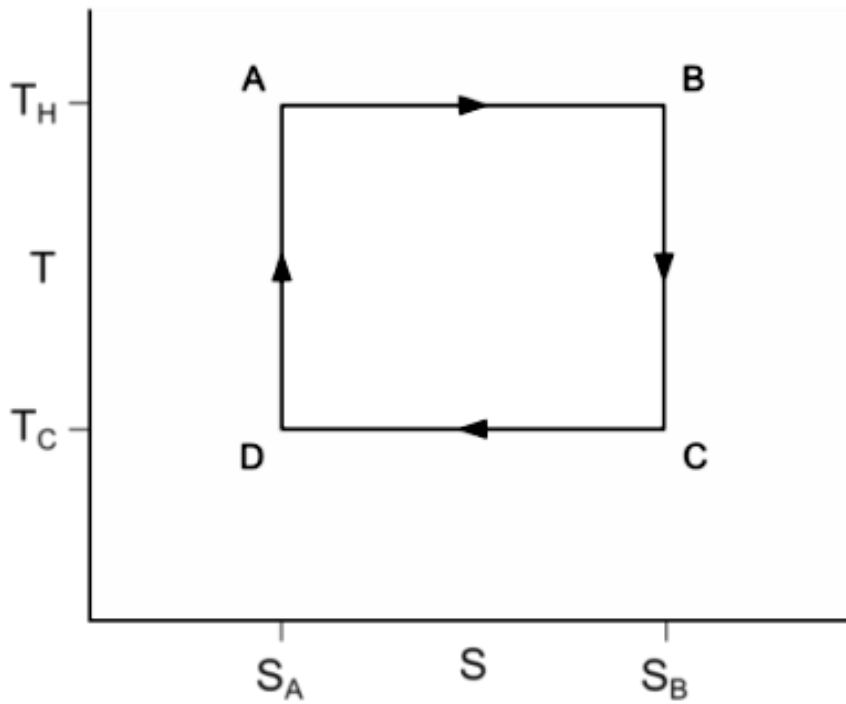
T-S Diagram

Figure : 6

Carnot Heat Engine

Now we understand Carnot engine physically in the following way.

Process A-B
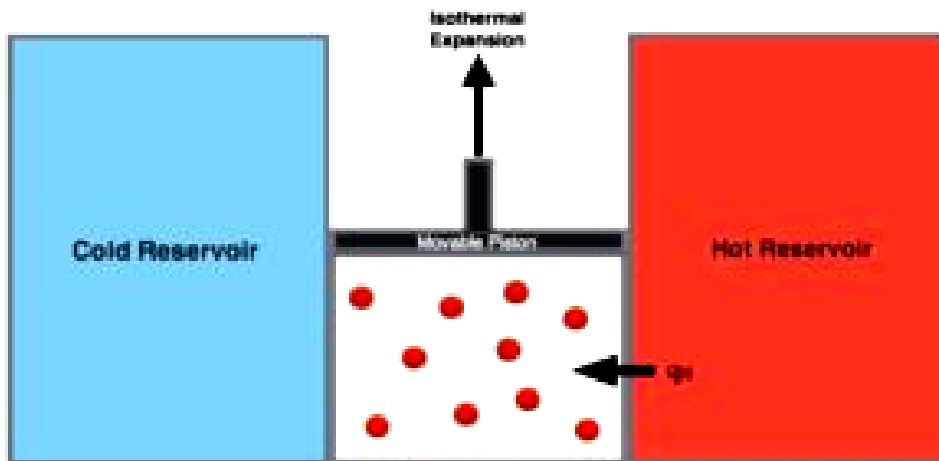
Figure : 7

In this process heat is released from the hot reservoir and is absorbed by the ideal gas particles within the system. Thus, the temperature of the system rises. The high temperature causes the gas particles to expand hence pushing the piston upwards and doing work on the surroundings.

Process B-C
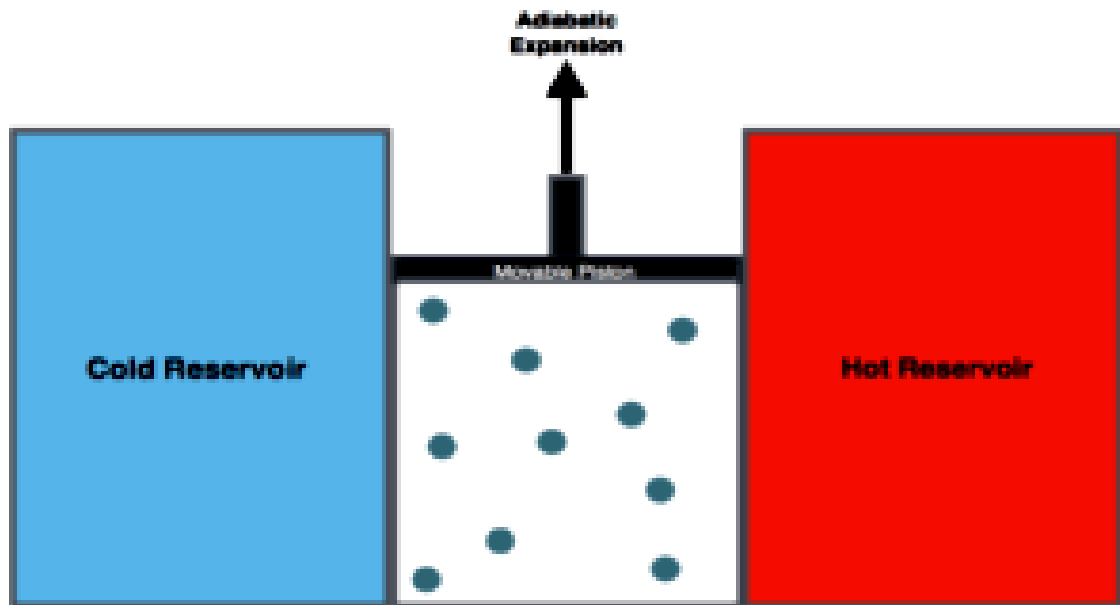
Figure : 8

In this process expansion continuous, however there is no heat exchange between the system and the surroundings. Thus, the system is undergoing adiabatic expansion. The expansion allows the ideal gas particles to cool, decreasing the temperature of the system.

Process C-D
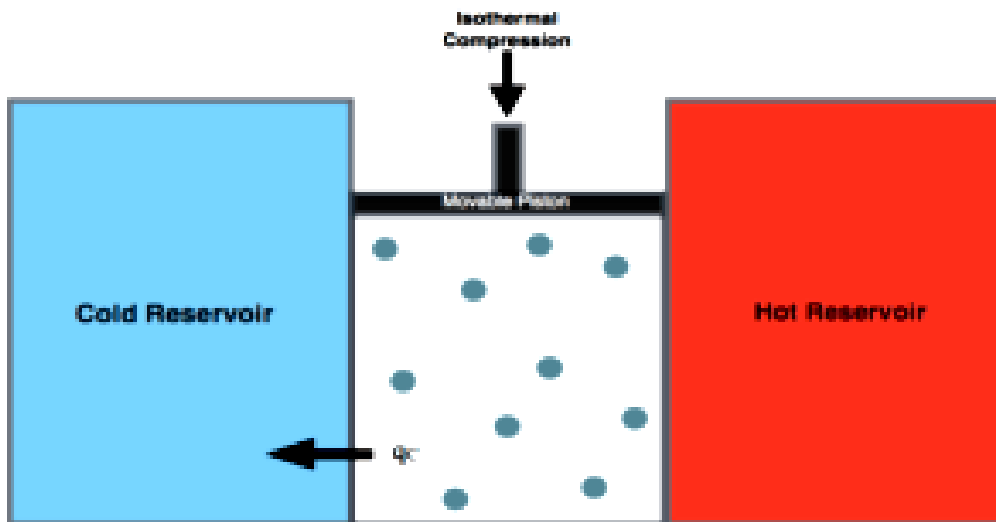
Figure : 9

In this process surroundings do work on the system which causes heat to be released. The temperature within the system remains the same. Thus, isothermal expansion occurs.

Process D-A
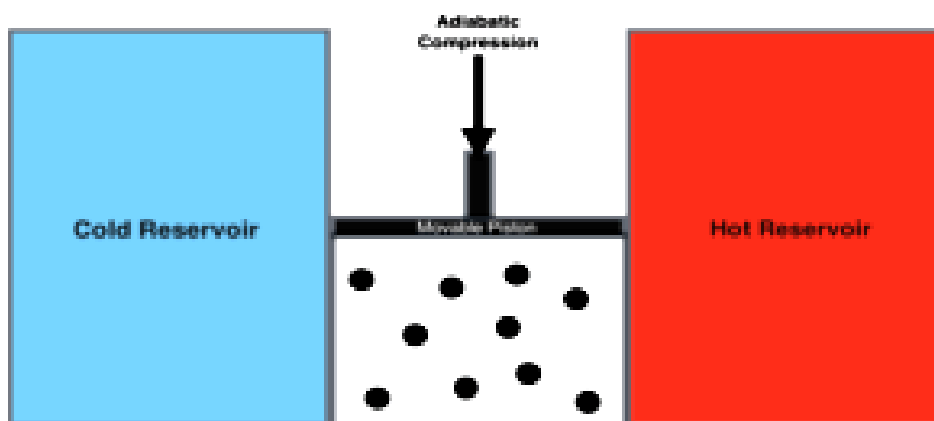
Figure : 10

No heat exchange occurs in this process however, the surroundings continue to do work on the system. Adiabatic compression occurs which raises the temperature of the system and puts the piston back to its original state (Prior to process A-B).

Below are P-V and T-S Diagrams of the Carnot Cycle.
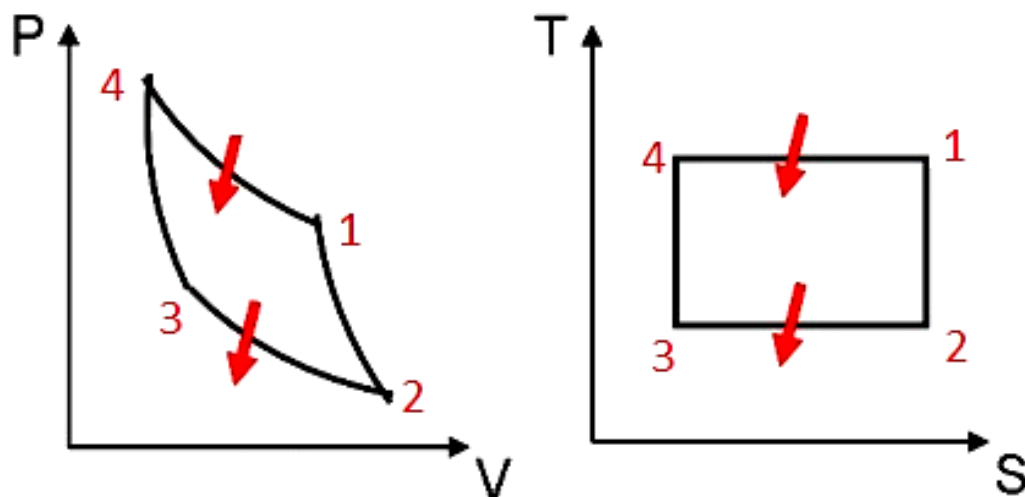
Figure : 11

We know $T_4 = T_1$, say it be T_A and $T_3 = T_2$, say it be T_B.

Below is the table which shows heat and work interactions of the Carnot cycle, along with the change in the internal energy.

Process	Change in Internal Energy	Work Interaction	Heat Interaction
Process 1-2	$C_V(T_2-T_1)$	$C_V(T_1-T_2)$	0
Process 2-3	0	$RT_B \ln(V_3/V_2)$	$RT_B \ln(V_3/V_2)$
Process 3-4	$C_V(T_4-T_3)$	$C_V(T_3-T_4)$	0
Process 4-1	0	$RT_A \ln(V_1/V_4)$	$RT_A \ln(V_1/V_4)$

Note: Negative value of heat interaction indicates heat rejected by the system and positive value of heat interaction indicates

heat added to the system. Positive value of work interaction indicates work done by the system and negative value of work interaction indicates work done on the system.

Efficiency of Carnot Cycle

Efficiency of the Carnot Cycle is the ratio of work output to the heat input.

Work output $= RT_A \ln(V_1/V_4) - RT_B \ln(V_2/V_3)$

Heat Input $= RT_A \ln(V_1/V_4)$

Efficiency = Work Output/Heat Input

After putting values of heat input and work output in the above formula, we get

$\eta = 1 - [(RT_B \ln(V_2/V_3))/(RT_A \ln(V_1/V_4))] \dots (1)$

Also, $V_1/V_4 = V_2/V_3$

It means

$\eta = 1 - (T_B / T_A)$

3.6   THERMAL EFFICIENCY

We define the **thermal efficiency**, η_{th}, of any heat engine as the ratio of the <u>work</u> it does, **W**, to the <u>heat</u> input at the high temperature, Q_H.

$$\eta_{th} = \frac{W}{Q_H}$$

The **thermal efficiency**, η_{th}, represents the fraction of **heat**, Q_H, converted **to work**. It is a dimensionless performance measure of a heat engine that uses thermal energy, such as a steam turbine, an internal combustion engine, or a refrigerator.

3.7   COEFFICIENT OF PERFORMANCE

The coefficient of performance or COP of a heat pump, refrigerator or air conditioning system is a ratio of useful heating or cooling provided to work required. Higher COPs equate to lower operating costs.
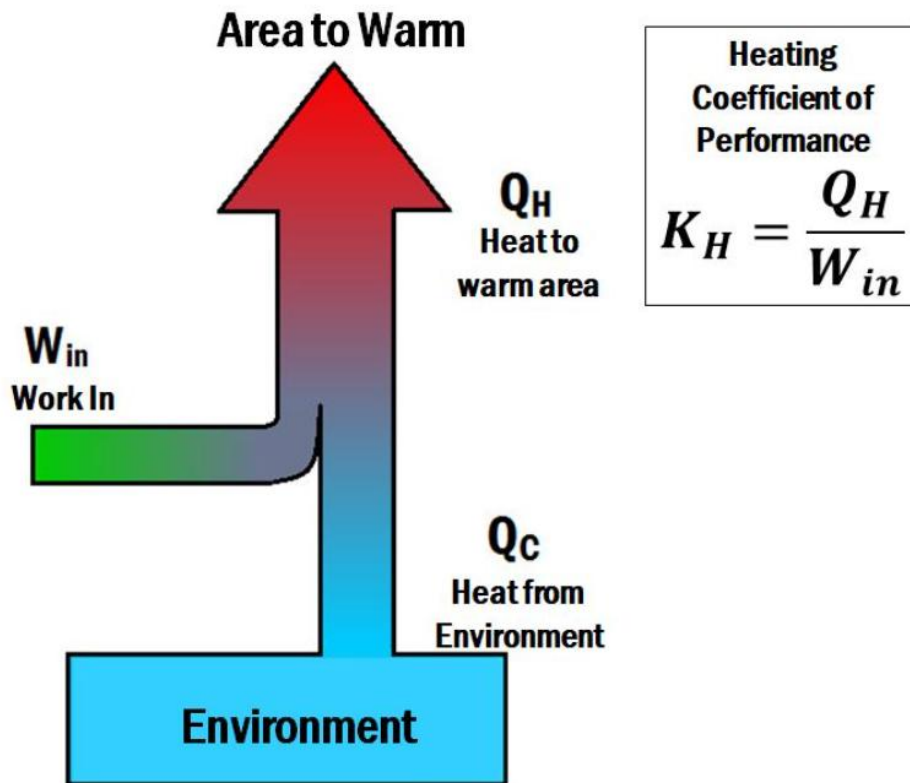
Figure : 12
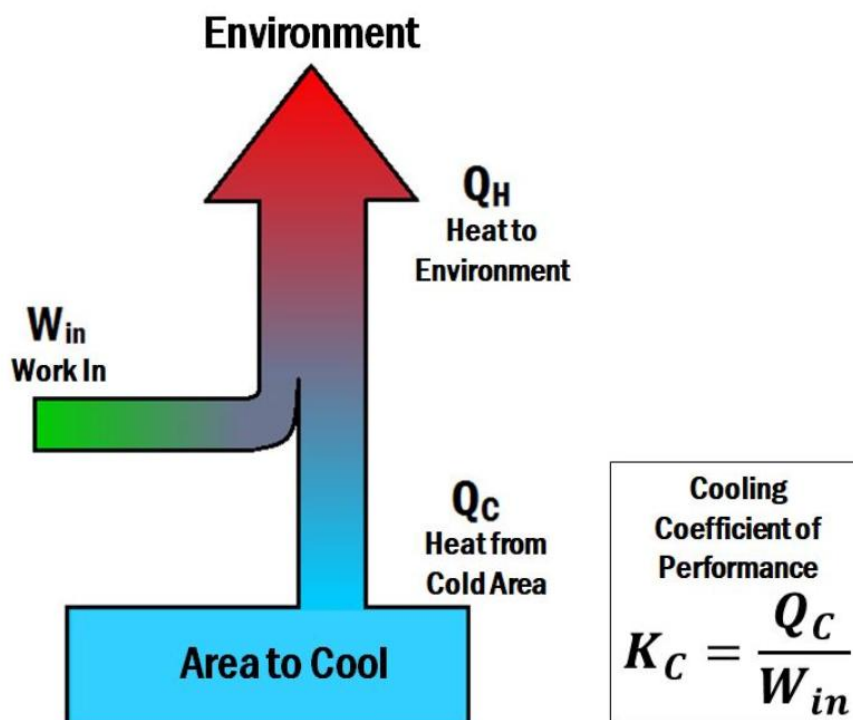
Figure : 13

3.8 CARNOT THEOREMS

Carnot's theorem also known as Carnot's rule was developed by Nicolas Léonard Sadi Carnot in the year 1824, with the principle that there are limits on maximum efficiency for any given heat engine. It depends mainly on hot and cold reservoir temperatures.
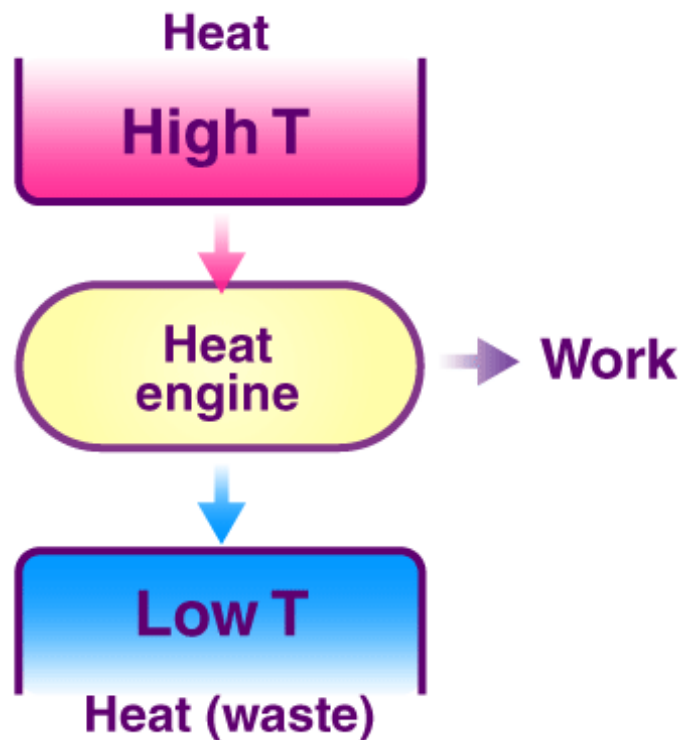

Figure : 14

3.8.1 Statement

This theorem consists of two parts and may be enunciated as follows :

(i) No engine working between two given temperatures can be more efficient than a reversible (Carnot) engine working between the same limits of temperature (i.e., between the same source and sink).

(ii) All reversible engines working between the same limits of temperature have the same efficiency, whatever be the working substance.

3.8.2 Proof
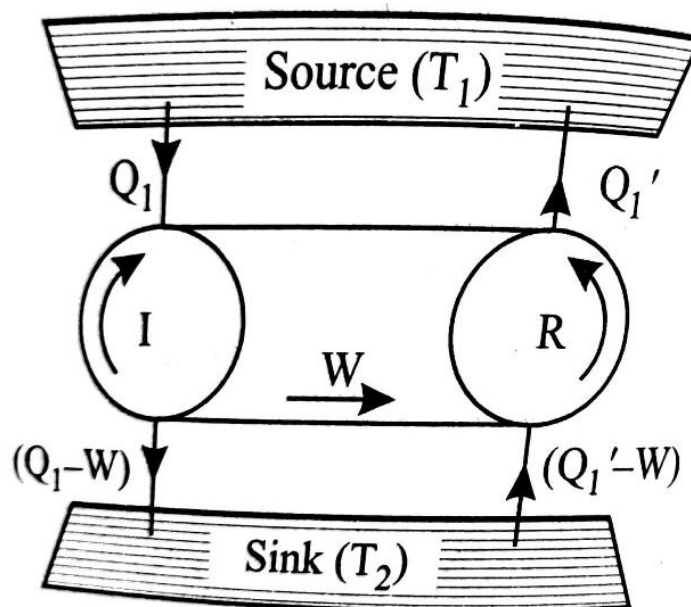
Figure : 15

In order to prove the first part of the theorem, let us consider two engines I and R working between the same source and sink.

Let I be irreversible and R reversible. Let the quantities of working substance in the two engines be so adjusted that the work performed by them per cycle is the same. Let the irreversible engine I absorb an amount of heat Q_1 from the source at a temperature T_1, perform an external work W and reject a quantity of heat $(Q_1 - W)$ to the sink at temperature T_2. Its efficiency η_1 is then equal to W/Q_1. Similarly, if the reversible engine R absorbs heat Q_1' from the source does an external work W and reject $(Q_1' - W)$ heat to be sink, then its efficiency η_R is equal to W/Q_1'.

Suppose that irreversible engine I is more efficient than reversible engine R, i.e.,

$$\eta_I > \eta_R$$

or $$\frac{W}{Q_1} > \frac{W}{Q_1'}$$

$$Q_I' > Q_1.$$

Thus $(Q_1' - W_1)$ is a positive quantity.

Now, suppose that the two engines I and R are coupled together by a belt in such a way that a engine I works directly i.e., forward, it derives engines R backward, as shown in Fig. 7. Engine R now works as a refrigerator driven by I, extracts heat $(Q_1' - W)$ from the sink at temperature T_2, requires work W to be done upon it and gives out heat Q_1' to the source at temperature T_1. The work W required to be done on R is directly supplied by I, working directly and in this way the engine I and refrigerator R coupled together form a self-acting device.

The source now loses Q_1 heat to I and gains Q_1' from R.

∴   Heat gained by the source = Q1' − Q1.

The sink gains $(Q_1 - W)$ heat from I and loses $(Q_1' - W)$ to R.

∴   Heat lost by the sink = (Q1' − W) − (Q1 − W)

$$= Q_1' - Q_1$$

which is a positive quantity (since $(Q_1' > Q_1)$.

Thus the coupled device is transferring in each cycle an amount of heat $Q_1' - Q_1$ from the sink at a temperature T_2 (lower temperature) to the source at a temperature T_1 (higher temperature) without the aid of any external energy. This transfer of heat from a lower to a higher temperature without any expenditure of work is contrary to the second law of thermodynamics and hence impossible. It follows, therefore, that our original assumption that the irreversible engine is more efficient that the reversible one is wrong. Hence no engine working between a given source and sink can be more efficient than reversible engine working between the same source and sink; or in other word a reversible (Carnot) engine operating between a given source and sink has maximum efficiency.

In order to prove second part of the theorem, let us imagine a reversible engine R' instead of the irreversible engine I. Thus we are having two reversible engines R and R' working between the same source and sink. Proceeding exactly as above we can show that if we assume R to the more efficient than R', it would lead to a result which would violate the second law of

thermodynamics, viz., the transfer of heat from a lower to a higher temperature without any expenditure of energy. Hence R cannot be more efficient than R'. Similarly, if we assume R' to be more efficient than R the same result would follow. Hence R' cannot be more efficient that R. It means that R and R' are both equally efficient. Thus the efficiency of all reversible engines, working between the same two temperatures, is the same irrespective of the nature and properties of the working substance or in other words, "the efficiency of a perfectly reversible engine is independent of the nature of the working substance."

3.8.3 Applications of Carnot's Theorem

- Carnot's theorem finds application in engines that convert thermal energy to work.

- Refrigeration: Method of removal of heat from the at low temperature and dissipating it to a higher temperature. This is a reversible process.

3.9 CLASSICS AND KELVIN STATEMENT OF SECOND LAW

Kelvin-Planck statement of the second law : As has already been described, the working substance in a heat engine extracts heat from a source, converts a part of it into work and rejects the rest to sink at a lower temperature. The steam which enters the cylinder of a steam engine from boiler is hotter than the steam which is rejected by the cylinder to surroundings. The heat lost by steam is utilized in doing work in the engine. Thus the mechanical energy obtained from the engine is the outcome of heat flow from a hotter to a colder body. If any how the boiler and surroundings would have been on the same temperature, no heat flow would occur and hence no mechanical energy would be obtained. Hence to convert heat into work, a difference of temperature is essential. No engine has ever been constructed which converts all the heat absorbed from the source into work without rejecting a part of it to the cold body. As the engine absorbs more and more heat from the hot body, the later suffers a continuous fall in temperature and if a continuous supply of

work is desired, the hot body will in the long run become as cold as its surroundings. Then no heat flow will be possible, the engine will stop working and hence no mechanical work will be obtained. It means that we can not obtain a continuous supply of work from a single supply of heat i.e., the presence of colder body is a must for the continuous conversion of heat into work. Such considerations led **Lord Kelvin** to state that :

"It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding object."

In the words of **Planck**,

"It is impossible to construct an engine which, working in a complete cycle, will produce no effect other than the raising of a weight and the cooling of a heat reservoir."

These two statements can be combined into one equivalent statement, known as the **Kelvin Planck statement** of the second law which is :

"It is impossible to construct a device which, operating in a cycle, has the sole effect of extracting heat from a reservoir and performing an equivalent amount of work."

According to this statement, a single reservoir at a single temperature can not continuously transfer heat into work. It is a **negative statement** and may be treated as the denial of what is known as a perpetual motion machine (working for ever) of the second kind. As an example, it is impossible to derive a steamship across the ocean by extracting heat from the ocean or to run a power plant by extracting heat from the surrounding air. Both the ocean and the surrounding air contain an enormous store of internal energy which, in principle, may be extracted in the form of a flow of heat. In doing so we will not violate the first law, because we do not plan to get work out of nothing, we are only planning to get motion from a single reservoir. The operation of a machine that utilizes the internal energy of a single heat reservoir, it called perpetual motion of the second kind. The impossibility of such a device is an essence of the second law of thermodynamics. **Ostwald** put the second law in

the form, **"Perpetual motion machine of the second kind is impossible."**

Clausius statement of the second law : This statements is based upon the performance of refrigerator-a heat engine working in the backward direction. In a refrigerator the working substance takes in heat from a cold body, a certain amount of work is done on it by some outside agency and rejects a larger amount of heat to a hotter body. Thus, a refrigerator transfers heat from a cold body to a hot body with the aid of a outside agency. No refrigerator has ever been constructed which can do this work without the supply of energy from an external agency. Considerations such as this led **Clausius** to state the second law in the form:

"It is impossible for a self-acting machine working in a cyclic process, unaided by any external agency, to transfer heat from a body at a lower temperature to a body at a higher temperature."

In other words it may be stated as "Heat cannot flow of itself from a colder to a hotter body."

Both the Statements of Second Law are Equivalent

The two enunciations of the seconds law of thermodynamics appear to the quite equivalent. To show this, suppose a refrigerator transfers an amount of heat Q_2 from a colder to a warmer body without having any work done on it by some outside agency; thus, violating the Clausius statements of the second law.
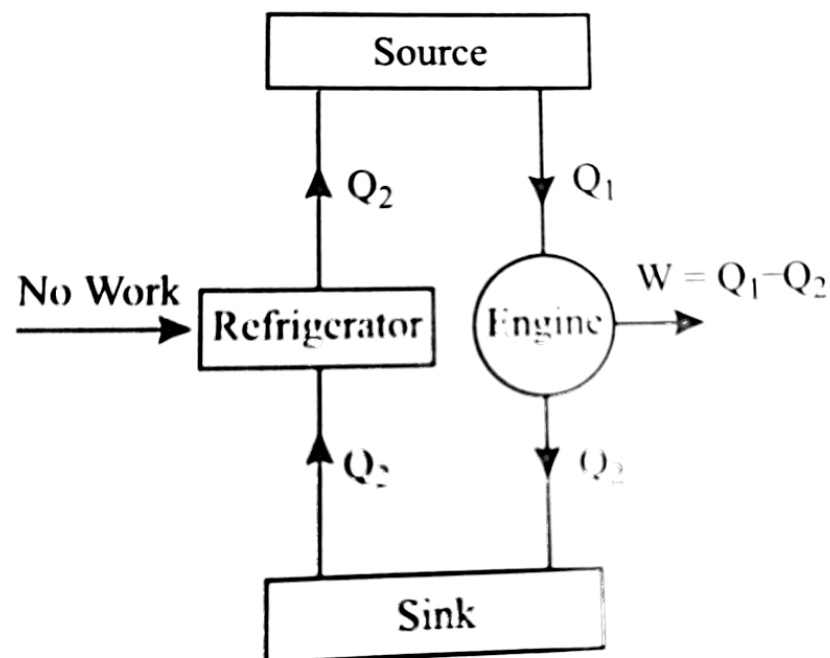

Figure : 16

Let us now suppose another heat engine also working between the same, hot and cold bodies, extracting heat Q_1 from hot body and giving back heat Q_2 to the cold body. This engine alone does not violate any law, but if the refrigerator and engine are coupled together, the net result is that the cold body is giving out amount of heat Q_2 and receiving back the same amount and thus there is no change in its heat contents. On the other hand, the hot body receives a heat Q_2 while gives out heat Q_1 and thus in each cycle it loses an amount of heat $Q_1 - Q_2$ which is completely converted into work without delivering any to the cold body. This system thus violates the Kelvin-Planck's statement of the second law.
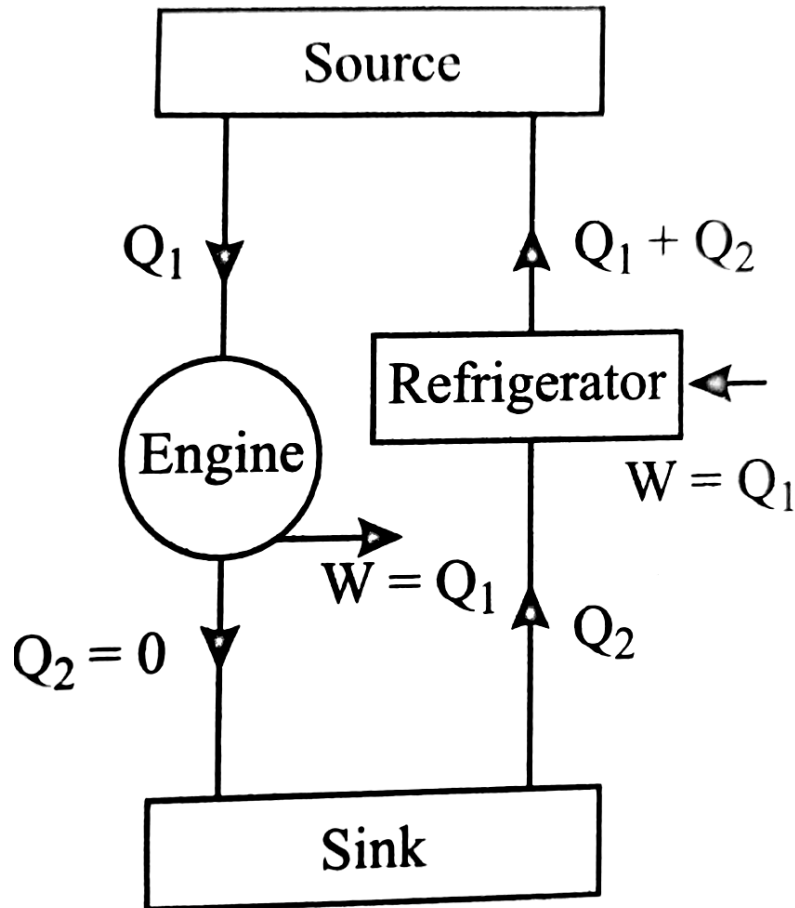
Figure : 17

In a similar way we can show that a violation of the Kelvin Planck's statements leads to a violation of Clausius statement. Let us think of an engine which extracts an amount of heat Q1 from a hot body and converts all into work without rejecting any to the cold body, thus violating the Kelvin-Plank statement. Now suppose that a refrigerator also works between the same hot and cold bodies while it extracts an amount of heat Q2 from the cold body and let an amount of work $W = Q_1$ be done upon

it so that finally it delivers an amount (Q_1 + Q_2) of heat to the hot body. If the engine and refrigerator are coupled together to work simultaneously, they will constitute a self acting machine, drawing a heat Q_2 from the cold body and transferring it to the hot body. Such a system violates the Clausius statements of second law.

Thus, we are that the violation of the conditions imposed by the Kelvin-Planck's statement also means a violation of the Clausius statements or vice versa. Hence both the enunciations of the law are completely equivalent to each other. No direct proof of the law can, however, be given; but the main evidence for its truth is that it has never been possible to construct a machine working against this law.

3.10 ABSOLUTE SCALE OF TEMPERATURE

On the absolute scale, temperature is expressed in Kelvin. **A temperature scale, zero of which is equivalent to -273.15 °C and 373.15 °C is equivalent to 100 °C**, is called absolute scale of temperature and -273.15 °C is called absolute zero.

Absolute zero

The temperature of -273°C is called absolute zero.

$$V = V_\circ \left(\frac{273 + t}{273} \right)$$

Volume at -273°C = $V_\circ \left(\dfrac{273 - 273}{273} \right) = 0$

Absolute or Kelvin scale of temperature

The temperature scale with its zero at -273°C and each degree equal to one degree on the Celsius scale is called Kelvin or the absolute scale of temperature.

Conversion of temperature from Celsius scale to Kelvin scale and vice versa

The value on the Celsius scale can be converted to the Kelvin scale by adding 273 to it.

Example:

20°C = 20 + 273 = 293 K.

3.11 SUMMARY

The second law of thermodynamics put restrictions upon the direction of heat transfer and achievable efficiencies of heat engines. The first law of thermodynamics states that the energy of the universe remains constant, though energy can be exchanged between system and surroundings, it can't be created or destroyed.

While the underlined first law of thermodynamics gives information about the quantity of energy transfer as a process, it fails to provide any insights about the direction of energy transfer and the quality of the energy. The first law cannot indicate whether a metallic bar of uniform temperature can spontaneously become warmer at one end and cooler at others. All that the law can state is that there will always be energy balance if the process occurs. It is the second law of thermodynamics that provides the criterion for the feasibility of any process. A process cannot occur unless it satisfies both the first and second laws of thermodynamics.

The second law of thermodynamics states that any spontaneously occurring process will always lead to an escalation in the entropy (S) of the universe. In simple words, the law explains that an isolated system's entropy will never decrease over time.

Nonetheless, in some cases where the system is in thermodynamic equilibrium or going through a reversible process, the total entropy of a system and its surroundings

remains constant. The second law is also known as the Law of Increased Entropy.

The second law clearly explains that it is impossible to convert heat energy to mechanical energy with 100 per cent efficiency. For example, if we look at the piston in an engine, the gas is heated to increase its pressure and drive a piston. However, even as the piston moves, there is always some leftover heat in the gas that cannot be used for carrying out any other work. Heat is wasted and it has to de discarded. In this case, it is done by transferring it to a heat sink or in the case of a car engine, waste heat is discarded by exhausting the used fuel and air mixture to the atmosphere. Additionally, heat generated from friction that is generally unusable should also be removed from the system.

Mathematically, the second law of thermodynamics is represented as;

$$\Delta S_{univ} > 0$$

where ΔS_{univ} is the change in the entropy of the universe.

Entropy is a measure of the randomness of the system or it is the measure of energy or chaos within an isolated system. It can be considered as a quantitative index that describes the quality of energy.

Meanwhile, there are few factors that cause an increase in entropy of the closed system. Firstly, in a closed system, while the mass remains constant there is an exchange of heat with the surroundings. This change in the heat content creates a disturbance in the system thereby increasing the entropy of the system.

Secondly, internal changes may occur in the movements of the molecules of the system. This leads to disturbances which further causes irreversibility inside the system resulting in the increment of its entropy.

Absolute Temperature

Absolute temperature is temperature on a scale where 0 is absolute zero. At absolute zero, atoms and molecules have minimum energy.

	Kelvin	Rankine	Celsius	Fahrenheit
Boiling point of water	373.15	671.67	100	212
Body temperature	310.15	558.27	37	98.6
Room Temperature	298.15	536.67	25	77
Freezing point of water	273.15	491.67	0	32
Absolute zero	0	0	-273.15	-459.67

Kelvin and Rankine are absolute temperature scales.

Celsius and Fahrenheit are relative temperature scales.
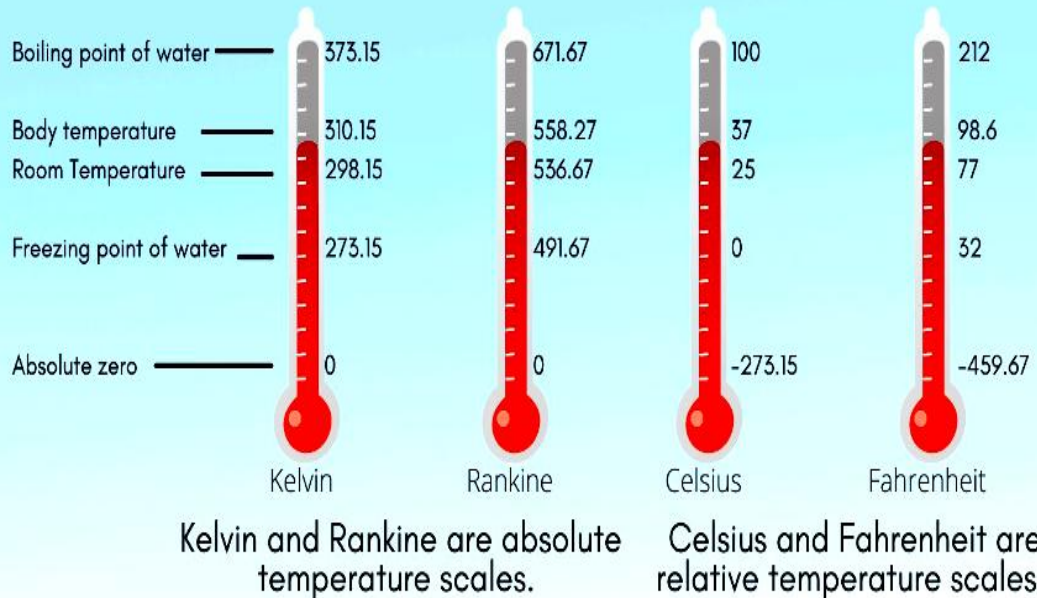
3.12 TERMINAL QUESTIONS

1. Describe Carnot's heat engine with the help of suitable diagrams. Why it can not be realized in practices?

2. Define Carnot's cycle and show how the work done in each operation is represented on a pressure volume diagram.

3. State and prove Carnot's theorem.

4. Define Absolute Scale of temperature.

5.   Explain Clausius and Kelvin statement of Second law of thermodynamics.

6.   What is coefficient of Performance.

7.   Why there is a need of Second law of thermodynamics.

8.   A Carnot's cycle contains

(a)   two isothermal processes only

(b)   two adiabatic processes only

(c)   two isothermal and two adiabatic processes

(d)   two isothermal and two isobaric processes

9.   A Carnot's engine works between a hot reservoir at temperature T1 and a cold reservoir at temperature T2. To increase its efficiency

(a)   T1 and T2 both should be increased

(b)   T1 and T2 both should be decreased

(c)   T1 should be increased and T2 decreased

(d) T1 should be decreased and T2 increased

10. If the temperature of the source is increased, the efficiency of Carnot engine

(a) increases

(b) decreases

(c) remains constant

(d) first increases and then becomes constant

11. Which is most effective for increase of efficiency of Carnot engine

(a) increase of temperature of source by 50oC

(b) decrease of temperature of sink by 50oC

(c) increase of temperature of source by 25oC and decrease of temperature of sink by 25oC

(d) all above are equally effective

12. Isotherms on T-S diagram are

(a)   Parallel to T-axis

(b)   Parallel to S-axis

(c)   Circular

(d)   None of these

3.13 ANSWER AND SOLUTION OF TERMINAL QUESTION

1.   Section 3.5

2.   Section 3.4

3.   Section 3.8

4.   Section 3.10

5.   Section 3.9

6.   Section 3.7

7.   Section 3.3

8.   (c)

9.   (c)

10.   (a)

11.   (b)

12.   (c)

3.14 SUGGESTED READINGS

1.   Thermal Physics: with Kinetic Theory, Thermodynamics: SC Garg.

2.   Thermal Physics: R. Murugeshan, Er. Kiruthiga Siva Prasath.

3.   Thermal Physics: C.B.P. Finn.

4.   Heat Thermodynamics and Statistical Physics: Brij lal, Dr. N. Subrahmanyam, P.S. Hemne.

UNIT - 04   ENTROPY

STRUCTURE

4.1   INTRODUCTION

The first law of thermodynamics was presented originally in terms of cycles, and it was demonstrated that the cyclic integral of heat equals the cyclic integral of work. When the first law was applied to thermodynamic processes, it revealed the existence of a property known as internal energy. Similarly, the second law was initially described in terms of system cycles. When applied to processes, the second law results in the definition of a new property called entropy. If the first law is called the law of internal energy, the second law is called the law of entropy. Indeed, thermodynamics is the study of the three E's: energy, equilibrium, and entropy.

Background of the concept of Entropy:

The second law of thermodynamics states that all spontaneous processes are, to some extent irreversible and are accompanied by a degradation of energy. It also means that it is impossible for any self-acting machine to transfer energy from a given state to a higher state of availability. To make these statements quantitative there is required some function that always changes in a certain way during a spontaneous process and therefore, will characterize such a change. Internal energy was defined to give quantitative significance to the first law. Internal energy does not change in a characteristic way in a spontaneous process, and it does not help in any way in the development of the second law. The function that is fundamental in the development of the second law is entropy. which means transformability(change) introduced by Clausius in 1815,

4.2 OBJECTIVES

After studying this unit, students will be able to:

Define the term Entropy and its applications

Explain the Concept of Entropy

Describe the Property and characteristics of Entropy

Define the Principle of Entropy

Define the Clausius theorem

Describe the Clausius Inequality of entropy

Explain the Change of Entropy in a System

Define Application of entropy principle

Explain the Absolute entropy

Describe the third Law of Thermodynamics (Entropy)

4.3   DEFINITION OF 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 RudolfClausius in 1850 is a highlight of 19th-century physics.The idea of entropy provides a mathematical way to encode the intuitive notion of which processes are impossible, even though they would not violate the fundamental law of conservationofenergy. For example, a block of ice placed on a hot stove surely melts, while the stove grows cooler. Such a process is called irreversible because no slight change will cause the melted water to turn back into ice while the stove grows hotter. In contrast, a block of ice placed in an ice-water bath will either thaw a little more or freeze a little more, depending on whether a small amount of heat is added to or subtracted from the system. Such a process is reversible because only an infinitesimal amount of heat is needed to change its direction from progressive freezing to progressive thawing. Similarly, compressed gas confined in a cylinder could either expand freely into the atmosphere if a valve were opened (an irreversible process), or it could do useful work by pushing a moveable piston against the force needed to confine the gas. The

latter process is reversible because only a slight increase in the restraining force could reverse the direction of the process from expansion to compression. For reversible processes the system is in equilibrium with its environment, while for irreversible processes it is not.
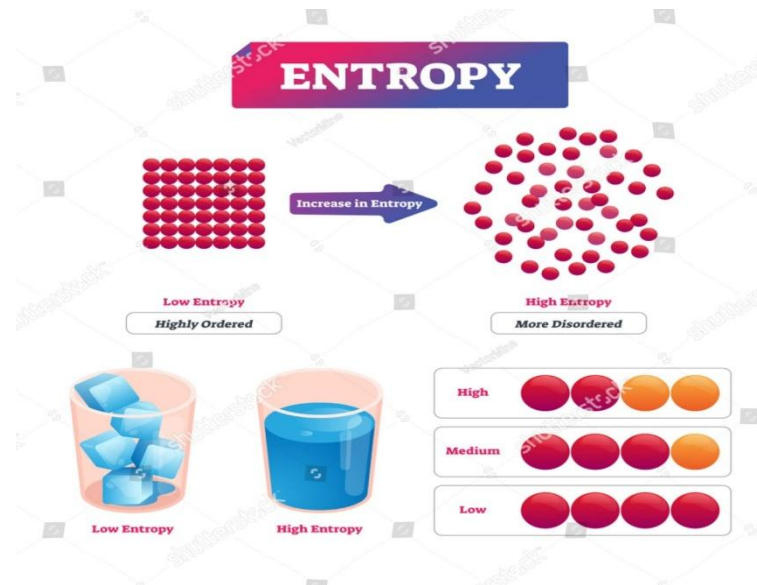

4.4   ENTROPY AND HEAT

The entropy is a measure of the unavailability of internal energy. Among the various forms, heat is the least available form of energy. Whenever a certain form of energy gets transformed to heat the total energy gets degraded with a corresponding increase in the entropy of the system. The word 'heat' often means 'entropy'. The word 'heat' takes on different meanings depending on the context. Often, the context implies that 'heat' is entropy.

The word 'heat' refers to 'entropy' specifically in expressions for the four laws of thermodynamics. Entropy acts as a fluid, so the flow of heat usually means a flow in entropy. Temperature is the pressure exerted by the entropy.

For example, if a molecule splits in half, the entropy doubles, but no heat transaction has occurred. Instead, the temperature (average energy per countable item) has dropped dramatically. The ability for that heat energy to be used usefully has dropped,

so you can interpret entropy as the useful work that can be done by a system. It can no longer do such useful work.

Second Law of Thermodynamics
shutterstock.com · 351766562
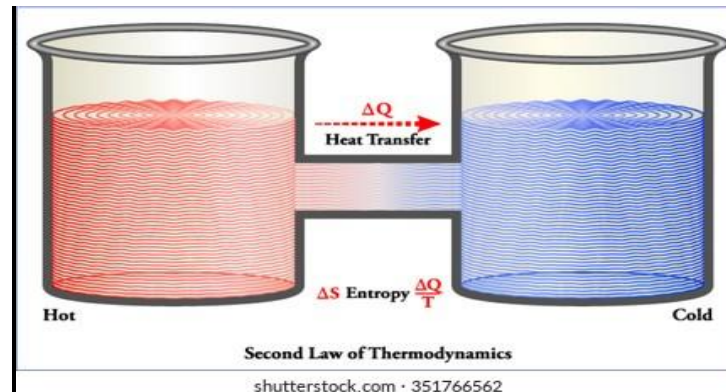
4.5 TWO REVERSIBLE ADIABATIC PATHS CAN NOT INTERSECT EACH OTHER

Assume that two reversible adiabatic AC and BC cross at point C. Let's design a reversible isotherm AB that intersects the reversible adiabatic at points A and B. A reversible cycle is made up of the three reversible processes AB, BC, and CA, and the area included indicates the network output in a cycle. However, such a cycle is impossible because of the process AB, the network is produced in a cycle by a heat engine exchanging heat with a single reservoir, which violates the Kelvin-Planck statement of the second law. As a result, the intersection of reversible adiabatic assumptions is incorrect. Only one reversible adiabatic can flow through a single location.

Because two constant property lines can never meet, it is assumed that a reversible adiabatic path represents a yet-to-be-identified property.
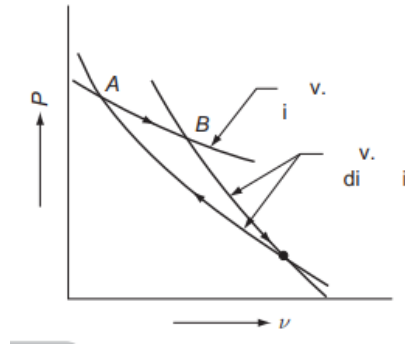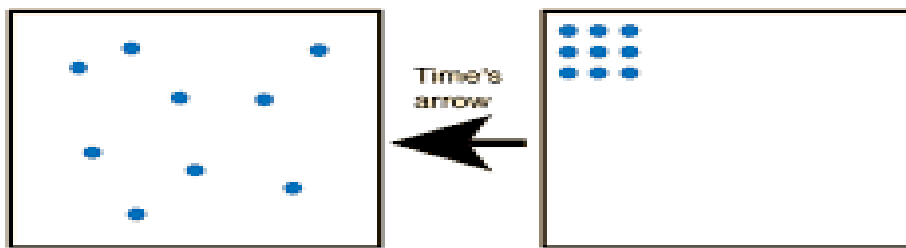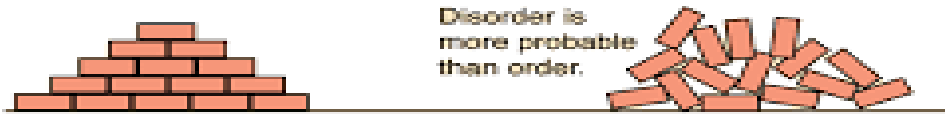
Fig 4.1 - Assumption of two reversible adiabatic intersecting each other

4.6 THE PROPERTY OF ENTROPY

Follow the reversible path R1 to get a system from an initial equilibrium state I to a final equilibrium state f. (Fig. 4.2). The system has been brought back from the dead. R2 is a reversible path that connects f and i. A reversible cycle is made up of two routes R1 and R2.
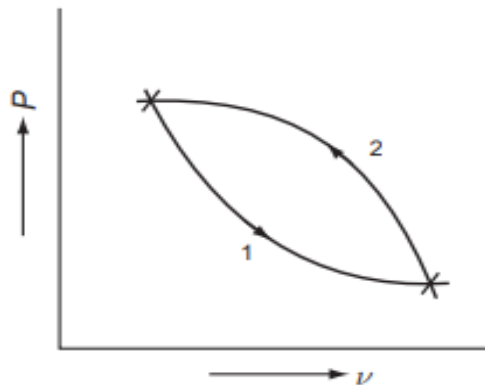

Fig 4.2- Two reversible paths R1 and R2 between two equilibrium states i and f

From Clausius theorem

$$\oint_{R1,R2} \frac{dQ}{T} = 0$$

The above integral may be replaced as the sum of two integrals,

One for path R1 and the other for path R2.

$$\oint_{R1} \frac{dQ}{T} + \oint_{R2} \frac{dQ}{T} = 0$$

$$\oint_{R1} \frac{dQ}{T} = - \oint_{R2} \frac{dQ}{T}$$

Since R2 is a reversible process -

$$\oint_{R1} \frac{dQ}{T} = \oint_{R2} \frac{dQ}{T}$$

Since R1 and R2 represent any two reversible paths, $\int_{i}^{f} \frac{dQ}{T}$ is independent of the reversible path connecting i and f. Therefore, there exists a property of a system whose value at the final state f minus initial state i is equal to $\int_{i}^{f} \frac{dQ}{T}$. This property is called entropy, and is denoted by S. If S_i is the entropy at the initial state i, and Sf is the entropy at the final state f, then

$$\oint_{R} \frac{dQ}{T} = S_f - S_i$$

When the two equilibrium states are infinitesimally near

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

Where ds is an exact differential because S is a point function and a property. The subscript R in d Q indicates that heat d Q is transferred reversibly.

The word entropy' was first used by Clausius, taken from the Greek word trope meaning transformation'. It is an extensive property and has the unit J/K. The specific entropy

$$s = \frac{S}{m} J / kg \ K$$

If the system is taken from an initial equilibrium state i to a final equilibrium state f by an irreversible path, since entropy is a point or state function, and the entropy change is independent of the path followed, the nonreversible path is to be replaced by a reversible path to integrate for the evaluation of entropy change in the irreversible process.

$$S_f \ - \ S_i \ = \ \int_i^f \frac{dQ_{rev}}{T} \ = \ (\Delta S)_{\text{irrev path}}$$

Integration can be performed only on a reversible path

4.6.1 Temperature-Entropy Plot

The infinitesimal change in entropy ds due to reversible heat transfer d −Q at temperature T is

$$dS = \frac{dQrev}{T}$$

If d −Q$_{rev}$ = 0, i.e., the process is reversible and adiabatic

dS = 0

And S = constant

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

dQ$_{rev}$ = TdS

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

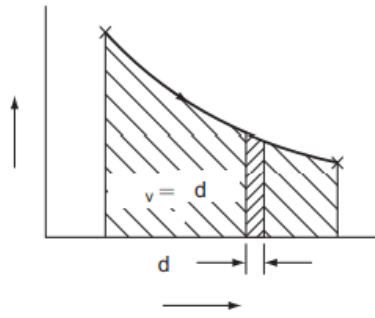Fig4.3 Area under a reversible path on the T-s plot

Fig 4.4 Reversible

isothermal represents heat transfer
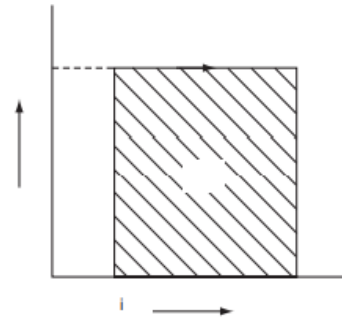
heat transfer

The system is taken from i to f reversibly (Fig. 4.3). The area under the curve $\int_{i}^{f} TdS$ is equal to the heat transferred in the process.

For reversible isothermal heat transfer (Fig. 4.4)

T = constant.

$$Q_{rev} = T\int_{i}^{f} dS = T(S_f - S_i)$$

For a reversible adiabatic process, dS = 0, S = C

4.7 ENTROPY PRINCIPLE

For any infinitesimal process undergone by a system, for the total mass $dS \geq d\!\!\!-\!Q\ T$ For an isolated system that does not undergo any energy interaction with the surroundings, $d\!\!\!-\!Q = 0$. Therefore, for an isolated system $dS_{iso} \geq 0$. For a reversible process, $dS_{iso} = 0$ or S = constant For an irreversible process $dS_{iso} > 0$. 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 the second law from the macroscopic viewpoint.

We can get the total mas from Eq. for any infinitesimal process that

a system goes through.

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

For an isolated system that does not undergo any energy interaction

With the surroundings, dQ = 0.

As a result, it can be demonstrated that the entropy of an isolated system can never decrease. When the process is reversible, it always grows and only stays constant. This is referred to as the entropy principle, or simply the entropy principle. It's all about the numbers.

From a macroscopic perspective, a generic version of the second law

Any system and its surroundings can always be included within a single boundary to produce an isolated system .The original system, which is thus only a part of the isolated system, is sometimes referred to as a subsystem.

Everything that is touched by the process is included in the system and its surroundings (the universe or the isolated system). For all potential procedures that a system can go through in its current environment

4.8   CLAUSIUS' THEOREM

Let a system be taken from an equilibrium state (1) to another equilibrium state (2) following the reversible path 1-2. Let (a) and (b) be two reversible adiabatic, which pass through the points (1) and (2) respectively. A reversible isotherm (c) is drawn, such that the area under 1-3-4-2 is equal to the area under the curve 1-2. From the first law,

From the first law,

$$Q = \Delta U + W$$

For process 1-2,

$$Q_{1-2} = U_2 - U_1 + W_{1-2} \text{ and for the process } 1-3-4-2$$

$$Q_{1-3-4-2} = U_2 - U_1 + W_{1-3-4-2}$$

As we have assumed that the area under 1-3-4-2 is equal to the area under 1-2.

i.e.

$$W_{1-2} = W_{1-3-4-2}$$

∴

$$Q_{1-2} = Q_{1-3-4-2}$$

$$= Q_{1-3} + Q_{3-4} + Q_{4-2}$$

But

$$Q_{1-3} = 0$$

and

$$Q_{4-2} = 0 \;(\because \text{adiabatic})$$

∴

$$Q_{1-2} = Q_{3-4}$$

Consider a reversible cycle as shown in Fig. 4.5. It is divided into a large number of strips by means of reversible adiabatic. Each strip may be closed at the top and bottom by means of reversible isotherms. The original closed cycle is thus replaced by a zig-zag closed path, consisting of alternate adiabatic and isothermal processes, such that the heat transferred during all the isothermal processes is equal to the heat transferred in the original cycle.
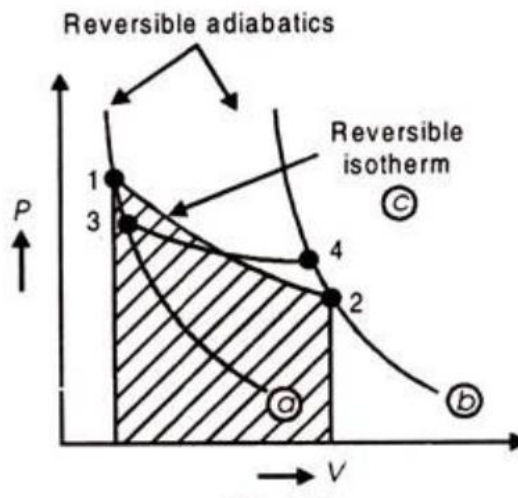

Fig 4.5

Now, for cycle $1 - 2 - 3 - 4$, δQ_1 is heat absorbed reversibly at T_1 and δQ_2 is heat rejected reversibly at T_2.

Then,
$$\frac{\delta Q_1}{T_1} = \frac{\delta Q_2}{T_2}$$

If heat supplied is taken as positive and heat rejected as negative, then

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

Similarly for another elemental cycle $5 - 6 - 7 - 8$

$$\frac{\delta Q_3}{T_3} + \frac{\delta Q_4}{T_4} = 0$$

If similar equation are written for all the elemental Carnot cycles, then for the whole (complete) original cycle

$$\left(\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} \right) + \left(\frac{\delta Q_3}{T_3} + \frac{\delta Q_4}{T_4} \right) + \cdots = 0$$

Thus the cyclic integral of $\delta Q/T$ for a reversible cycle is equal to zero. This is known as Clausious Theorem.
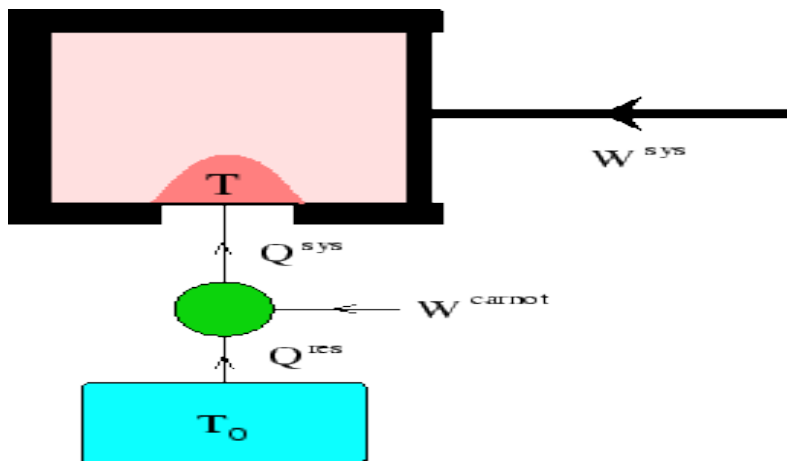

Fig-4.5(a)

4.8.1 Clausius Inequality of entropy

According to Clausius Theorem

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

In the II-Law, during Carnot theorem, we have proved that the efficiency of the Reversible engine is more than that of an Irreversible engine.

$$\eta_R > \eta_I$$

or $$\eta_I < \eta_R \qquad \qquad ...(1)$$

We also know that,

$$\eta \text{ of any engine } = \frac{\text{Heat supplied } - \text{ Heat rejected}}{\text{Heat supplied}} = \frac{Q_1 - Q_2}{Q_1}$$

or For small amount of heat δQ,

$$\eta = \frac{\delta Q_1 - \delta Q_2}{\delta Q_1} = 1 - \frac{\delta Q_2}{\delta Q_1}$$

Hence the Eq. (1) will therefore be,

$$\left[1 - \frac{\delta Q_2}{\delta Q_1}\right]_I < \left[1 - \frac{\delta Q_2}{\delta Q_1}\right]_R$$

But for reversible engine,

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

$$\left[1 - \frac{\delta Q_2}{\delta Q_1}\right] = 1 - \frac{T_2}{T_1}$$

$$\therefore \qquad 1 - \left(\frac{\delta Q_2}{\delta Q_1}\right)_I < 1 - \frac{T_2}{T_1}$$

$$\therefore \qquad \left(\frac{\delta Q_2}{\delta Q_1}\right)_{II} > \frac{T_2}{T_1}$$

or opposite $$\left(\frac{\delta Q_1}{\delta Q_2}\right)_I < \frac{T_1}{T_2}$$

or $$\left(\frac{\delta Q_1}{T_1}\right)_I - \left(\frac{\delta Q_2}{T_2}\right)_I < 0$$

We know that, heat added is positive. Therefore δQ_1 is positive and heat rejected is negative. Therefore δQ_2 is negative

$$\therefore \qquad \left(\frac{\delta Q_1}{T_1}\right)_I + \left(\frac{\delta Q_2}{T_2}\right)_I < 0$$
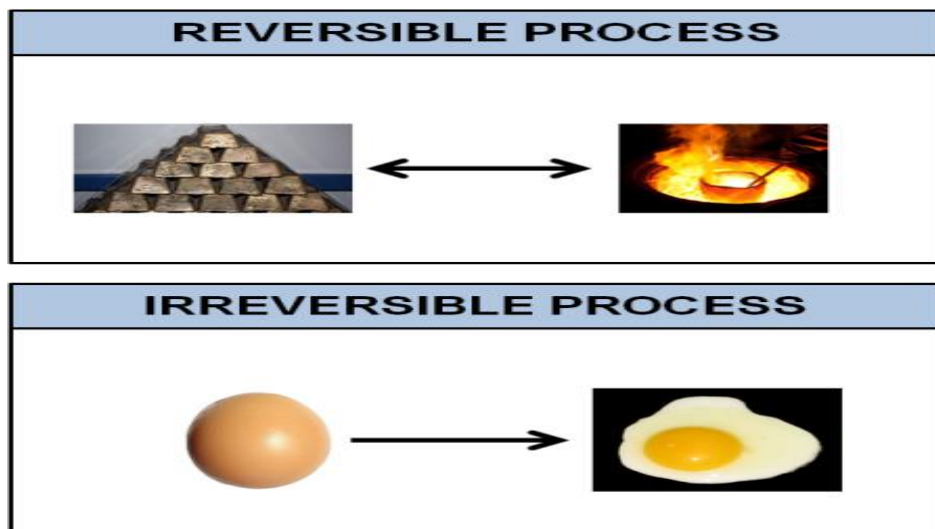
i.e., The algebraic sum of $\delta Q/T$, for an irreversible cycle is always less than zero.

$$\therefore \qquad \oint_R \frac{\delta Q}{T} < 0 \text{ for an Irreversible cycle.}$$

And we know that from Clausius theorem $\oint \frac{\delta Q}{T} = 0$ for a reversible cycle. Combining results for reversible and irreversible cycle, we may write,

$$\oint \frac{\delta Q}{T} \leq 0$$

4.9   CHANGE OF ENTROPY IN A SYSTEM

4.9.1 Change of Entropy in an Irreversible Process

We know that, a change in entropy for a reversible process is given by,

$$\left(\frac{\delta Q}{T}\right)_R = (dS)_R \qquad \qquad ...(1)$$

Now to find the value of change in entropy in an Irreversible process.

Consider a system, which change its state from state point (1) to state point (2) by following the reversible path a and returns from state point (2) to state point (1) by following the irreversible path b as shown in Fig. 4.6.
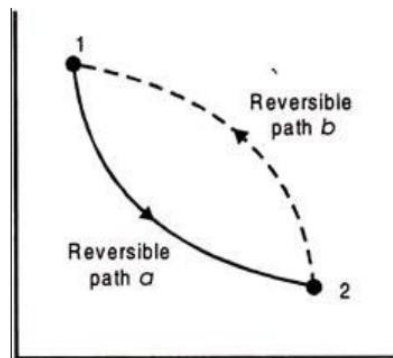

Fig 4.6

Since cyclic integral of any property is zero and entropy is a property we can write,

$$\oint dS = a\int_1^2 (dS)_R + b\int_2^1 (dS)_I = 0 \qquad \qquad ...(2)$$

Now, from Eq. (1), for a reversible process we have,

$$a\int_1^2 (dS)_R = a\int_1^2 \left(\frac{\delta Q}{T}\right)_R \qquad \qquad ...(3)$$

Substituting this in Eq. (2) we get,

$$a\int_1^2 \left(\frac{\delta Q}{T}\right)_R + b\int_2^1 (dS)_I = 0 \qquad \qquad ...(4)$$

Since the processes $1-a-2$ and $2-b-1$ together will form Irreversible cycle. Applying Clausius inequality,

$$\oint_I \frac{\delta Q}{T} < 0$$

We get from Eq. (4),

$$a\int_1^2 \left(\frac{\delta Q}{T}\right)_R + b\int_2^1 \left(\frac{\delta Q}{T}\right)_I < 0 \qquad \qquad ...(5)$$

Subtracting Eq. (5) from Eq. (4) we get,

$$b\int_1^2 (dS)_I > a\int_2^1 \left(\frac{\delta Q}{T}\right)_I$$

In general, $\quad (dS)_I > \left(\frac{\delta Q}{T}\right)_I \qquad \qquad ...(6)$

Combining Eqs (1) and (6), we can write,

$$dS \geq \delta Q / T$$

Where equality sign is for reversible process and inequality sign is for an Irreversible process (from Eq. 6).

Note:

The effect of irreversibility is always to increase the entropy of the system.

4.9.2 Change of Entropy for an Isolated System

We know that, in an isolated system, matter, work or heat cannot cross the boundary of the system. Hence according to the first law of thermodynamics, the IE of the system will remain constant.

Since for an isolated system $\delta Q = 0$,

From equation,

$$dS = \frac{\delta Q}{T} \qquad \qquad ...(1)$$

We get, $\qquad (dS)$ isolated $\geq 0 \qquad \qquad ...(2)$

Equation (2) states, that entropy of an isolated system either increases or remains constant and never decreases. This is known as the Principle of increase of entropy.

4.10 ENTROPY AND DIRECTION: THE SECOND LAW—A DIRECTIONAL LAW OF NATURE

The entropy of an isolated system can never decrease, only natural processes that result in an increase in entropy for the system and its surroundings are possible (the universe).In nature, all spontaneous processes occur exclusively in one direction, from a greater to a lower potential, and these activities are accompanied by an increase in the universe's entropy. When the potential gradient is tiny (or non-existent), the entropy change of the cosmos is zero in the limit, and the process is reversible.

The second law specifies the direction in which a process occurs. A process always proceeds in such a way that the entropy of the universe increases.

The macroscopic change stops only when the potential gradient disappears, and the equilibrium is established when the universe's entropy reaches its maximum value. To calculate the equilibrium state of an isolated system, the entropy must be expressed as a function of certain system properties are then used to maximize the function. At equilibrium, the system (isolated) is at the top of the entropy hill, and dS = 0.
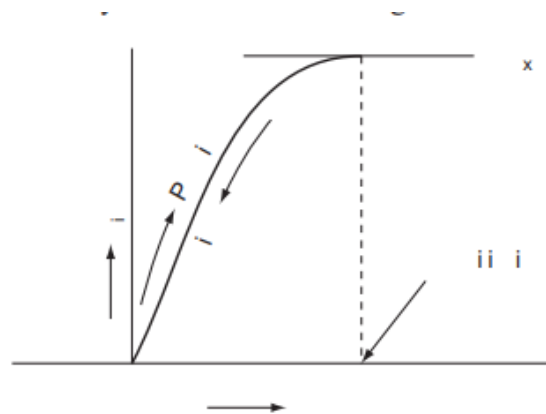

Fig 4.7 Equilibrium state of an isolated system

The natural direction of events in which entropy increases indicates the arrow of time' which results from the universe not being in thermodynamic equilibrium. It undergoes a natural evolution, and inexorably approaches the state of equilibrium.

4.11 APPLICATIONS OF ENTROPY PRINCIPLE

One of the most fundamental laws of physical science is the notion of increasing entropy. It expresses the second rule of thermodynamics quantitatively. Every irreversible process causes the universe's entropy to rise, and this entropy increase quantifies the process's irreversibility. The greater the increase in entropy of the universe, the greater the irreversibility of the process. The following are some examples of entropy principle applications.

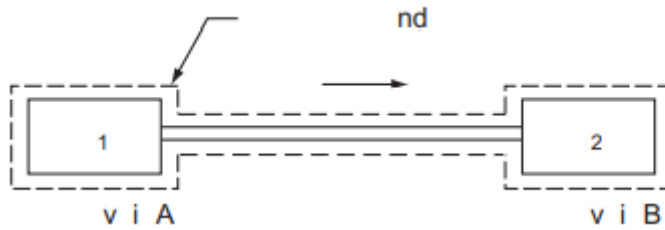### 4.11.1 Transfer of Heat through a Finite Temperature Difference

Fig 4.8 Heat transfer through a finite temperature difference

Let Q be the rate of heat transfer from reservoir A at T1 to reservoir B at T2, T1 > T2 (fig 4.8)

For reservoir, $\Delta S_A = -$ Q/T1. It is negative because heat Q is escaping from the reservoir. SB = + Q/T2 for reservoir B. It is positive because heat is being absorbed by the reservoir. The rod linking the reservoirs experiences no entropy change because once in the reservoir, its coordinates do not change in a stable condition. Therefore, for the isolated system comprising the reservoirs and the rod, and since entropy is an additive property

$$S = S_A + S_B$$

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

$$\Delta S_{uni} = -\frac{Q}{T1} + \frac{Q}{T2}$$

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

Since T1 > T2, ΔS_{univ} is positive, and the process is irreversible and possible. If $T_1 = $ T2, ΔS_{univ} is zero, and the process is reversible. If $T_1 < T_2$, ΔS_{univ} is negative and the process is impossible.
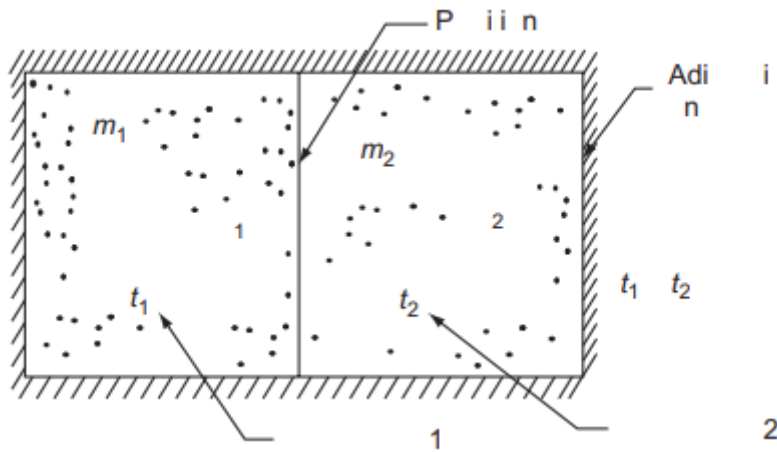
4.11.2 Mixing of Two Fluids

Fig 4.9 -Mixing of fluids

A composite system in an adiabatic enclosure includes subsystem 1 with a fluid of mass m_1, specific heat c_1, and temperature t_1, and subsystem 2 with a fluid of mass m_2, specific heat c_2, and temperature t_2 (Fig. 4.9)

When the partition is removed, the two fluids mix, and at equilibrium, let t_f denote the final temperature and $t_2 < t_f < t_1$, since energy contact is limited to the two fluids, the system is isolated

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

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

Entropy change for the fluid in subsystem 1

$$\Delta S_1 = \int_{ti}^{tf} \frac{dQrev}{T} = \int_{ti}^{tf} \frac{m_1 c_1 dT}{T} = m_1 c_1 \ln \frac{T_f}{T_1}$$

$$= m_1 c_1 \ln \frac{tf + 273}{t_1 + 273}$$

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

$$\Delta S_2 = \int_{ti}^{tf} \frac{dQrev}{T} = \int_{ti}^{tf} \frac{m_2 c_2 dT}{T} == m_2 c_2 \ln \frac{T_f}{T_2}$$

$$= m_2 c_2 \ln \frac{tf + 273}{t_1 + 273}$$

This will be positive, since $T_2 < T_f$

$\therefore \Delta S_{univ} = \Delta S_1 + \Delta S_2$

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

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 per formed. If m1 = m2 = m and c1 = c2 = c.

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

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

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

$$\Delta S_{univ} = 2mc \ln \frac{T_1 + T_2 / 2}{\sqrt{T_1 + T_2}}$$

This is always positive, since the arithmetic mean of any two numbers is always greater than their geometric mean.

4.12 ENTROPY TRANSFER MECHANISMS

Heat transfer and mass flow are two ways entropy can be moved into or out of a system. Work, on the other hand, transfers energy. Entropy transfer is identified as entropy crosses the system border and indicates the entropy gained or lost by a system during a process. Because heat transfer is the sole type of entropy interaction associated with a fixed mass or closed system, the entropy transfer for an adiabatic closed system is zero. More information is provided below:

(a) **Heat Transfer**-Since $dS = \dfrac{dQ_{rev}}{T}$ when heat is added to a system, $d\!-\!Q$ is positive, and the entropy of the system increases. When heat is removed from the system, $d\!-\!Q$ is negative, and the entropy of the system decreases.

Heat given to a system of fixed mass raises the internal energy of the system, causing the molecules (of a gas) to move with higher kinetic energy and collide more frequently, increasing the system's disorder. Heat is thus defined as a chaotic or disordered energy transfer that contributes to molecular chaos.

If heat Q flows reversibly from the system to the surroundings at T_0, the environment's entropy increases.
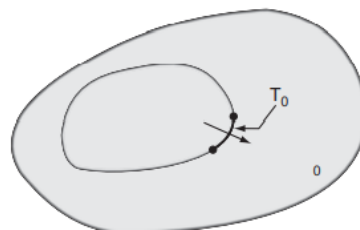

Fig 4.8 Entropy transfer along with heat flow

$$\Delta S_{sur} = \frac{Q}{T_0}$$

The entropy of the system is reduced by

$$\Delta Ssys = \frac{Q}{T_0}$$

T_0 is the constant temperature at the boundary where heat transfer occurs. It is possible to say that the system has lost entropy to its surroundings. Alternatively, the surrounds may have received entropy from the system. As a result, entropy transfer from the system to the surroundings occurs in addition to heat movement.

(b) **Mass Flow** - Both entropy and energy are contained in mass, and a system's entropy and energy are proportional to its mass. When a system's mass is doubled,

so are its entropy and energy. Streams of matter transmit entropy and energy into and out of a system, and the rates of entropy and energy transport are related to the mass flow rate. Closed systems do not have mass flow and thus no entropy transmission. When an amount of mass m enters or exits a system, it is accompanied by an entropy of amount ms, where s is the specific entropy. As a result, when a mass of amount m enters a system, its entropy increases by ms and reduces by the same amount when it departs it in the same state.

4.13 ABSOLUTE ENTROPY

It's vital to remember that the amount by which the system's entropy changes from its initial to end state, not the value of absolute entropy, is what matters. In some circumstances, a zero value of entropy is ascribed to the system at an arbitrarily defined standard state, and the entropy changes are determined using this standard state as a reference.

4.14. Third Law of Thermodynamics (Entropy)

Statistical analysis suggests that the entropy of a substance tends to zero as absolute zero temperature is reached.

This point has been so intensely investigated, that it is probably safe to say that at absolute zero temperature, the entropy of a pure substance in some perfect crystalline form becomes zero, a generalization known as the Third law.

It is found that the specific heats approach zero as temperature tends to zero and the difference $C_p - C_v$ also approaches zero, because the co-efficient of thermal expansion approaches zero.
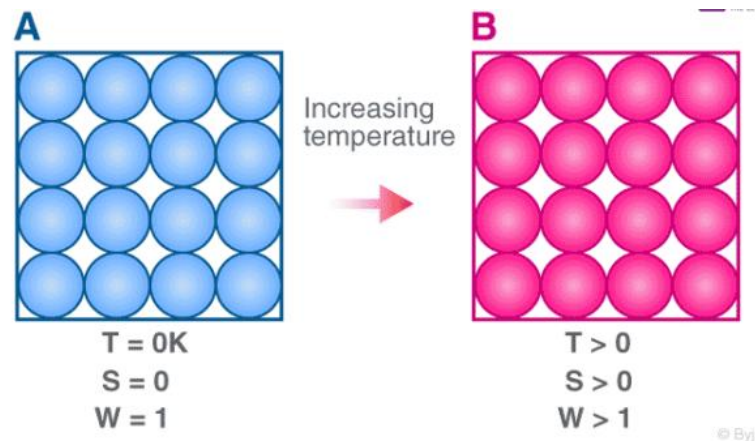
4.15 SUMMARY

The law of entropy, the amount of energy in a system that is not available for work, or the degree of disorder in a system. When heat is added to a system that is kept at a constant temperature, the change in entropy is proportional to the change in energy, pressure, temperature, and volume. Its magnitude ranges from 0 to the total energy in a system. The concept, first proposed by German physicist Rudolf Clausius in 1850, is sometimes referred to as the second law of thermodynamics, which states that entropy increases during irreversible processes such as spontaneous mixing of hot and cold gases, uncontrolled expansion of a gas into a vacuum, and fuel combustion. Entropy is commonly used in nontechnical contexts as a measure.

4.16 TERMINAL QUESTIONS

1.   Show that through one point there can pass only one reversible adiabatic?

2.   State and prove Clausius' theorem?

3.   Show that entropy is a property of a system?

4.   How is the entropy change of a reversible process estimated will it be different for an irreversible process between the same end states?

5.   Why is the Carnot cycle on T–s plot a rectangle?

6.   Establish the inequality of Clausius?

7. Give the criteria of reversibility, irreversibility and impossibility of a thermodynamic cycle?

8. What do you understand by the entropy principle?

9. Show that the adiabatic mixing of two fluids is irreversible?

10. Why the second law called a directional law of nature?

11. For any irreversible process, the net entropy change is

   A   Positive

   B   Zero

   C   Negative

   D   Infinite

12. A system in which there may exchange energy but not mass called

   A   Open system

   B   Close system

   C   Insulated system

   D   Isolated system

13. For thermodynamics constant pressure process, boundaries are

   A   Partially fixed

   B   Movable

   C   Fixed

   D   Infinite

14. The unit of entropy is

   A   J.K

   B   J/K

   C   J/K.s

   D   J.s/K

15. A certain perfect gas has Cp = 0.846KJ/kgK and Cv = 0.657KJ/kgK.The molar mass of gas will be

    A   40kg/kmol

    B   44kg/kmol

    C   48kg/kmol

    D   38kg/kmol

16. Change of entropy depends upon

    A   Initial states

    B   End states

    C   Process between end states

    D   None of the above

17. The entropy of process remains constant, if process is

    A.   Irreversible

    B.   Isobaric

    C   Reversible

    D   Isochoric

18. The entropy equation ds = dQ/T is true only for

    A   Reversible process

    B   Irreversible process

    C   Both A and B

    D   None

19. For reversible adiabatic process,change in entropy is

    A   Maximum

    B   Minimum

    C   zero

    D   Negative

20. If there is no heat transferred during the process, it is called

    A.   Isobaric

    B.   Isothermal

    C.   Polytrophic

    D.   Adiabatic

4.17 ANSWERS OF TERMINAL QUESTIONS

11. A	16. B
12. B	17. C
13. B	18. A
14. B	19. C
15. B	20. D

4.18 SUGGESTED READINGS

HEAT AND MASS TRANSFER THERMODYNAMICS, P K NAAG

CHEMICAL ENGINEERING THERMODYNAMICS, K V NARAYAN

ADVANCED ENGINEERING THERMODYNAMICS, R.W BENSON

Bachelor of Science
DCEPHS -106
Thermal Physics

U. P. Rajarshi Tandon
Open University

Block

2 Thermodynamic relations

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UNIT-05   MAXWELL'S RELATIONS

STRUCTURE

5.1 INTRODUCTION

In thermodynamics, the **fundamental thermodynamic relation** are four fundamental equations that demonstrate how four important thermodynamic quantities depend on variables that can be controlled and measured experimentally. Thus, they are essentially equations of state and using the fundamental equations, experimental data can be used to determine sought-after quantities like G or H. The relation is generally expressed as a microscopic change in internalenergy in terms of microscopic changes in entropy and volume for a closedsystem in thermal equilibrium in the following way.

$$dU = TdS - pdV$$

Here, U is internalenergy, T is absolutetemperature, S is entropy, P is pressure,

and V is volume. This relation applies to a reversible change, or to a change in a closed system of uniform temperature and pressure at constant composition.

This is only one expression of the fundamental thermodynamic relation. It may be expressed in other ways, using different variables (e.g. using thermodynamicpotentials). For example, the fundamental relation may be expressed in terms of the enthalpy as

$$dH = dU + pdV + Vdp$$

in terms of the Helmholtzfreeenergy (F) as

$$dF = dU - TdS - SdT$$

and in terms of the Gibbsfreeenergy (G) as

$$dG = dH - TdS - SdT$$

5.2 Objectives

After studying this unit, students will be able to:

Define Maxwell's equation

Describe Reciprocal theorem

Explain Thermodynamic potential

 Define Enthalpy, Gibbs free energy

Discuss Heat capacity

Discuss Specific heat capacity

5.3   RECIPROCAL THEOREM

Maxwell's reciprocal theorem, sometimes called Maxwell's reciprocal rule, is a technical relationship that equates two separate distortions in an elastic structure under load. It can either be used to reduce the number of factors calculated in a given circumstance or used as a check that the calculation has correctly predicted the equality of two separate distortions. Maxwell's rule is one of the basic tools of structural engineering.
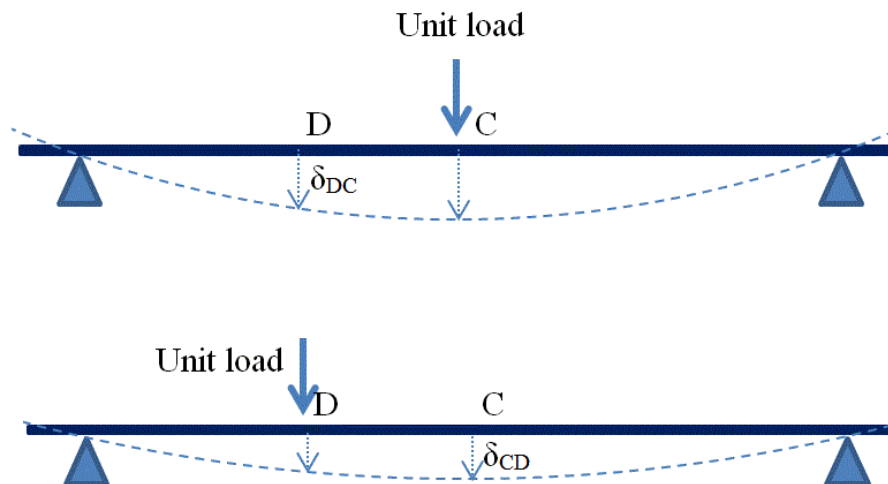
A simple example of the general rule is illustrated in the figure 1. A beam is supported near either end. A unit load is applied in the Centre (for simplicity as an example), at point C. The beam is not deflected at the centre but all along its length. Let the deflection at a point D be δ_{DC}. Maxwell's reciprocal theorem says that the

deflection at D due to a unit load at C is the same as the deflection at C if a unit load were applied at D. in our notation, $\delta_{CD} = \delta_{DC}$. The lower diagram illustrates the second situation.

> Applying unit load at C, the work done against
> the elastic forces on the beam is $\frac{1}{2}\delta_{CC}$.
> Applying in addition a unit load at D,
> the additional work is $\frac{1}{2}\delta_{DD} + \delta_{CD}$.
>
> If the forces are applied in the reverse order,
> the work done at D is $\frac{1}{2}\delta_{DD}$.
> Adding the load at C, the extra work done is $\frac{1}{2}\delta_{CC} + \delta_{DC}$.
>
> Since the total work in both case must be the same,
> $\frac{1}{2}\delta_{CC} + \frac{1}{2}\delta_{DD} + \delta_{CD} = \frac{1}{2}\delta_{DD} + \frac{1}{2}\delta_{CC} + \delta_{DC}$
> Giving Maxwell's theorem that $\delta_{CD} = \delta_{DC}$.

5.4 MAXWELL'S EQUATIONS

Maxwell's relations are a set of equations in <u>thermodynamics</u> which are derivable from the <u>symmetry of second derivatives</u> and from the definitions of the <u>thermodynamic potentials</u>. These relations are named for the nineteenth-century physicist <u>James clerk Maxwell</u>

EQUATION -

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

For a pure substance undergoing an infinitesimal reversible process

(a) $dU = TdS - pdV$

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

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

(d) dG = dH − TdS − SdT = Vdp − SdT

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

dz = M dx + N dy, then

$$\left[\frac{\partial M}{\partial y}\right]_x = \left[\frac{\partial N}{\partial x}\right]_y$$

Applying this to the four equations

$$\left[\frac{\partial T}{\partial V}\right]_S = -\left[\frac{\partial p}{\partial S}\right]_V$$

$$\left[\frac{\partial T}{\partial p}\right]_S = \left[\frac{\partial V}{\partial S}\right]_P$$

$$\left[\frac{\partial p}{\partial T}\right]_V = \left[\frac{\partial S}{\partial V}\right]_T$$

$$\left[\frac{\partial V}{\partial T}\right]_P = -\left[\frac{\partial S}{\partial p}\right]_T$$

These four equations are known as Maxwell's e Equations.

5.5 TdS EQUATIONS

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

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

$$TdS = T\left[\frac{\partial S}{\partial T}\right]_V dT + T\left[\frac{\partial S}{\partial V}\right]_T dV$$

Since $T\left[\frac{\partial S}{\partial T}\right]_V = C_V,$ heat capacity at constant volume, and

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

$$TdS = CvdT + T\left[\frac{\partial p}{\partial T}\right]_V dV$$

This is known as the first TdS equation.

If S = S (T, p)

$$dS = \left[\frac{\partial S}{\partial T}\right]_P dT + \left[\frac{\partial S}{\partial p}\right]_T dP$$

$$TdS = T\left[\frac{\partial S}{\partial T}\right]_P dT + T\left[\frac{\partial S}{\partial p}\right]_T dP$$

$$T\left[\frac{\partial S}{\partial T}\right]_P = Cp, \quad \left[\frac{\partial S}{\partial p}\right]_T = -\left[\frac{\partial V}{\partial T}\right]_P$$

Then,

$$TdS = C\,p\,dT - T\left[\frac{\partial V}{\partial T}\right]_P$$

This is known as the second TdS equation.

5.6   DIFFERENCE IN HEAT CAPACITIES

Equating the first and second TdS equation,

$$TdS = C\,p\,dT - T\left[\frac{\partial V}{\partial T}\right]_P dp = CvdT + T\left[\frac{\partial p}{\partial T}\right]_v dV$$

$$(C\,p - Cv)\,dT = T\left[\frac{\partial p}{\partial T}\right]_v dv + T\left[\frac{\partial V}{\partial T}\right]_P dp$$

$$dT = \frac{T\left[\frac{\partial p}{\partial T}\right]_v}{Cp - Cv}dV + \frac{T\left[\frac{\partial V}{\partial T}\right]_P}{Cp - Cv}dp$$

$$\left[\frac{\partial T}{\partial V}\right]_P dV + \left[\frac{\partial T}{\partial P}\right]_v dP$$

$$\frac{T\left[\frac{\partial p}{\partial T}\right]_v}{Cp - Cv}dV = \left[\frac{\partial T}{\partial P}\right]_v \text{ and } \frac{T\left[\frac{\partial V}{\partial T}\right]_P}{Cp - Cv}dp = \left[\frac{\partial T}{\partial P}\right]_v$$

Both these equations give

$$Cp - Cv = T\left[\frac{\partial p}{\partial T}\right]_v\left[\frac{\partial V}{\partial T}\right]_P$$

But,
$$\left[\frac{\partial p}{\partial T}\right]_v\left[\frac{\partial T}{\partial V}\right]_P\left[\frac{\partial V}{\partial p}\right]_T = -1$$

$$Cp - Cv = -T\left[\frac{\partial V}{\partial T}\right]^2\left[\frac{\partial p}{\partial V}\right]_T$$

5.7 RATIO OF HEAT CAPACITIES

At constant S, the two TdS equations become

$$C\,p\,dT_s = T\left[\frac{\partial V}{\partial T}\right]_P dp_s$$

$$CvdT_s = -T\left[\frac{\partial p}{\partial T}\right]_v dV_s$$

$$\frac{Cp}{Cv} = -\left[\frac{dV}{dT}\right]_P\left[\frac{dT}{dp}\right]_v\left[\frac{dp}{dV}\right]_S = \frac{\left[\dfrac{dp}{dV}\right]_S}{\left[\dfrac{dp}{dV}\right]_T} = \gamma$$

$$\left[\frac{dp}{dV}\right]_S > \left[\frac{\partial p}{\partial V}\right]_T$$

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

$$Ws = h2s - h1 = \int_1^{2S} vdp = \text{Area } 1\text{–}2S\text{–}3\text{–}4\text{–}1$$

For reversible and isothermal compression, the work done would be

$$WT = h2T - h1 = \int_1^{2T} vdp = \text{Area } 1\text{–}2T - 3 - 4 - 1$$
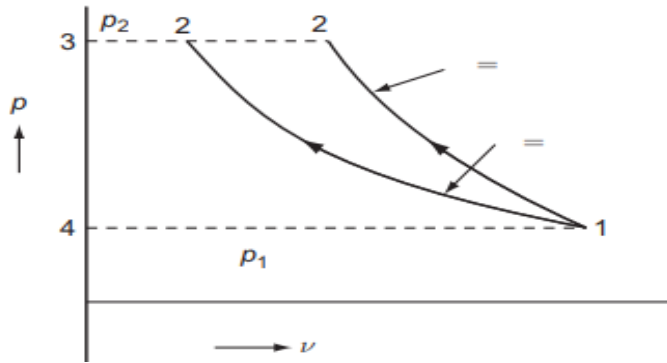
$W_T < W_S$

Fig 2 - Compression work in different reversible processes

For polytropic compression with $1 < n < \gamma$, the work done will be between these two values. So, isothermal compression requires minimum work. The adiabatic compressibility (ks) is defined as

$$ks = -\frac{1}{V}\left[\frac{\partial V}{\partial p}\right]_S$$

$$\frac{Cp}{Cv} = \frac{-\frac{1}{V}\left[\frac{\partial V}{\partial p}\right]_T}{-\frac{1}{V}\left[\frac{\partial V}{\partial p}\right]_S} = \gamma$$

$$\gamma = \frac{K_T}{K_S}$$

5.8   Thermodynamic Potentials

Thermodynamic Potentials; the term Ts represents the energy you can get from the system's environment by heating; the term pV represents the expansion work.

Thermodynamic potentials are scalar quantities used to represent state functions. Together with the corresponding equations of state, thermodynamic potentials describe the equilibrium behavior of a system as a function of so-called"natural variables".

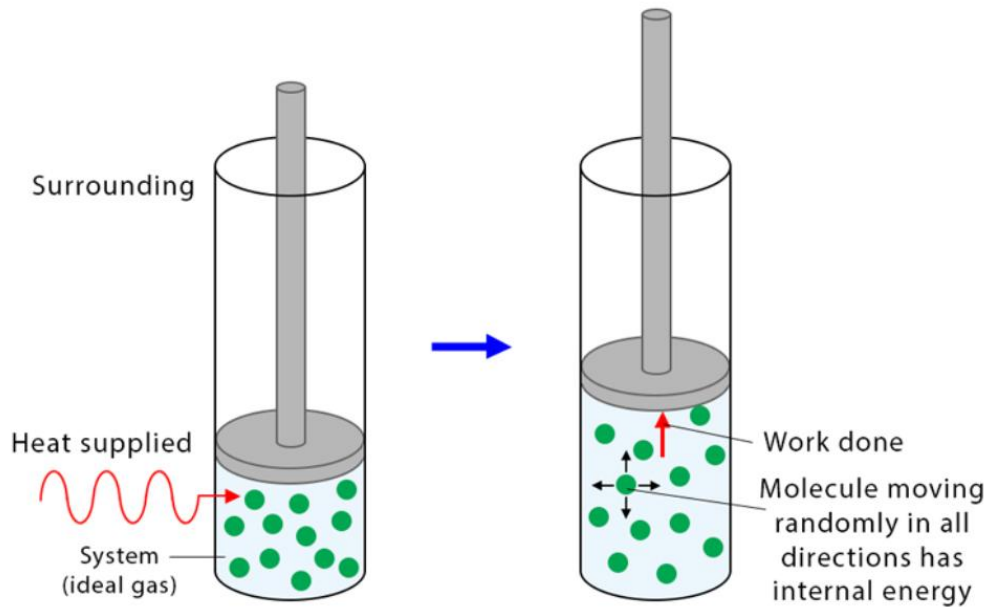Four common **thermodynamic potentials** are
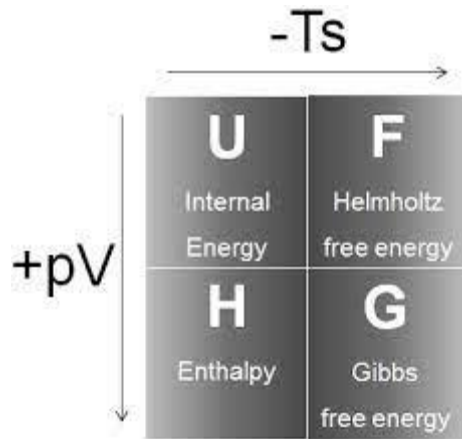
5.8.1 Internal Energy

Internal energy (also called the **thermal energy**) is defined in thermodynamics as the energy associated with tiny kinds of energy. It is a large quantity that varies depending on the size of the system or the amount of stuff it contains. The joule is the SI unit of internal energy (J). It is the energy contained inside the system, excluding the system's total kinetic energy of motion and potential energy. Microscopic kinds of energy include those produced by the rotation, vibration, translation, and interactions of a substance's molecules. Although none of these types of energy can be directly measured or evaluated, methodologies have been devised to assess the change in the total amount of all these microscopic forms of energy.
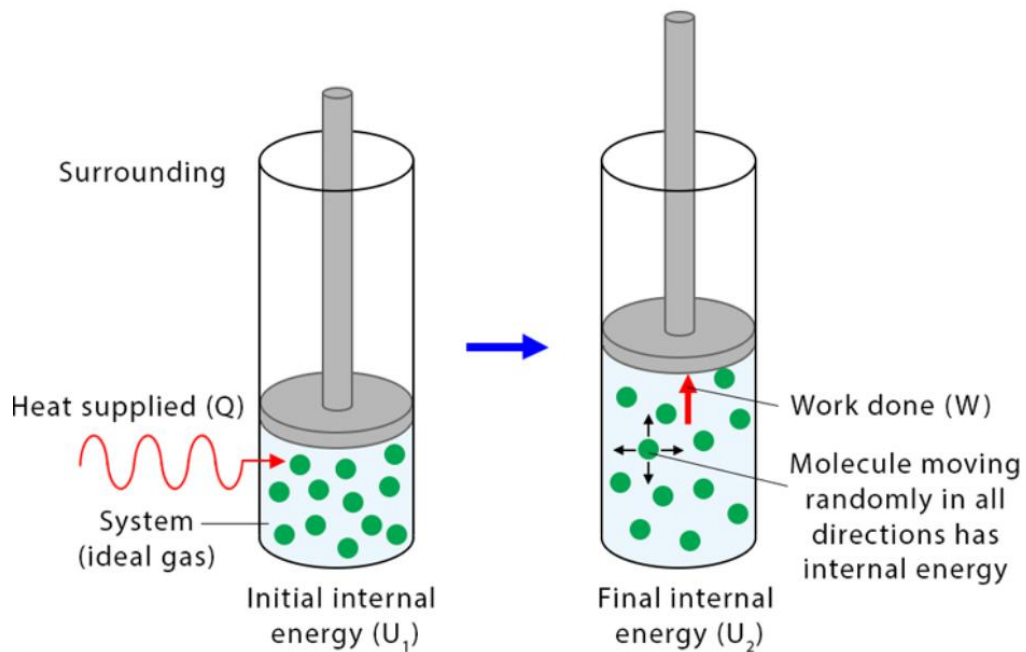
Internal Energy

The sum of kinetic energy and potential energy of all molecules in a substance

Surrounding

Heat supplied

System
(ideal gas)

Work done

Molecule moving
randomly in all
directions has
internal energy

Internal Energy Equation

$$U_2 - U_1 = \Delta U = Q - W$$

Surrounding

Heat supplied (Q)

System
(ideal gas)

Initial internal
energy (U_1)

Work done (W)

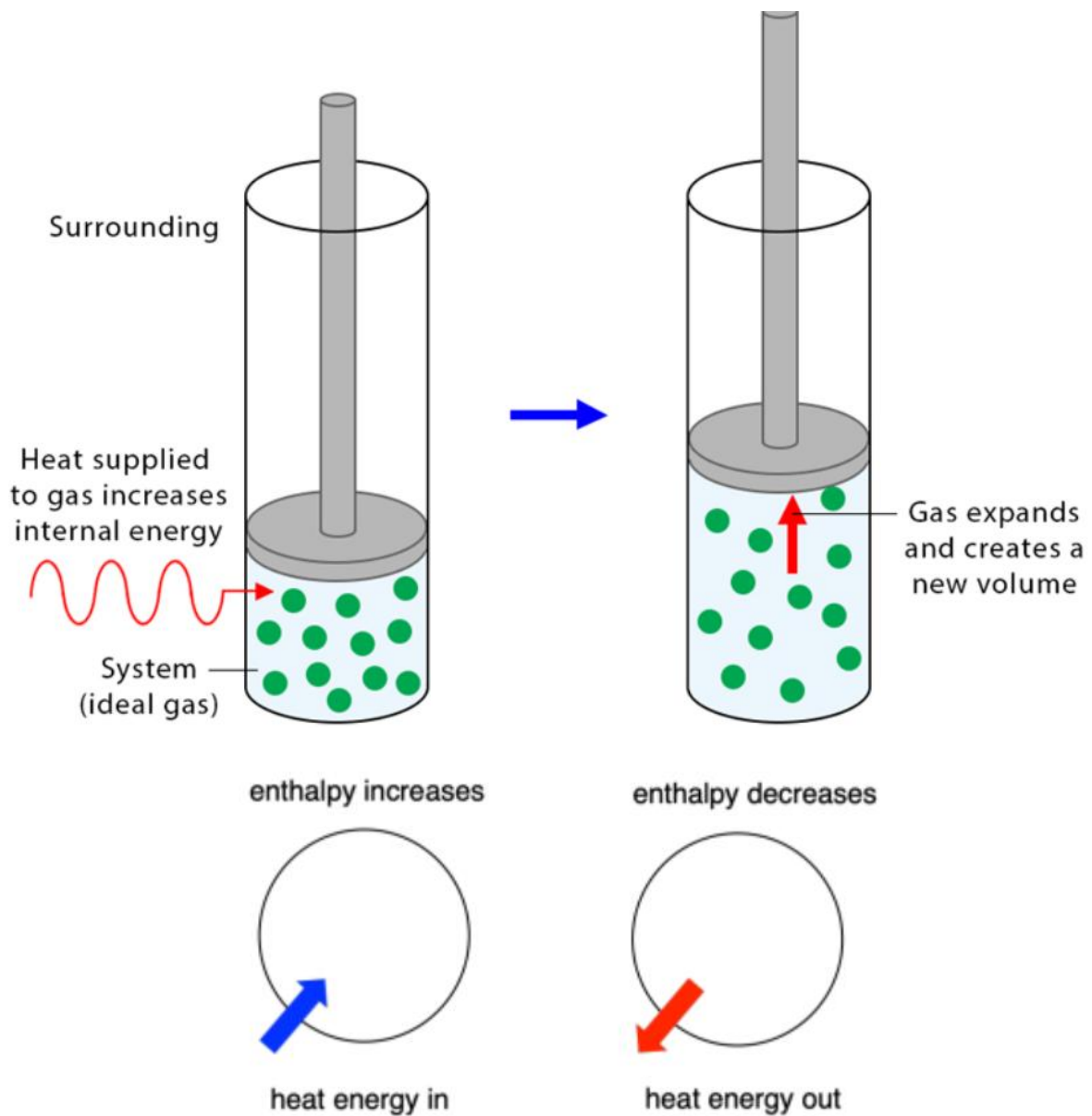Molecule moving
randomly in all
directions has
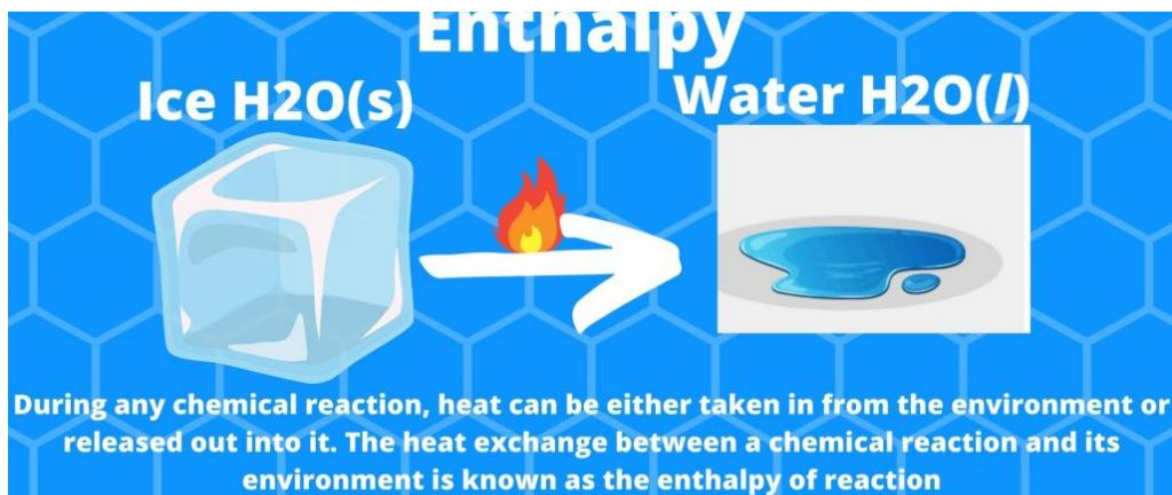internal energy

Final internal
energy (U_2)

5.8.2 Enthalpy

The enthalpy is a measurement of energy in a thermodynamic system. It's the thermodynamic quantity that equals a system's total heat content. The enthalpy is defined as the sum of the internal energy E plus the product of pressure p and volume V. Because the sum of the internal energy U and the product of pressure p and volume V appears in many thermodynamic analyses, it is convenient to name the combination enthalpy and to give it a distinct symbol, H.

$$H = U + pV$$

Surrounding

Heat supplied to gas increases internal energy

System (ideal gas)

Gas expands and creates a new volume

enthalpy increases

enthalpy decreases

heat energy in

heat energy out

During any chemical reaction, heat can be either taken in from the environment or released out into it. The heat exchange between a chemical reaction and its environment is known as the enthalpy of reaction

5.8.3 Helmholtz Free Energy:

The Helmholtz free energy is a thermodynamic potential defined as the internal energy of the system minus the product of the temperature and the entropy of the system in thermodynamics. It determines how much "useful" work a closed thermodynamic system can produce at constant volume and pressure. The free energy of Helmhotz is defined as:

$$F = U - TS,$$

$$dF = -SdT - pdV$$

The internal energy, U, is the sum of all the kinetic and potential energies of all the particles in the system, and it has a precise physical meaning. The amount of spontaneous energy transfer, TS, is the second term, where S is the system's final entropy. The Helmholtz free energy provides all reversible work in a constant temperature process. When physicists use the term "free energy" without specifying Helmholtz or Gibbs, they almost always mean Helmholtz free energy.

5.8.4 Gibbs free energy:

In thermodynamics, the Gibbs free energy is a thermodynamic potential that is defined as the enthalpy of the system minus the product of the temperature times the entropy of the system. Since the enthalpy is defined to be the sum of the internal energy E plus the product of the pressure p and volume V, the Gibbs free energy is defined as:
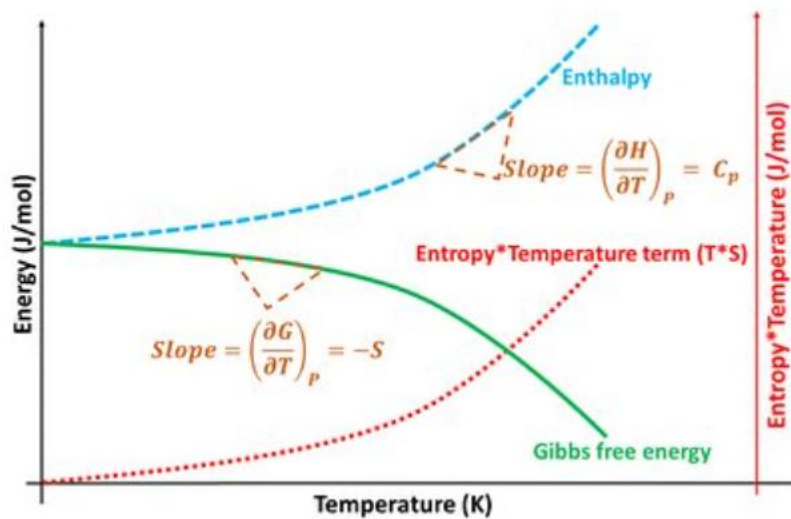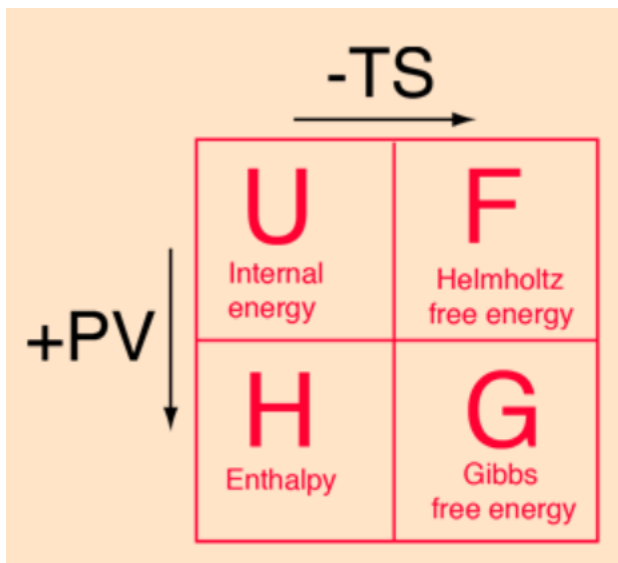
$$G(p, T) = U + pV - TS$$
$$G(p, T) = H - TS$$

The change in **Gibbs free energy, ΔG**, in chemistry, is a very useful parameter. It can be thought of as the maximum amount of work obtainable from a reaction.

Absolute temperature → Absolute pressure →

$$G = U - TS + PV$$

Gibbs free energy | Internal energy | Final entropy | Final volume

Energy you can get from the system's environment by heating

Work to give the system final volume V at constant pressure P

-TS →

+PV ↓

| U Internal energy | F Helmholtz free energy |
| H Enthalpy | G Gibbs free energy |

Enthalpy

$Slope = \left(\dfrac{\partial H}{\partial T}\right)_P = C_p$

Entropy*Temperature term (T*S)

$Slope = \left(\dfrac{\partial G}{\partial T}\right)_P = -S$

Gibbs free energy

Energy (J/mol)

Entropy*Temperature (J/mol)

Temperature (K)

5.9 Equilibrium conditions

Our discussion of thermodynamic potentials dealt hitherto mostly with the equilibrium state. The second law of thermodynamics-

$$T\,dS \geq \delta Q = dU + P\,dV - \mu dN \qquad\qquad\text{………………….(1)}$$

Allows however also to study the impact of irreversible processes, that is the evolution of the system toward the equilibrium. We have used for (1) the differential form of (4.6) together with the generalized first law

$$dU = \delta Q + \delta W + \mu d\,,$$

$$\delta W = -P\,dV\,,$$

Where we have taken the δW appropriate for a gas

Equilibrium internal energy. The entropy is an exact differential $dS = \delta Q/T$ at equilibrium. One can then consider situations like

$$dU = T\,dS - P\,dV \Rightarrow dU = -P\,dVS = \text{const. (work)}$$

$$dU = T\,dSV = \text{const. (heat)}$$

Where selected state variables are constant. We will now generalize this discussion

5.10 Heat capacity

Thermodynamics in its totality is concerned about heat. The meaning of heat today is energy in transit. Before the development of thermodynamic laws, the heat was considered as the measure of an invisible fluid, caloric, present in any matter. The capability of a substance to hold this fluid was then referred to as the heat capacity of that substance. The development in thermodynamics and dependence of heat transfer on temperature changed the definition of heat.

Modern thermodynamics defines ***heat as the measure of the total internal energy of a system.*** In order to quantify the heat energy associated with matter and its dependence on temperature, two properties were defined. These properties were named as specificheatcapacity and heat capacity of the system.

Mathematically,

Q=CΔT

Where Q is the heat energy required to bring about a temperature change of ΔT and C is the heat capacity of the system under study.

5.11 Specific Heat Capacity:

Specific heat capacity is the amount of heat energy required to raise the temperature of a substance per unit of mass. The specific heat capacity of a material is a physical property. It is also an example of an extensive property since its value is proportional to the size of the system being examined.

In SI units, specific heat capacity (symbol: c) is the amount of heat in joules required to raise 1 gram of a substance 1 Kelvin. It may also be expressed as J/kg·K. Specific heat capacity may be reported in the units of calories per gram degree Celsius, too. Related values are molar heat capacity, expressed in J/mol·K, and volumetric heat capacity, given in J/m^3·K.

Heat capacity is defined as the ratio of the amount of energy transferred to a material and the change in temperature that is produced:

C = Q / ΔT

Where C is heat capacity, Q is energy (usually expressed in joules), and ΔT is the change in temperature (usually in degrees Celsius or in Kelvin). Alternatively, the equation may be written:

Q = CmΔT

Specific heat and heat capacity are related by mass:

C = m * S

Where C is heat capacity, m is mass of a material, and S is specific heat. Note that Since specific heat is per unit mass, its value does not change, no matter the size of the sample. So, the specific heat of a gallon of water is the same as the specific heat of a drop of water.

It's important to note the relationship between added heats, specific heat, mass, and temperature change *does not apply during a phase change*. The reason for this is because heat that is added or removed in a phase change does not alter the temperature.

Specific Heat Capacity

The specific heat capacity of a substance is the amount of energy required to raise the temperature of 1 kg of the substance by 1°C.

$$c = \frac{\Delta E}{m \Delta \theta}$$

$$\Delta E = mc\Delta \theta$$

m = mass (kg)
c = specific heat capacity (J/kg°C)
ΔE = change in thermal energy (J)
$\Delta \theta$ = change in temperature (°C)

Specific Heat Capacity	Heat Capacity
Specific heat capacity is the amount of heat required to raise the temperature of one gram of a substance by 1 °C or 1 °K	Heat capacity is the amount of heat required to raise the temperature of a substance by 1 °C or 1 °K
It is the amount of heat added or removed to change the temperature	It is the ability of a body to absorb heat without increasing the temperature
It is not an intrinsic property	It is an intrinsic property of a substance
Formula c= q/mT	Formula C= q/T
The unit of specific heat capacity is J/g°C	The unit of heat capacity is J/°C
It is an intensive property so it depends on the amount of a substance	It is an extensive property so it is independent of amount of a substance
Specific heat is specific for specific objects	Heat capacity is a non-specific property
Examples of specific heat capacity are: Water = 1 calorie or 4.182 J/g$^{\circ}$C Copper = 0.385 J/g$^{\circ}$C	Examples of heat capacity are: 1 liter of water = 4182 J/kg$^{\circ}$C 100 g of copper = 38.5 J/$^{\circ}$C

5.12 Summary:

A system's thermodynamic state can be defined by its properties, which canbe classified as measured, fundamental, or derived. We want to create relationships that relate changes in fundamental and derived properties to measured properties that can be obtained directly from laboratory measurements. P, v, T, composition, cp, and cv are among the properties measured. Small letters are used to denote specific quantities, such as v for volume. Internal energy u and entropy s are the fundamental properties. These characteristics result from the first and second laws of thermodynamics.The first law states that energy is conserved, while the second law states that the universe's entropy always increases. The derived properties are defined to aid in the energy balance of systems that frequently combine internal energy and other properties. The mass that crosses the boundary between the surroundings and the system contributes to two terms in the energy balance in open systems: internal energy and flow work (Pv). Enthalpy (h) can be defined as follows for convenience:
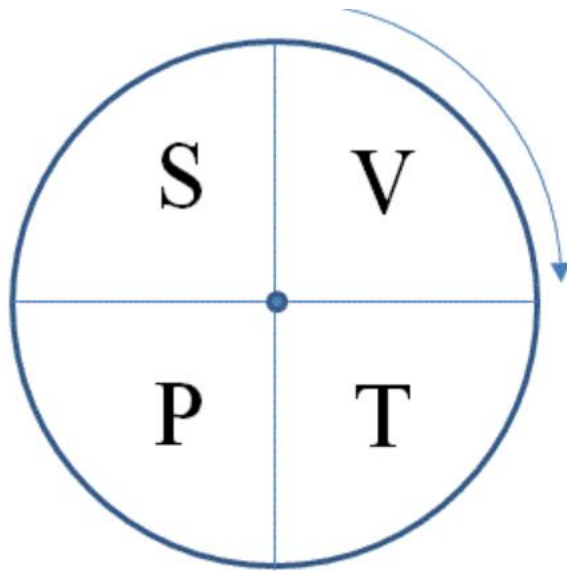
Maxwell's Relations

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

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

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

The four principal thermodynamic energies, their differential expressions, and the corresponding Maxwell relations.

Thermodynamic energy	Differential expression	Corresponding Maxwell relations
U	$dU = TdS - PdV$	$\left(\dfrac{\partial T}{\partial V}\right)_S = -\left(\dfrac{\partial P}{\partial S}\right)_V$
H	$dH = TdS + VdP$	$\left(\dfrac{\partial T}{\partial P}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_P$
A	$dA = -SdT - PdV$	$\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$
G	$dG = -SdT + VdP$	$\left(\dfrac{\partial S}{\partial P}\right)_T = -\left(\dfrac{\partial V}{\partial T}\right)_P$

5.13 Terminal question

1. Derive Maxwell's equations.

2. What is the use of the Gibbs entropy equation?

3. Define reciprocal theorem?

4. What is heat capacity?

5. Explain specific heat capacity?

6. Define chemical potential of a component in terms of U, H, and G.

7. Maxwell's thermodynamic relation are valid for

A. Closed system only

B. All process of thermodynamics

C. Only reversible process

D. A thermodynamic system in equilibrium

8. $\left[\dfrac{\partial p}{\partial T}\right]_v \left[\dfrac{\partial T}{\partial V}\right]_P \left[\dfrac{\partial V}{\partial p}\right]_T = ?$

A. Zero

B. 1

C. -1

D. Infinity

9. The ratio of specific heat $\gamma = \dfrac{Cp}{Cv}$ is always greater than unity, because ….

A. Cp = Cv +R

B. Cv = Cp + Cp.R

C. Cv = Cp +R

D. Cp = Cv- R

10. What is the unit of gibbs free energy ?

A. Kelvin

B. Kilowatt

C. Newton

D. Joule

5.14 ANSWERS OF TERMINAL QUESTIONS

7. [D]

8. [C]

9.[A]

10. [D]

5.15 SUGGESTED READING

1. *"Differential Forms of Fundamental Equations"*. *Chemistry LibreTexts. 2 October 2013.*

2. *Gao, Xiang; Gallicchio, Emilio; Roitberg, Adrian (2019). **"The generalized Boltzmann distribution is the only distribution in which the Gibbs-Shannon entropy equals the thermodynamic entropy"**. The Journal of Chemical Physics. 151 (3): 034113. **doi**:**10.1063/1.5111333**.*

3. *Gao, Xiang (March 2022). **"The Mathematics of the Ensemble Theory"**. Results in Physics. 34: 105230. **doi**:**10.1016/j.rinp.2022.105230**.*

4.   Thermal Physics: with Kinetic Theory, Thermodynamics: SC Garg.

5.   Thermal Physics: R. Murugeshan, Er. Kiruthiga Siva Prasath.

6.   Thermal Physics: C.B.P. Finn.

7.   Heat Thermodynamics and Statistical Physics: Brij lal, Dr. N. Subrahmanyam, P.S. Hemne.

UNIT - 06   PHASE TRANSITION

STRUCTURE

6.1 INTRODUCTION

Transitions between distinct physical states (phases) of the same substance are referred to as phase transitions. Ice melting and water boiling are common instances of phase transitions, as is the change of graphite into diamond at high pressures. Figure 1 is a diagram that illustrates temperature-pressure phase diagrams of matter (T−P) and temperature-volume (T−V).

Obviously, these necessarily simplified schemes do not reflect the whole variety of phase diagrams and phase transitions. For example, the melting curve of ice actually has a negative slope (dT /dP< 0), while in Fig. 1 the melting curve is depicted with a positive slope. Moreover, the melting curves can have a maximum, or, due to quantum effects, terminate at absolute zero temperature. The solid-state region (Fig. 1) can include numerous phase transitions associated with changes in their crystalline and electronic structure. Finally, in the case of special forms of interparticle interaction, the critical liquid-vapor point may not appear on the phase diagram of matter. In the above examples, phase transitions are accompanied by abrupt changes in the specific volume and entropy. Such transitions are called phase transitions of the first order, which usually occur at changing an aggregate state of matter and a radical transformation of the crystalline structure of solids.
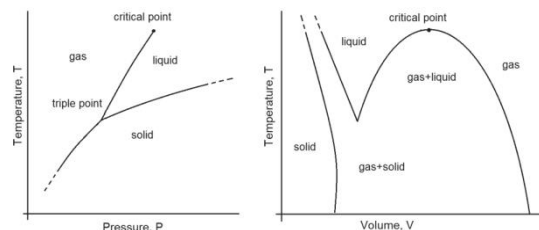

Figure 1: Typical form of phase diagram of one-component systems.

6.2 OBJECTIVE

After studying this unit, students will be able to:

1. First order phase transition

2. Clausiusclapeyron equation

3. Ehrenfest equation.

4. Latent heat equation from maxwells relation.

5. Effect of pressure on melting points of solid and boiling point of liquids.

6. Joules expansion.

7. Joule coefficient.

8. Free expansion and conservation of internal energy.

9. Change of entropy in isothermal irreversible process.

6.3   CONCEPT OF PHASE

Phases are states of matter characterized by distinct macroscopic properties. Typical phases we will discuss in this chapter are liquid, solid and gas. Other important phases are superconducting and magnetic states.

First and second order phase transitions. States of matter come with their stability regions, the phase diagram. The properties of the microscopic state change by definition at the phase boundary. This change is
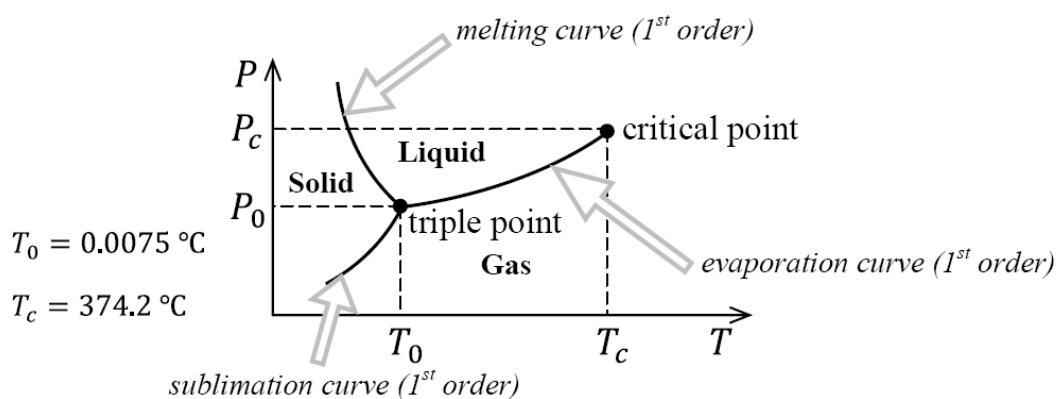

Fig 2 - The appropriate variables for phase diagram of water are the pressure P and the temperature T. critical point:

The first-order phase boundary between gas and liquid becomes second order right at the critical point. The two phases have then equal densities and specific entropies (entropy per particle). There is no critical point for the liquid-solid transition.

Triple point: The point at which gas, liquid and solid coexist.

6.4 EXPLAIN 1st ORDER PHASE TRANSITION WITH CLAUSIUS-CLAPEVRON EQUATIONS

In general, matter is divided into three phases. Solid, liquid, and gas are the three states of matter. A phase is a system with a homogeneous physical structure and chemical composition. A substance with the same chemical content but a distinct physical structure can exist in solid, liquid, or gas phases. 1st order phase transitions are transitions from one phase to another, such as vaporization, fusion, and sublimation. It's also possible that a second-order phase transition exists. When dealing with phase transitions that occur at constant temperature and pressure, the Gibb's potential G is particularly useful.

Theory:

Consider an equilibrium system composed of two phases of the same substance. The system is made up of two phases that are in equilibrium with liquid and vapour in an insulator cylinder with a piston. The system is in thermal contact with a reservoir at temperature T and is kept at that temperature and constant pressure P.
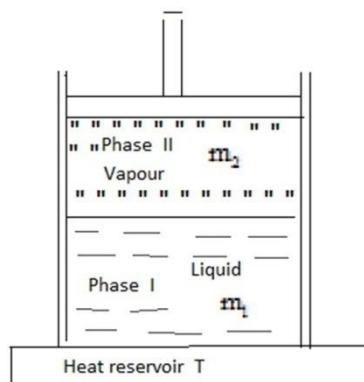
Fig 3 – Heat reservoir

Let the masses of the liquid and vapour phases be m_1 and m_2,

The specific Gibb's free energy be g_1 and g_2 respectively. Both phases are in equilibrium have the constant Gibb's potential. Therefore,

$$m_1 \, g_1 + m_2 \, g_2 = G \qquad \ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

at constant pressure P and temperature T (P, T)

Now, we consider a phase transition like evaporation is in effect a transfer of mass from the liquid to the vapour phase. If dm amount mass of the liquid vaporizes and complete system is in equilibrium. The total Gibb's free energy G_b of the system remains constant, then

$$(m_1 - dm)g_1 + (m_2 + dm)g_2 = Gb \rightarrow \text{(constant P, T)} \ldots..\text{(2)}$$

Or

$$(m_1 \, g_1 + m_2 g_2) + dm(g2 - g1) = Gb \rightarrow \text{(constant P, T)} \ldots\ldots\ldots.\text{(3)}$$

$$Ga + dm(g_2 - g_1) = Gb \rightarrow \qquad \text{(constant P, T)} \ldots\ldots\ldots.\text{(4)}$$

$$dm(g_2 - g_1) = dG \rightarrow \qquad \text{(constant P, T)} \quad \ldots\ldots\ldots\ldots\ldots.\text{(5)}$$

The transition take place but Gibb's free energy remain constant, therefore $G_a = G_{,b}$. A system is in equilibrium at a constant temperature T and constant pressure P has a minimum value of G and for a reversible transformation under these conditions dG = 0, therefore

$$g_1 = g_2$$

The specific Gibb's function has the same value in both phases. Next, we consider a neighboring isothermal corresponding to temperature T + dT and pressure P + dP. In this case specific Gibb's functions for the liquid and vapour phases now be ' g_1 and ' g_2, since the g's are function of T and P.

Since the two phases are in equilibrium at neighboring points a ' and b' on the T + dT

isothermal, we again arrive at the conclusion that

$g'_1 = g'_2$ (T+dT , P+dP).

We may write g'1= g_1 + dg_1 , where 1 dg is the change in g1 as T increases by dT and

P increases by dP. Similarly, $g_2' = g_2$+ dg_2, we then have

g_1+ dg_1 = g_2 + dg_2 →   (T + dT, P + dP)

Therefore,

 dg_1 = dg_2

The increment in the specific Gibb's function for the two phases are equal. The

specific Gibb's potential in terms thermodynamic function may be written as

dg = - SdT + VdP

Where S and V are the specific entropy and the specific volume respectively at

temperature T and pressure P.

For the liquid and vapour phases, we have

dg_1 = - S_1dT + V_1dP

dg_2 = - S_2dT + V_2 dP

since,

 dg_1 = dg_2 , then

- S_1dT + V_1 dP = - S_2dT + V_2dP ……………….(6)

Or

$$\frac{dP}{dT} = \left(\frac{S_2 - S_1}{V_2 - V_1} \right)_T \qquad …………………………. (7)$$

Now,

$$(S_2 - S_1)_T = \frac{L_{vap}}{T}$$

Where L_{vap} is the latent heat of vaporization at temperature T, hence

$$\left(\frac{dP}{dT}\right) = \frac{L_{vap}}{T(V_2 - V_1)_T}$$

This is the Clausius-Clapeyron equation for liquid-vapour equilibrium. It gives the rate at which the pressure must vary with temperature in order that the two phases remain in equilibrium. The phase equilibrium line on the P-T diagram is the locusof points representing states in which at which the liquid and vapour phases are in equilibrium.
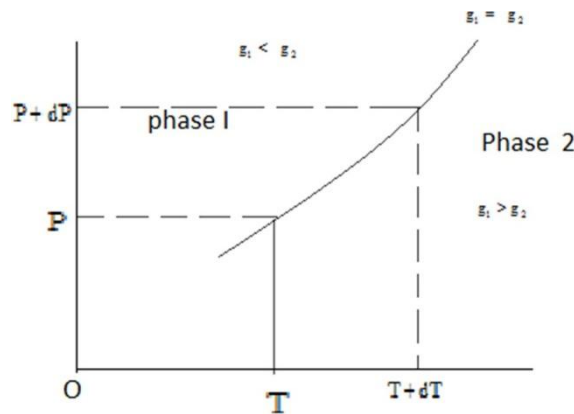

Fig. 4 Phase equilibrium plot on P – T diagram.

If both phases are to coexist at a given temperature the pressure is automatically determined thereby.Evidently, the same reasoning applied to the solid-liquid and solid-vapour phases gives the Clausius-Clapeyronrelations.

$$\left(\frac{dP}{dT}\right)_{fusion} = \frac{L_{fus}}{T(V_2 - V_1)_T}$$

$$\left(\frac{dP}{dT}\right)_{sub\lim ation} = \frac{L_{sub}}{T(V_2 - V_1)_T}$$

Although the latent heat varies with temperature it is always positive as is the temperature. The specific volume of the vapour phase is always greater than the specific volumes of the liquid or solid phases, $(V_2 > V_1$ and $V_2 > V3)$, so that the slope of the vapour pressure curve and sublimation pressure curves are always

positive. In general the specific volume of the liquid phase is greater than that of the solid phase ($V_1 > V_3$) and the slope of the melting curve is also positive.

Discussion for water:

There are some substance like water which contract on melting so that ($V_1 - V_3$) is negative. The three phase equilibrium lines meet at a common point A called the triple point. At this unique temperature and pressure all three phases coexist in equilibrium, so that $g_1 = g_2 = g_3$. For water the triple point temperature is 273.16K and the triple point pressure is 4.58mmHg. The triple point of water is the fundamental fixed point of thermometry.
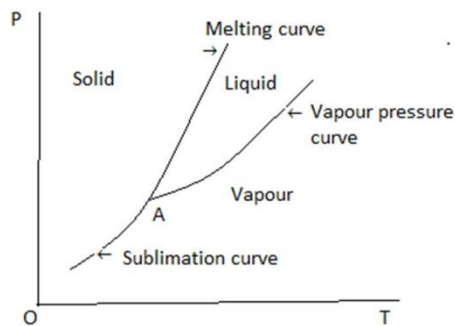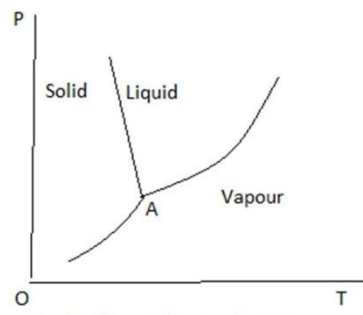

Fig. 2a: Phase diagram for simple substance

Fig. 2b: Phase diagram for water

The Clausius- Clapeyron equation is one of the most useful relations in thermodynamics. It is used to predict the effect of pressure changes on transition temperatures and for calculations of the latent heats. It may be integrated to give in a rough way of the saturation vapour pressure as a function of temperature.

6.5   Second-order phase transition and its characteristics

In a second-order phase transition the first derivatives of G vanish and the Clapeyron equation is replaced by a condition involving second derivatives.

Phase transition satisfying following condition-

1. No change in entropy and volume.

2. Discontinuity appear in specific heat (Cp) at constant pressure and isobaric volume expansion (α).

6.5.1 Ehrenfest equation

The entropy remains constant at phase transition –

So, for change of phase at T and P

$$[S_i = S_f]$$

So, for a change of phase at T+dT and P+dP

S+dSi = S$_f$ + dS$_f$

So, (dS$_i$ = dS$_f$)

(S$_i$=S$_f$)

Take S as dependent variable T and P as independent variable

S = S (T,P)

$$ds = \left(\frac{dS}{dT}\right)_P dT + \left(\frac{dS}{dP}\right)_T dP$$

$$Tds = T\left(\frac{dS}{dT}\right)_P dT + T\left(\frac{dS}{dP}\right)_T dP \qquad \text{(Multiply both side by T)}$$

$$\left(Cp = T\left(\frac{dS}{dT}\right)_P \right)$$

$$Tds = CpdT - T\left(\frac{dV}{dT}\right)_P dP \text{ (From Maxwellrelation } \left(\frac{dS}{dP}\right)_T = -\left(\frac{dV}{dT}\right)_P dP \text{)}$$

$$\alpha = \text{ Volume coefficient of expansion } \frac{1}{V}\left(\frac{dV}{dT}\right)_P$$

$$dS = Cp\frac{dT}{T} - V\alpha dP$$

$$dS_i = (Cp)_i \frac{dT}{T} - V\alpha_i dP$$

$$dS_f = (Cp)_f \frac{dT}{T} - V\alpha_f dP$$

$$dS_i = dS_f$$

$$\frac{dP}{dT} = \frac{(Cp)_f - (Cp)_i}{TV(\alpha_f - \alpha_i)}$$

This equation is Ehrenfest equation

6.6   Joule expansion

The Joule expansion is an irreversible thermodynamic process in which a volume of gas is held in one side of a thermally isolated container (via a small partition), while the other side is evacuated; the partition between the two parts of the container is then opened, and the gas fills the entire container. This procedure is a helpful exercise in classical thermodynamics since the consequent increase in entropy is simple to calculate.

One mole of an ideal gas (at pressure Pi and temperature Ti) is restricted to the left-hand side (as shown) of a thermally isolated container, occupying volume V0. The container's right side, which similarly has a volume V_0, is evacuated. The tap (solid line) connecting the two halves of the container is then abruptly opened, allowing the gas to fill the whole volume $2V_0$ container.

We propose that both the previous and new temperature and pressure (T_f, P_f) obey the Ideal Gas Law, so that $P_iV_i = RT_i$ initially and $P_fV_f = RT_f$ after the tap is opened, where R is the ideal gas constant.

Because the system is thermally isolated, the change in internal energy U = 0, and because internal energy is simply a function of temperature for perfect gases, we know that T = 0, and hence $T_i = T_f$. This means that $P_iV_0 = P_f(2V_0)$, and so the pressure is divided in half, i.e. $P_f = P_i/2$.
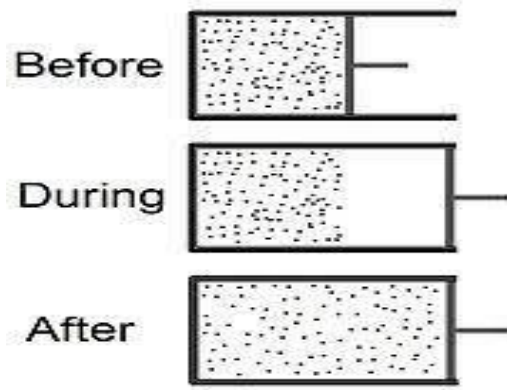
Fig 6 - Joule expansion

6.7 Derivation of joule coefficient

Joule coefficient. Here we are interested in how the temperature changes with volume in an experiment in which the internal energy is constant. That is, we want to derive the Joule coefficient, $\eta = (\partial T/\partial V)U$.

Now entropy is a function of state – i.e. of the intensive state variables P, V and T. (V = molar volume.) But the intensive state variables for a particular substance are related by an equation of state, so we need express the entropy as a function of only two of P, V or T, and, since we are seeking a relation between V and T, let us choose to express S as a function of V and T, so that

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT \qquad \ldots\ldots\ldots\ldots\ldots(1)$$

Let us look at these three terms in turn.

First, dS. In the Joule experiment, the internal energy of the gas is constant, so that

$$TdS - PdV = 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

That is,

$$dS = \frac{PdV}{T}$$

From the gibbs function –

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{............................(3)}$$

For the second term on the right hand side we obtain

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial H}\right)_P \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \Big/ \left(\frac{\partial H}{\partial S}\right)_P = \frac{C_P}{T} \qquad \text{..............(4)}$$

Then,

$$\frac{-VdP}{T} = -\left(\frac{\partial V}{\partial T}\right)_P dP + \frac{C_p dT}{T} \qquad \text{...............(5)}$$

Multiply through by *T*, and divide by *dP*, taking the infinitesimal limit as $dP \to 0$, recalling that we are dealing with an experiment in which the enthalpy is constant, and we arrive at

$$-V = -T\left(\frac{\partial V}{\partial T}\right)_P + C_P\left(\frac{\partial T}{\partial P}\right)_H \qquad \text{...............(6)}$$

From which we immediately obtain

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \qquad \text{...............(7)}$$

This is known as joule- coefficient.

6.8 Entropy

Entropy is a *state* function defined by (per unit mass)

$$ds \equiv \frac{dq_{rev}}{T}$$

Entropy is a state function ,this statement itself means that entropy change for a process is independent of the path taken by the process. Thus entropy change for same initial and final state is always same whether process is reversible or irreversible.Entropy is defined for both reversible and irreversible processes. Entropy

is a property of the system so its value is independent of the path followed i.e. It is a point function. So it is defined for both reversible and irreversible processes.

When we calculate entropy for any process we consider that process to be the reversible cause at the end **Entropy is a point function.**

For reversible process change in entropy of the system and surrounding (Universe) combined is zero. For irreversible process, it is non zero positive that's entropy generation. And for impossible processes, it's negative (refer to Clausius inequality).

But calculating absolute entropy is impossible but not necessary too. So we calculate the change in entropy during the process.
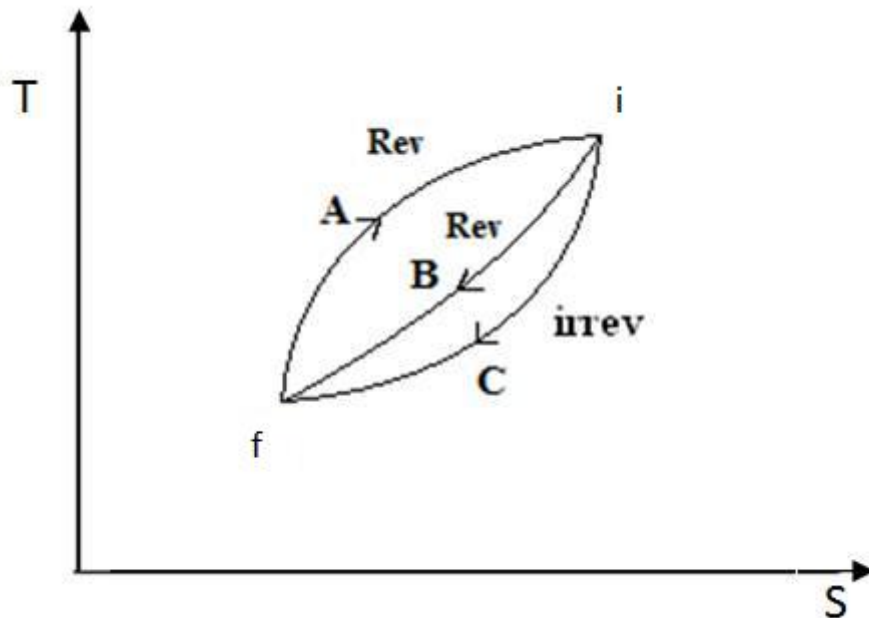

Fig 7-Graph of reversible and irreversible method.

If we take a system from state i to state f, then the change in entropy would be S_f - S_i, irrespective of the path taken, because they have specifically started and ended up at the same state.

6.8.1 Change of Entropy in an isothermal irreversible process

Let a system at higher temperature T1 and its surrounding at lower temperature T2 – 'q' amount of Δ goes irreversibility from system to surroundings.

$$\Delta S_{\text{system}} = -\frac{q}{T_1}$$

$$\Delta S_{\text{surrounding}} = +\frac{q}{T_2}$$

$$\Delta S_{\text{process}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$= -\frac{q}{T_1} + \frac{q}{T_2}$$
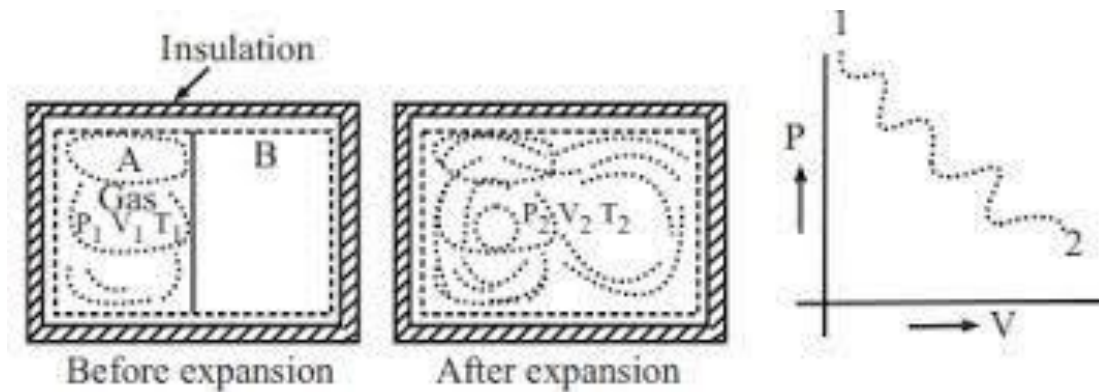
$$= q\left[\frac{T1 - T2}{T1T2}\right]$$

But T1>T2

So, T1-T2 = +Ve

$\Delta S_{\text{process}} > 0$

Hence, entropy increses in an irreversible process

6.9 Free expansion and conservation of internal energy in it

Before expansion   After expansion

In a free expansion, gas is allowed to expand into a vacuum. This happens quickly, so there is no heat transferred. No work is done, because the gas does not displace anything. According to the First Law, this means that:

$\Delta E_{\text{int}} = 0$

There is no change in internal energy, so the temperature stays the same.

On a PV diagram all you can do is plot the end-points. The process follows a path on the diagram that is not well-defined. Because the temperature is constant, the connection between the initial and final states is:

$P_1V_1 = P_2V_2$

Consider a rigid container that is thermally insulated. The container is divided into two compartments separated by a valve that is initially closed. One compartment, of volumeV1, contains the gas under investigation. The other compartment is empty. The initial temperature of the system is T1. The valve is now opened, and the gas is free to expand so as to fill the entire container, whose volume is V2. What is the temperature, T2, of the gas after the final equilibrium state has been reached?

Because the system consisting of the gas and the container is adiabatically insulated, no heat flows into the system: that is,

$$Q = 0.$$

Furthermore, the system does no work in the expansion process: that is,

$$W = 0.$$

Follows from the first law of thermodynamics that the total energy of the system is conserved: that is,

$$\Delta E = Q - W = 0.$$

Let us assume that the container itself has negligible heat capacity (which, it turns out, is not a particularly realistic assumption--see later), so that the internal energy of the container does not change. Under these circumstances, the energy change of the system is equivalent to that of the gas. The conservation of energy, thus reduces to

$$E(T_2, V_2) = E(T_1, V_1),$$

Where E(T,V) is the gas's internal energy.

6. 10 First and second latent heat equation from maxwell's relation

6.10.1 Maxwell Relations (MR)

Maxwell's equations are based on Euler's test for exact differentials, i.e. the mixed second derivates of nice functions must be equal. For a function f (x,y) :

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

Let's look at the Helmholtz equation as an example, as it is directly connected to the Clausius-Clapeyron equation

$$F = U - TS$$
i.e.
$$dF = dU - TdS - SdT$$
From the fundamental equation of thermodynamics:
$$dU = TdS - pdV$$
i.e.
$$dF = -SdT - pdV$$
Euler's test :
$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V}$$
Which will give us:
$$\frac{\partial S}{\partial V}_T = \frac{\partial p}{\partial T}_V$$

F=Helmholtz, T=temperature, P=pressure,V=volume, U=internal energy, S=entropy
Similarly, using Legendre's transforms and the above Euler test, a number of relations can be derived. These relations help draw connections between different system properties.

6.10.2 Clausius-Clapeyron Relation (CCR)

ClausiusClapeyron equation is related to phase transitions. Phase transitions for a single component are discontinuous, and occur at specific states. Both, change in volume, v (changes in density) and entropy are discontinuous. The condition for co-existence of two phases, is determined by laws of thermodynamics. This equilibrium condition for a single component system consisting of two phases, alpha (a) and beta (b), is Ta=Tb, Pa=Pb, μa=μb.

Let's consider two phases represented by state variables, U, V and N.

S1 (U1, V1, N1) S1 (U1, V1,N1) is the entropy of state 1/phase 1.

S2 (U2, V2, N2) S2 (U2, V2,N2) is the entropy of state 2/phase 2.

From thermodynamics, the conditions of equilibrium are given by minimum energy or maximum entropy.max(S1(U1,V1,N1)+S2(U2,V2,N2))

At maximum we have:

$dS_1+dS_2=0$

$$dS = \frac{dU}{T} + P\frac{dV}{T} - \mu\frac{dN}{T}$$

Hence, we derive at T1=T2; P1=P2 and μμ1=μμ2 unless the above three are satisfied, only one state exists
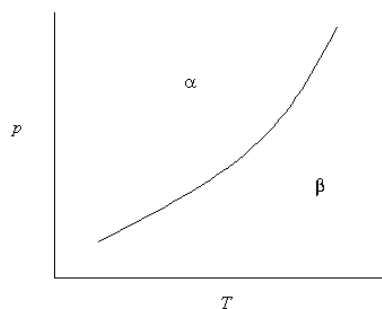

Fig 6 -In the above phase diagram, alpha and beta represent two different phases. And the phase line represents points of coexistence, i.e. both alpha and beta phases are in equilibrium along this curve.

CCR gives us a relationship on how pressure changes with temperature (i.e. slope of the tangent of the coexistence curve) for a pure system under phase transition. Here is the equation:

dPdT=LTΔvdPdT=LTΔv

Here, L is the latent heat or enthalpy or energy.

6.10.3 Effect of pressure in melting in solid and boiling in liquid

Both the melting and boiling point increase with increase in pressure and decrease with decrease in pressure as it is directly proportional to the pressure. Pressure cooker is the best example for it. We know that in pressure cooker the pressure of gas is very high because of that the water boils at high temperature that that of 100° C. In pressure cooker water boils at 120° Celcius instead of 100° Celcius. This is the main reason why food get cooked at lower time in Pressure cooker. Melting, it would take large volume than that of solidification (exception in case of water). If we increase the pressure it become harder for the substance to change into shape as the pressure increases volume get decreases, but for the substance to change the sate it requires much so it results in the rise of melting point. But melting point decrease with increase in pressure in case of water as it is an exception.
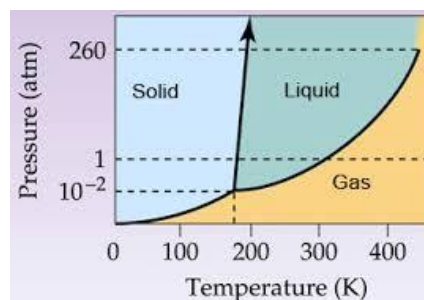

Fig 7 effect of pressure in solid and liquid.

Summary

Some important points -

The free expansion or unregistered expansion process is an irreversible non flow process. A free expansion occurs when a fluid is allowed to expand suddenly into a vacuum chamber through an orifice of large dimension.

For a free expansion process,

Heat Q= 0

Work W= 0

Internal Energy U = 0

Following points are important for free expansion of the gas.

1. Expansion may be called as a adiabatic expansion since there is no heat transfer.

2. Free expansion process is irreversible.

3. This is known as a unregistered expansion process since there is no work done by the system.

4. Since dU=zero → U2 =U1

5. Free expansion process is known as a constant internal energy process.

6. Enthalpy and temperature on both are constant during the free expansion process of ideal gas.

4.11 TERMINATED QUESTIONS -

1. A _____ transformation, in which a two-component single-phase liquid is cooled and transforms into two solid phases

    A. peritectic

    B. metastable

    C. spinodal decomposition

    D. eutectic

2. Which of the following is not a basic states of matter?

    A. Solid

    B. Liquid

C.   Air

D.   Plasma

3.   Phase transitions occur when the thermodynamic free energy of a system is non-analytic for some choice of thermodynamic variables.

A.   Yes

B.   No

C.   Can be yes or no

D.   Can not say

4.   Which of the following are also called continuous phase transitions?

A.   First-order phase transitions

B.   Second-order phase transitions

C.   Third-order phase transitions

D.   Fourth-order phase transitions

5.   Which of the following is a measure of the degree of order across the boundaries in a phase transition system?

A.   Critical points

B.   Relevance

C.   Both A and B

D.   Order Parameter

6.   Which of the following is a spontaneous exothermic process?

A.   Ice melting

B.   Removal of sugar from the coffee

C.   Rusting

D.   Dissolution of sand in water

7.   If we consider that there are no volume and enthalpy changes caused by mixing, then the only contribution to the entropy will be_____

A.   Thermal

B.   Hydrostatic

C.   Rotational

D.   Configurational

8.   Properties of metallic material primarily depends on _____

A.   Processing

B.   Type of crystal structure

C.   Microstructure

D.   Grain size

9.   According to Gibbs rule the number of phases (P) present in a system in equilibrium is given as_____

A.   P=C+F-N

B.   P=C+N-F

C.   P=F+N-C

D.   P=C+N+F

10.   First-order phase transitions are those that involve a latent heat.

A.   TRUE

B.   FALSE

C.   Can be true or false

D.   Can not say

ANSWERS

1-Ans : C

Explanation: phase transitions (or phase changes) are the physical processes of transition between the basic states of matter: solid, liquid, and gas, as well as plasma in rare cases.

2-Ans : D

Explanation: A eutectic transformation, in which a two-component single-phase liquid is cooled and transforms into two solid phases. The same process, but beginning with a solid instead of a liquid is called a eutectoid transformation.

3-Ans : A

Explanation: Yes, Phase transitions occur when the thermodynamic free energy of a system is non-analytic for some choice of thermodynamic variables

4-Ans : B

Explanation: Second-order phase transitions are also called continuous phase transitions. They are characterized by a divergent susceptibility, an infinite correlation length, and a power law decay of correlations near criticality.

5-Ans : D

Explanation: An order parameter is a measure of the degree of order across the boundaries in a phase transition system; it normally ranges between zero in one phase (usually above the critical point) and nonzero in the other.

6-Ans: C

Explanation: Rusting is spontaneous exothermal process .Melting of ice is a spontaneous endothermic process and the last two are non-spontaneous in nature.

7- Ans: D

Explanation: The only contribution to the entropy will be Configurational. Configurational entropy comes from the possibility of arranging the atoms A and B in different ways for a particular macro state

8-Ans: A

Explanation: The properties of metallic material primarily depends on chemical composition and processing. This is the property that decides the microstructure that gets developed into the material.

9- Ans: B

Explanation: $P+F=C+N$, where F is the degree of freedom, N is the non-compositional variable and C is the number of components. Here the degree of freedom is an intensive variable hence can be varied independently while still maintaining the equilibrium.

10 –Ans: A

Explanation: True, First-order phase transitions are those that involve a latent heat

6.13 Suggested Reading

1.   Thermal Physics: with Kinetic Theory, Thermodynamics: SC Garg.

2.   Thermal Physics: R. Murugeshan, Er. Kiruthiga Siva Prasath.

3.   Thermal Physics: C.B.P. Finn.

4.   Heat Thermodynamics and Statistical Physics: Brij lal, Dr. N. Subrahmanyam, P.S. Hemne.

UNIT - 7   THIRD LAW OF THERMODYNAMICS

7.1 INTRODUCTION

The bench of Chemical Science which deals with the study of different forms of Energy and the Quantitative relationships between them is known as Thermodynamics. The confined study of chemical changes and chemical substances only, the restricted branch of Thermodynamics is known as chemical Thermodynamics. The Third Law of Thermodynamics states that the Entropy of a pure Crystal at Absolute Zero is Zero. The 3rd Law of Thermodynamics explains Entropy. Entropy is the measure of the disorder in a system, and while a perfect Crystal is by definition perfectly ordered so that the Entropy of that Crystal is Zero. Whenever asked to explain the Third Law of Thermodynamics it is necessary to mention the pure Crystal state of the matter.

Decrease in temperature — More decrease in temperature — 0 K or -273.15 °C
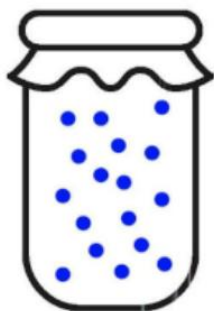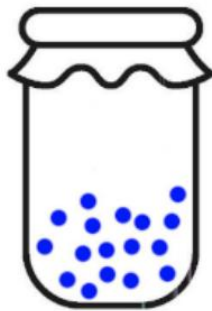
Decrease in kinetic energy — More decrease in kinetic energy — ZERO kinetic energy

"The value of entropy of a completely pure crystalline substance is zero at absolute zero temperature"

7.2 OBJECTIVES

After studying this Unit, student should able to :

- Understand the concept of Joule's Thomson expansion effect.

- Define inversion curve in thermodynamics.

- Explain the concept of Third law of Thermodynamics.

- Define Throttling Process.

7.3 JOULE'S THOMSON EFFECT

In thermodynamics, the effect called Joule Thomson effect was discovered in 1852. This effect was named after two physicists James Prescott Joule (1818-1889) and William Thomson (1824-1907). This effect describes the change in temperature of a real gas or liquid when it is forced to pass through porous plug or valve while it is kept insulated so that exchange of heat with the environment is not possible. This process is called throttling process or Joule Thomson effect. This effect is mainly used in thermal machines such as refrigerators, heat pumps and air conditioners.

**Joule-Thomson effect, also called Joule-Kelvin effect**, the change in temperature that accompanies expansion of a gas without production of work or transfer of heat.

Let the stream of gas which is at high pressure is allowed to expand by passing through porous plug into region of low pressure or vacuum. The gas gets cool under adiabatic conditions. But hydrogen and helium are exceptions as they get

warmed up under similar circumstances. The temperature below which a gas becomes cooler on expansion is known as the inversion temperature. For example, the inversion temperature of hydrogen is –48°C while that of helium is –242°C. Thus Joule-Thomson effect can be defined as the phenomenon of temperature change produced when a gas is allowed to expand adiabatically from a region of high pressure to a region of extremely low pressure. This cooling of the gas is basicallydue to the decrease in the kinetic energy of the gaseous molecules as some part of this kinetic energy is utilized in overcoming intermolecular van der Waals force of attraction during expansion. The Joule-Thomson effect is very small when a gas approaches ideal behavior. Thus for an ideal gas, Joule Thomson effect is zero. Therefore, no absorption or evolution of heat takes place when expansion of an ideal gas occurs i.e. q = 0.This is because in an ideal gas there are no intermolecular van der Waals forces of attraction thus there is no expenditure of energy in overcoming these forces during expansion. Further, when expansion of ideal gas occurs in vacuum then no work is

done since pressure against which it expands is zero. From the first law equation we can say that ΔU is also equal to zero. Thus, when an ideal gas undergoes expansion under adiabatic conditions in vacuum, no change takes place in its internal energy. In other words, the internal energy of a given quantity of an ideal gas at a constant temperature is independent of its volume, i.e., $(\partial U / \partial V)_T = 0$. An ideal gas may, therefore, be defined thermodynamically by the following two equations: (i) PV = constant, at constant temperature (ii) $(\partial U / \partial V)_T = 0$ The quantity $(\partial U / \partial V)_T$ is called the internal pressure and it is zero for ideal gas.

Joule and Thomson derived the relationship between fall of pressure of gas on expansion and resulting lowering of temperature by performing the following technique:
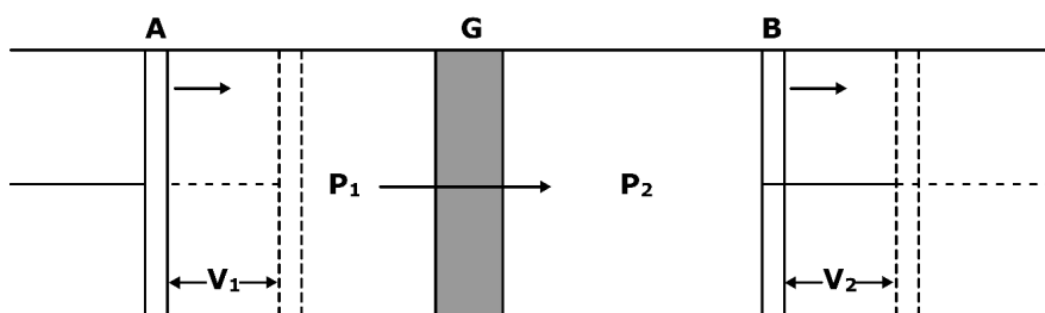
A tube made of a non-conducting material is fitted with a porous plug G in the middle and two pistons A and B on the sides, as shown. The tube is thoroughly insulated to ensure adiabatic conditions. Let the volume of gas enclosed between the piston A and the porous plug G at pressure P_1 is V_1. This volume is forced to pass through porous plug by moving the piston A inwards. At the same time the volume of gas enclosed between porous plug G and piston B i.e. V_2 is allowed to expand at a lower pressure P_2 by moving the piston B outward, as shown. Therefore, work done on the system at the piston A $= +P_1V_1$ and work done by the system at the piston B $= -P_2V_2$

Then, net work done by the system $= -P_2V_2 + P_1V_1$ Since the expansion of the gas is done adiabatically i.e. no exchange of heat takes place between the system and surroundings. Thus the work is done by the system at the expense of internal energy only. Let the internal energy of the system changes from U_1 to U_2.

$$-P_2V_2 + P_1V_1 = U_2 - U_1$$

$$U_2 + P_2V_2 = U_1 + P_1V_1$$

$$H_2 = H_1$$

$$H_2 - H_1 = 0$$

$$\text{i.e. } \Delta H = 0$$

This states that the Joule-Thomson expansion of a real gas occurs with constant enthalpy and not with constant internal energy. According to this the process is known as isoenthalpic process. Taking enthalpy as the function of temperature and pressure, then the total differential of the enthalpy H can be written as

$$dH = (\partial H / \partial P)_T \, dP + (\partial H / \partial T)_P \, dT$$

But $(\partial H / \partial T)_P = C_P$

Substituting equation (4) in (3) we get

$$dH = (\partial H / \partial P)_T \, dP + C_P \, dT$$

Since for adiabatic expansion, $dH = 0$, hence

$$(\partial H / \partial P)_T \, dP + C_P \, dT = 0$$

Rearranging the above equation $dT/dP = (\partial H / \partial P)_T / C_P$

i.e., $(\partial T / \partial P)_H = - (\partial H / \partial P)_T / C_P$

The quantity $(\partial T / \partial P)_H$ is called Joule-Thomson coefficient and it is denoted as $\mu_{J.T}$. For small pressure range the equation 6 can also be written as

$$\Delta T = - \frac{(\partial H / \partial P)_T}{C_P} \Delta P$$

In the above equation ΔT is the fall of temperature and ΔP is fall of pressure.
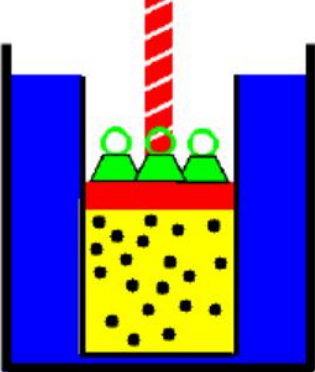
7.4 ENTHALPY EQUATION

In symbols, the enthalpy, H, equals the sum of the internal energy, E, and the product of the pressure, P, and volume, V, of the system: **H = E + PV**. According to the law of energy conservation, the change in internal energy is equal to the heat transferred to, less the work done by, the system.

Enthalpy is the measurement of energy in a thermodynamic system. The quantity of enthalpy equals to the total content of heat of a system, equivalent to the system's internal energy plus the product of volume and pressure.

Technically, enthalpy describes the internal energy that is required to generate a system and the amount of energy that is

required to make room for it by establishing its pressure and volume and displacing its environment.

The enthalpy can be made into an **intensive**, or "specific", variable by dividing by the mass.

E = Internal Energy Q = Heat Transfer
T = Temperature W = Work
p = Pressure C_p = Heat Capacity
V = Volume (constant pressure)

Define a new state variable that is a combination of other state variables.

Enthalpy = H = E + pv

h = Specific Enthalpy = $e + pv = \dfrac{\text{Enthalpy}}{\text{mass}}$

1st Law: $E_2 - E_1 = Q - W$

For a constant pressure process, the work is given:
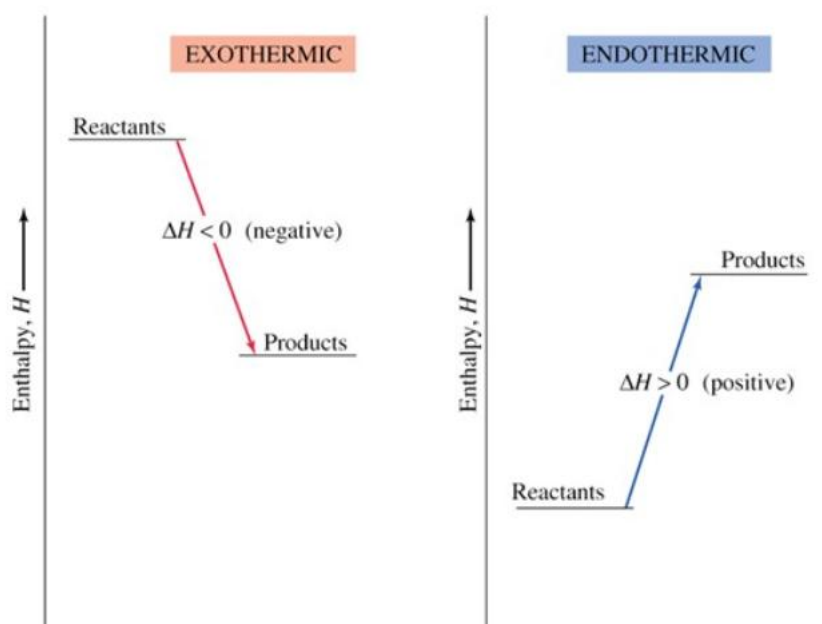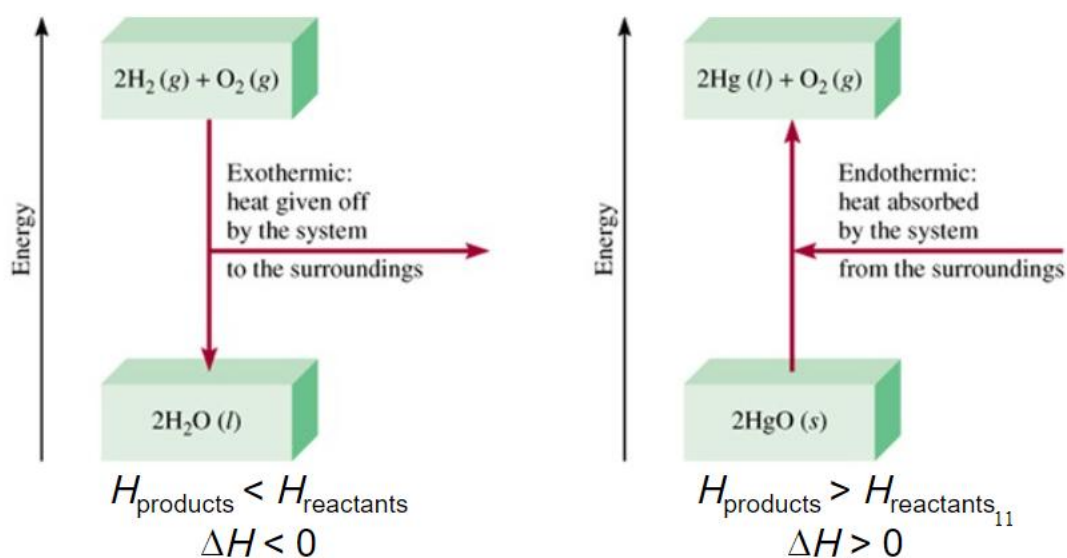
$$W = p(V_2 - V_1)$$

$$E_2 - E_1 = Q - p(V_2 - V_1)$$

Re-group: $(E_2 + pV_2) - (E_1 + pV_1) = (H_2 - H_1)_p = Q = C_p(T_2 - T_1)_p$

(specific enthalpy) $\quad (h_2 - h_1)_p = c_p(T_2 - T_1)_p$

$$\Delta H = H_{(products)} - H_{(reactants)}$$

ΔH = heat given off or absorbed during a reaction **at constant pressure**

Energy

$2H_2\,(g) + O_2\,(g)$

Exothermic:
heat given off
by the system
to the surroundings

$2H_2O\,(l)$

$H_{products} < H_{reactants}$
$\Delta H < 0$

Energy

$2Hg\,(l) + O_2\,(g)$

Endothermic:
heat absorbed
by the system
from the surroundings

$2HgO\,(s)$

$H_{products} > H_{reactants}$
$\Delta H > 0$

EXOTHERMIC

Enthalpy, H

Reactants

$\Delta H < 0$ (negative)

Products

ENDOTHERMIC

Enthalpy, H

Products

$\Delta H > 0$ (positive)

Reactants

$$\Delta H_{rxn} = \Delta H_{products} - \Delta H_{reactants}$$

7.5 INVERSION CURVE

The Joule–Thomson inversion curve (JTIC), defined as **the locus in the p–T plane where the adiabatic Joule–Thomson (JT) coefficient is zero, separates regions for which heating**

and cooling occur upon an isenthalpic expansion. JTIC calculation for mixtures is a clear matter for single-phase conditions.
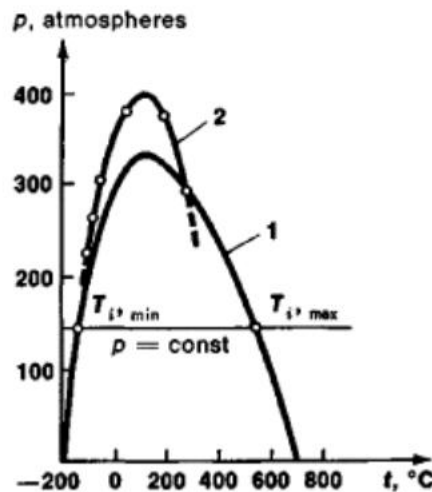
7.6 DIFFERENT TYPES OF COOLING SYSTEMS

- Central Air Conditioner. The most common type of air conditioner is the central cooling system. ...

- Ductless Mini-Split Systems. Ductless systems are ideal for homes and apartments. ...

- Heat Pumps. ...

- Evaporative Air Conditioners.

7.7 COMPARISION OF JOULE-THOMSON EXPANSION WITH JOULE EXPANSION AND ADIABATIC EXPANSION

Since, all the three processes are adiabatic in nature i.e., heat can neither enter the system nor leave the system.

But still there are differences in

(i)   Joule Expansion

(ii) Joule Thomson Expansion

(iii) Adiabatic Expansion

(i)   In Joule Expansion, the net work done by the system or on the system is zero i.e., the system is mechanically isolated from the surrounding.

> **In Joule Expansion, we observe cooling effect.**

(ii) In Joule Thomson Expansion, although the system is mechanically isolated from the surrounding, but the external work done by the gas in passing through the porous plug is not zero.

> **In Thomson Expansion, we observe both cooling and heating effect.**

(iii) In Adiabatic Expansion, neither the system is mechanically isolated from the surrounding nor the pressure of the gas is made to keep constant. The adiabatic expansion of gas performs external work against the atmospheric pressure.

In Adiabatic Expansion, we observe cooling effect.

Adiabatic Expansion	Joule Thomson Effect/Expansion	
1	In thermodynamics, Adiabatic expansion is a reversible process.	In thermodynamics, the Joule-Thomson effect is an irreversible process.

| 2 | In this expansion, only cooling is produced. | For the case of the Joule-Thomson effect, both cooling and heating are produced.

It depends on the **Inversion temperature** of the gas.

If gas is below the Temperature of Inversion, then, it produces a cooling effect. And if the gas is above the temperature of inversion, it produces |

a heating effect.

But, if the gas is at the Temperature of Inversion, then, at this temperature the Joule-Thomson effect becomes Zero.

For example, If try to expand hydrogen or helium gases with the help of the Joule-Thomson effect then, must do pre-cooling of these gases before further expansion. This is because at ordinary temperature these gases produce

		heating effects.
3	Even, cooling is produced in adiabatic expansion in the case of a perfect gas.	In the Joule-Thomson effect there no heating and cooling is produced in the case of a perfect gas.
4	The entropy of the gas remains constant in this expansion.	Enthalpy of the gas remains constant in this effect.
5	In this expansion, work is done only by gas.	In the Joule-Thomson effect, the work is done is by the gas as well as on the gas.

6	The fall in the temperature range is much larger in the case of adiabatic expansion, for the same pressure difference.	Here the change in the temperature range is small, for a given pressure difference.
7	No is no need for the Porous-Plug arrangement.	A Porous-Plug is required to complete the Joule-Thomson effect.

7.8   THROTTLING PROCESS

Throttling is a process where a high-pressure fluid is converted into low-pressure by using a throttle valve. In a throttling process, the enthalpy remains constant and the work done is zero.

An example of a throttling process is **an ideal gas flowing through a valve in mid position**. From experience we can observe that: Pin > Pout, velin < velout (where P =

pressure and vel = velocity). These observations confirm the theory that hin = hout.

An application of the throttling process occurs in **vapor-compression refrigerators**, where a throttling valve is used to reduce the pressure and reduce the temperature of the refrigerant from the pressure at the exit of the condenser to the lower pressure existing in the evaporator.

The throttling processes are considered as adiabatic. The pressure losses throughout the system are neglected.

What is the difference between throttling process and free expansion process?

Enthalpy = PV. In Free expansion process dQ=0,du=0,dw=0,enthalpy =0(const). **Throttling process is also called isenthalpic process in which enthalpy remains constant before and after throttling process** so it's not a correct answer.
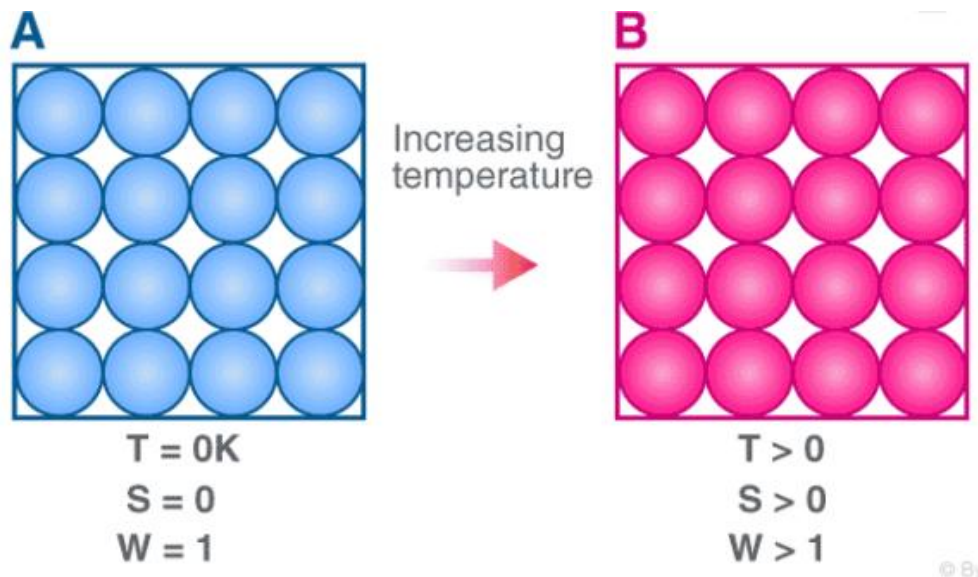
7.9   THIRD LAW OF THERMODYNAMICS

The third law of thermodynamics states that the entropy of a perfect crystal at a temperature of zero Kelvin (absolute zero) is equal to zero.

Entropy, denoted by 'S', is a measure of the disorder/randomness in a closed system. It is directly related to the number of microstates (a fixed microscopic state that can be occupied by a system) accessible by the system, i.e. the greater the number of microstates the closed system can occupy, the greater its entropy. The microstate in which the energy of the system is at its minimum is called the ground state of the system.

At a temperature of zero Kelvin, the following phenomena can be observed in a closed system:

- The system does not contain any heat.
- All the atoms and molecules in the system are at their lowest energy points.

Therefore, a system at absolute zero has only one accessible microstate – it's ground state. As per the third law of thermodynamics, the entropy of such a system is exactly zero.

A

T = 0K
S = 0
W = 1

B

Increasing temperature

T > 0
S > 0
W > 1

This law was developed by the German chemist Walther Nernst between the years 1906 and 1912.

Alternate Statements of the 3rd Law of Thermodynamics

The Nernst statement of the third law of thermodynamics implies that *it is not possible for a process to bring the entropy of a given system to zero in a finite number of operations.*

The American physical chemists Merle Randall and Gilbert Lewis stated this law differently: *when the entropy of each and every element (in their perfectly crystalline states) is taken as 0 at absolute zero temperature, the entropy of every substance must have a positive, finite value. However, the entropy at absolute zero can be equal to zero, as is the case when a perfect crystal is considered.*

The Nernst-Simon statement of the 3rd law of thermodynamics can be written as: *for a condensed system undergoing an isothermal process that is reversible in nature, the associated entropy change approaches zero as the associated temperature approaches zero.*

Another implication of the third law of thermodynamics is: *the exchange of energy between two thermodynamic systems (whose composite constitutes an isolated system) is bounded.*

Why is it Impossible to Achieve a Temperature of Zero Kelvin?

For an isentropic process that reduces the temperature of some substance by modifying some parameter X to bring about a change from 'X_2' to 'X_1', an infinite number of steps must be performed in order to cool the substance to zero Kelvin.

This is because the third law of thermodynamics states that the entropy change at absolute zero temperatures is zero. The entropy v/s temperature graph for any isentropic process attempting to cool a substance to absolute zero is illustrated below.
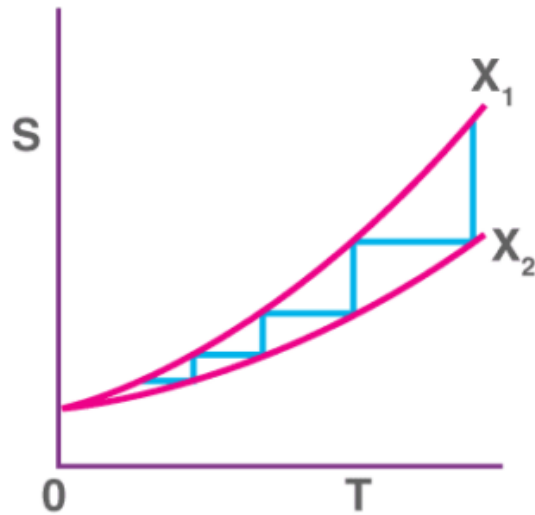
From the graph, it can be observed that – the lower the temperature associated with the substance, the greater the number of steps required to cool the substance further. As the temperature approaches zero kelvin, the number of steps required to cool the substance further approaches infinity.

Mathematical Explanation of the Third Law

As per statistical mechanics, the entropy of a system can be expressed via the following equation:

$$S - S_0 = k_B \ln\Omega$$

Where,

- S is the entropy of the system.

- S_0 is the initial entropy.

- k_B denotes the Boltzmann constant.

- Ω refers to the total number of microstates that are consistent with the system's macroscopic configuration.

Now, for a perfect crystal that has exactly one unique ground state, $\Omega = 1$. Therefore, the equation can be rewritten as follows:

$S - S_0 = k_B \ln(1) = 0$ [because $\ln(1) = 0$]

When the initial entropy of the system is selected as zero, the following value of 'S' can be obtained:

$S - 0 = 0 \Rightarrow S = 0$

Thus, the entropy of a perfect crystal at absolute zero is zero.

Applications of the Third Law of Thermodynamics

An important application of the third law of thermodynamics is that it helps in the calculation of the absolute entropy of a substance at any temperature 'T'. These determinations are based on the heat capacity measurements of the substance. For any solid, let S_0 be the entropy at 0 K and S be the entropy at T K, then

$$\Delta S = S - S_0$$
$$\Delta S = \int_0^T \frac{C_p dT}{T}$$

According to the third law of thermodynamics, $S_0 = 0$ at 0 K,

$$S = \int_0^T \frac{C_p}{T} dT$$

The value of this integral can be obtained by plotting the graph of C_p/T versus T and then finding the area of this curve from 0 to T. The simplified expression for the absolute entropy of a solid at temperature T is as follows:
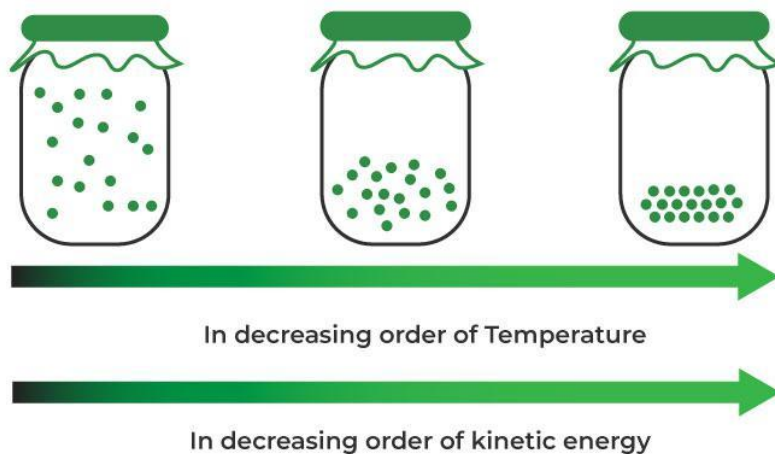
$$S = \int_0^T \frac{C_p}{T} dT$$
$$S = \int_0^T C_p d\ln T$$
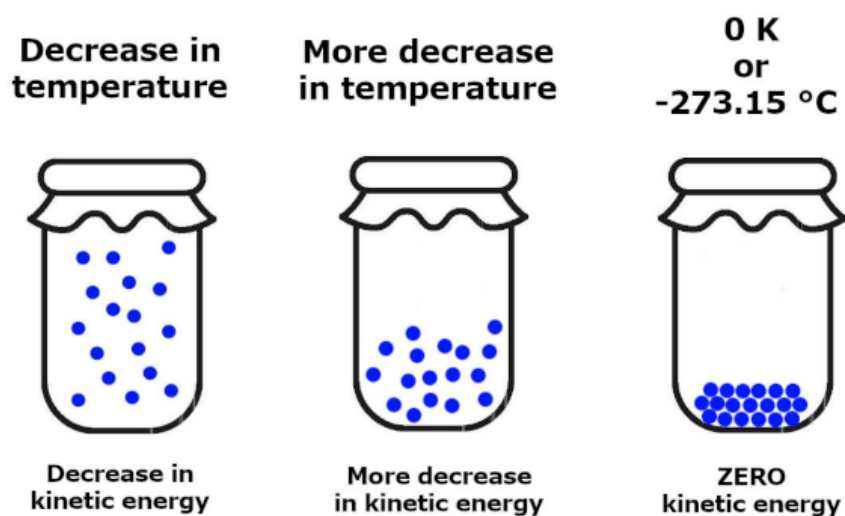$$= C_p \ln T = 2.303 \, C_p \log T$$

Here C_p is the heat capacity of the substance at constant pressure and this value is assumed to be constant in the range of 0 to T K.

7.9 SUMMARY

Third Law of Thermodynamics

In decreasing order of Temperature

In decreasing order of kinetic energy

Third Law of Thermodynamics

Decrease in temperature

More decrease in temperature

0 K or -273.15 °C

Decrease in kinetic energy

More decrease in kinetic energy

ZERO kinetic energy

Third Law of Thermodynamics statement:
"The value of entropy of a completely pure crystalline substance is zero at absolute zero temperature"

In this Unit we studied about Joule's Thomson expansion, inversion curve and later on we understand the concept of Third law of Thermodynamics etc.`

- The temperature below which a gas becomes cooler on expansion is known as the **inversion temperature**.
- Thus **Joule-Thomson effect** can be defined as the phenomenon of temperature change produced when a gas is allowed to expand adiabatically from a region of high pressure to a region of extremely low pressure.
- Joule-Thomson expansion of a real gas occurs with constant enthalpy and not with constant internal energy and thus is also known as isenthalpic process.
- Joule Thomson coefficient is given by $(\partial T / \partial P)_H = - (\partial H / \partial P)_T / C_P$
- Joule Thomson coefficient for ideal gas is zero
- Joule Thomson coefficient for real gas is given by

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right]$$

7.10 TERMINAL QUESTIONS

1. Explain Joule's Thomson effect.

2. Define Inversion Curve in Thermodynamics.

3. Comparison of Joule expansion, Joule Thomson expansion and Adiabatic expansion.

4. State and explain third law of thermodynamics.

5. What is Throttling Process.

7.11 ANSWER AND SOLUTION OF TERMINAL QUESTION

1. Section 7.3

2. Section 7.5

3. Section 7.7

4. Section 7.9

5. Section 7.8

7.12 SUGGESTED READINGS

1. Thermal Physics: with Kinetic Theory, Thermodynamics: SC Garg.

2. Thermal Physics: R. Murugeshan, Er. Kiruthiga Siva Prasath.

3. Thermal Physics: C.B.P. Finn.

4.   Heat Thermodynamics and Statistical Physics: Brij lal, Dr.

N. Subrahmanyam, P.S. Hemne.

Bachelor of Science
DCEPHS -106
Thermal Physics

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Block

3 **Heat**

UNIT - 8	KINETIC THEORY OF GASES
UNIT - 9	CONDUCTION AND CONVECTION
UNIT - 10	RADIATION

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UNIT - 8   KINETIC THEORY OF GASES

8.1 INTRODUCTION

Firstly ,in this unit we understand the concept of Heat in Thermodynamics

In thermodynamics, heat has a very specific meaning that is different from how we might use the word in everyday speech. Scientists define heat as *thermal energy transferred between two systems at different temperatures that come in contact*. Heat is written with the symbol **q** or **Q**, and it has units of Joules (J).

Heat is sometimes called a *process quantity*, because it is defined in the context of a process by which energy can be transferred. We don't talk about a cup of coffee containing heat, but we can talk about the heat *transferred* from the cup of hot coffee to your hand. Heat is also an extensive property, so the change in temperature resulting from heat transferred to a system depends on how many molecules are in the system.

Heat is a form of energy that produces the sensation of hotness. Thermodynamics is the branch of physics that deals with the energy relationships involving heat, mechanical energy and other forms of energy. The entire formulation of

thermodynamics is based on a few fundamental laws which have been established on the basis of the human experience of the experimental behaviour of macroscopic aggregates of matter collected over a long period of time.

Methods of Heat Transfer

Conduction: Conduction is the transfer of heat from the hotter part of the body to the colder part of the body without the actual movement of the particles in between.

Convection: The transmission of heat due to the actual movement of the medium is called convection.

Radiation: Radiation is the process by which the heat gets transmitted from one point to another without the action of any material in between.

In this unit we will discuss about terms related to kinetic theory of gases.

The kinetic theory of gases explains the three macroscopic properties of a gas in terms of the microscopic nature of atoms and molecules making up the gas. Usually, the physical properties of solids and liquids can be described by their size,

shape, mass, volume etc. However, when we talk about gases, they have no definite shape, size while mass and volume are not directly measurable. The Kinetic theory of gases is useful and can be applied in this case.

With the help of the kinetic theory of gases, the physical properties of any gas can be defined generally in terms of three measurable macroscopic properties. The pressure, volume and temperature of the container where the gas is stored or present

8.2 OBJECTIVES

After studying this unit, student should able to :

➢ Concept of Ideal Gas Equation.

➢ Comparison of Ideal gas and Red gas.

➢ What is critical constants.

➢ Explain the concept of Brownian's Motion.

➢ Define Mean free Path.

8.3 IDEAL GAS EQUATION

What is Ideal Gas?

An ideal gas is a theoretical gas composed of a set of randomly-moving point particles that interact only through elastic collisions.

The ideal gas concept is useful because it obeys the ideal gas law, a simplified equation of state and is amenable to analysis under statistical mechanics.

Ideal Gas Laws

The laws which deal with ideal gases are naturally called ideal gas laws and the laws are determined by the observational work of Boyle in the seventeenth century and Charles in the eighteenth century.

- *Boyles Law* – states that for a given mass of gas held at a constant temperature the gas pressure is inversely proportional to the gas volume.

- *Charles Law* – states that for a given fixed mass of gas held at a constant pressure the gas volume is directly proportional to the gas temperature

Ideal Gas Equation

The Ideal gas law is the equation of state of a hypothetical ideal gas. It is a good approximation to the behaviour of many gases under many conditions, although it has several limitations. The ideal gas equation can be written as

$$PV = nRT$$

Where,

- P is the pressure of the ideal gas.

- V is the volume of the ideal gas.

- n is the amount of ideal gas measured in terms of moles.

- R is the **universal gas constant**.

- T is the temperature.

According to the Ideal Gas equation-

The product of Pressure & Volume of a gas bears a constant relation with the product of Universal gas constant, number of moles of gas and temperature.

i.e.

$$pv = nRT$$

Universal Gas Constant (R)

R is a universal gas constant and it is the molar equivalent of boltzmann constant having the units of energy increased per temperature per mole. It is denoted by R.

From the SI system the value of the universal gas constant is 8.314 kJ/mole.K

Derivation of the Ideal Gas Equation

Let us consider the pressure exerted by the gas to be '**p**'

The volume of the gas be – '**v**'

Temperature be – "**T**"

"**n**" – be the number of moles of gas

Universal gas constant – **R**

According to **Boyle's Law**,

At constant **n** & **T,** the volume bears an inverse relation with the pressure exerted by a gas.

i.e.

$$v \propto \frac{1}{p}$$

……………………………….(i)

According to **Charles' Law**,

When **p** & **n** are constant, the volume of a gas bears a direct relation with the Temperature.

i.e.

v ∝ T

……………………………….(ii)

According to **Avogadro's Law**,

When **p** & **T** are constant, then the volume of a gas bears a direct relation with the number of moles of gas.

i.e.

v ∝ n

………………………………(iii)

Combining all the three equations, we have-

$$v \propto \frac{nT}{p}$$

or

pv = nRT

where **R** is the **Universal gas constant**, which has a value of

8.314 J/mol-K

8.4   COMPARISION OF IDEAL GAS AND REAL GAS

The three states of matter that are recognised by their characteristics are solids, liquids and gases. Solids have definite mass and shape due to the strong molecular attraction. In liquids, the molecules are moving so they result in taking the shape of the container. In gases, the molecules are free to move anywhere in the container. Two types of gases exist. Real gas and Ideal gas. As the particle size of an ideal gas is extremely small and the mass is almost zero and no volume Ideal gas is also considered a point mass. The molecules of real gas occupy space though they are small particles and also have volume.

Ideal gas:

An ideal gas is defined as a gas that obeys gas laws at all conditions of pressure and temperature. Ideal gases have velocity and mass. They do not have volume. When compared to the total volume of the gas the volume occupied by the gas is negligible. It does not condense and does not have triple point.

Real gas:

A real gas is defined as a gas that does not obey gas laws at all standard pressure and temperature conditions. When the gas

becomes massive and voluminous it deviates from its ideal behaviour. Real gases have velocity, volume and mass. When they are cooled to their boiling point, they liquefy. When compared to the total volume of the gas the volume occupied by the gas is not negligible.

Difference between Ideal gas and Real gas	
IDEAL GAS	**REAL GAS**
No definite volume	Definite volume
Elastic collision of particles	Non-elastic collisions between particles
No inter-molecular attraction force	Inter molecular attraction force
Does not really exists in the environment and is a hypothetical gas	It really exists in the environment
High pressure	The pressure is less when compared to Ideal gas

Independent	Interacts with others
Obeys PV = nRT	Obeys P+((n2a)V2)(V−nb)=nRT

8.5 VANDER WAAL EQUATION OF STATE

According to the ideal gas law, PV = nRT, where P is the pressure, V is the volume, n is the number of moles, T is the temperature, and R is the universal gas constant. The Van der Waals equation is also known as the Van der Waals equation of state for real gases which do not follow ideal gas law. The Van der Waals Equation derivation is explained below.

Derivation of Van der Waals equation

For a real gas, using the Van der Waals equation, the volume of a real gas is given as (Vm – b), where b is the volume occupied per mole.

Therefore, ideal gas law when substituted with V = V_m – b is given as:

$$P(V_m - b) = nRT$$

Because of intermolecular attraction, P was modified as below.

$$(P + \tfrac{a}{V_m^2})(V_m - b) = RT$$
$$(P + \tfrac{an^2}{V^2})(V - nb) = nRT$$

Where,

V_m: molar volume of the gas

R: universal gas constant

T: temperature

P: pressure

V: volume

Thus, Van der Waals equation can be reduced to ideal gas law as $PV_m = RT$.

8.6 VANDER WAAL CONSTANTS

The Van der Waal constant **'a' signifies the magnitude of attraction between the gas molecules, and the constant 'b' signifies the effective volume occupied by the gas molecules**

The constants a and b are called as van der waals constants. They are the correction factors for pressure and volume in the ideal gas equation which corrects two properties of real gas: the excluded volume of gas particles and attractive force between gas molecules. The van der Waals equation of state proposes the ideal gas law PV=nRT where the value of these constants

approaches zero.

Complete step by step solution

The van der Waal equation is represented as:

$$\left(P + \frac{a}{nV^2}\right)(V - nb) = nRT$$

Where P is the pressure, V is the volume, R is the universal gas constant, T is the absolute temperature and n is the total number of moles.

It was derived by van der Waal in 1873. It modifies the ideal gas law (PV=nRT). The constants a and b have positive values and are specific for each gas.
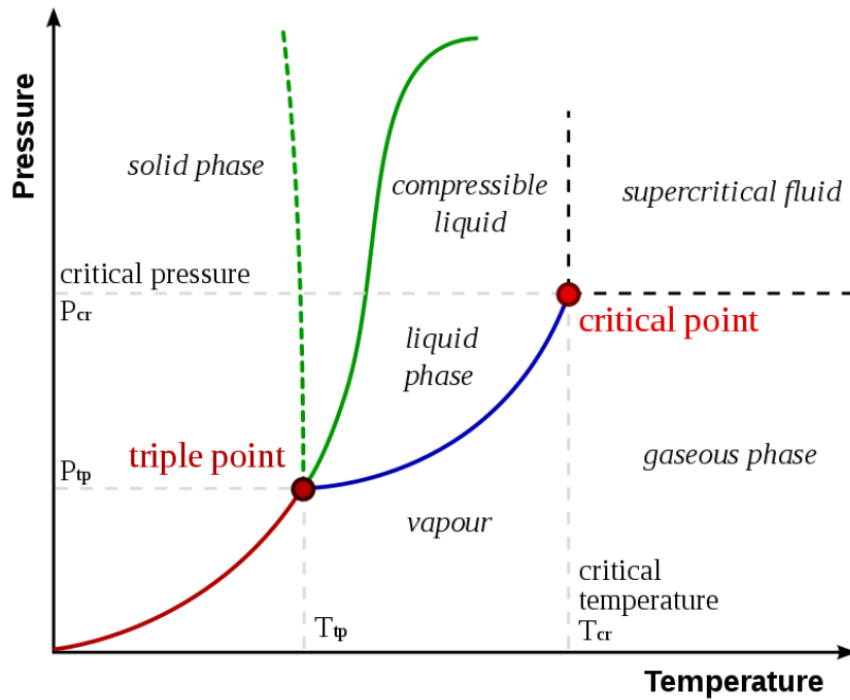
"a" corrects for intermolecular attraction. Attractive force between molecules decreases the pressure of real gas, slowing the molecules and reducing collisions with the wall. Higher the value of a , greater will be the attraction among molecules and the more easily gas will compress.

'b' term represents the excluded volume of the gas or the volume occupied by the gas particles.

8.7 CRITICAL CONSTANTS

Critical constant is the critical temperature, critical pressure, or critical density of any substance. This term is usually taken as a plural noun because it can refer to three conditions (temperature, pressure or density) at the same point. We can abbreviate critical temperature as Tc, critical pressure as Pc, and critical density as Vc. Moreover, we can calculate critical constants using the values of the Van der Waals constants.

Typically, critical constant values are given for the critical point of a substance. The critical point of a substance is the endpoint of the phase equilibrium curve of that substance. A phase equilibrium curve or a phase diagram is the graph of pressure versus temperature in which the phase changes of the substance are shown. This shows the temperatures and pressure at which the substance exists as a solid, liquid, or gas. The critical point is the temperature and pressure at which the liquid and vapour phases coexist.

Critical Temperature, Pressure, Volume

The critical temperature, pressure, and volume simply represent

T_C, P_C, and V_C respectively, and above which the gases cannot

be liquefied.

What is critical temperature?

The Critical temperature (T_C) is the maximum temperature at which the gas can be liquefied and the temperature above which the liquid cannot exist.

What is critical pressure?

Critical pressure (P_C) is the maximum pressure required for the liquefaction of gases at the critical temperature.

What is critical volume?

Critical volume (V_C) is the volume occupied by one gram mole of gaseous substances at critical temperate and pressure.

Continuity of state

An examination of the PV curve at the temperature below the critical temperature may be discontinuous or break down during the transformation of gas to liquid. The continuity of the state of matter from the gas to liquid can be explained from the above Andrews isotherm ABCD at temperature, T_1.

Suppose the gas is heated with the specific heat at constant volume along with AB. Then the gas gradually cooling at constant pressure along with BC, and the volume will be

reduced considerably. On reaching D the process liquefaction would appear.

At point D, the system contains highly compressed gas. But from the Andrews curve, the critical temperature point is the representation of the liquefaction point of the gases. Hence there is hardly a distinction between the liquid and the gaseous state. There is no line of separation between the two phases. This is known as the principle of continuity of the state.

Critical temperature pressure and volume formula
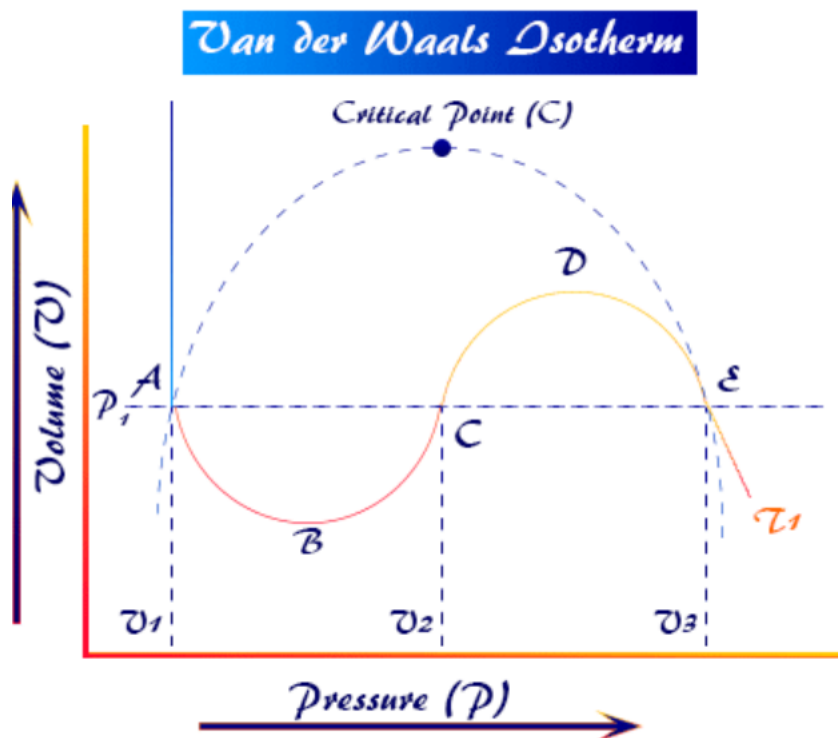
With the increase in temperature, the minimum and maximum points come close to each other and at the critical point (C) both

maximum and minimum coalesce. The slope and curvature both become zero at this point.

In these conditions, we can calculate the critical temperature, pressure, and volume formula for real gases from the Van der walls equation.

Critical constants V_c, T_c and P_c

Van der waals equation for 1 mole gas,

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{dP}{dV}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

$$\left(\frac{d^2P}{dV^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$$

At critical state, $\left(\frac{dP}{dV}\right)_T = 0$ and $\left(\frac{d^2P}{dV^2}\right)_T = 0$

$$\therefore \frac{RT_C}{(V_C-b)^2} = \frac{2a}{V_C^3} \text{ and } \frac{2RT_C}{(V_C-b)^3} = \frac{6a}{V_C^4}$$

From the above two equation,

$$V_C = 3b$$

$$T_C = \frac{8a}{27Rb}$$

$$P_C = \frac{a}{27b^2}$$

8.8 MEAN FREE PATH

In a gaseous system, the molecules never move in a straight path without interruptions. This is because they collide with each other and change speed and direction. Between every two collisions, a molecule travels a path length. The average of all the path lengths between collisions is the mean free path. In this article, we will derive an expression for the mean free path.


The mean free path λ of a gas molecule is its average path length between collisions.

Mathematically the mean free path can be represented as follows:

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 \frac{N}{V}}$$

Let's look at the motion of a gas molecule inside an ideal gas, a typical molecule inside an ideal gas will abruptly change its direction and speed as it collides elastically with other molecules of the same gas. Though between the collisions the molecule will move in a straight line at some constant speed, this is applicable for all the molecules in the gas.

It is difficult to measure or describe this random motion of gas molecules thus we attempt to measure its mean free path λ.


Random path followed by a gass molecule
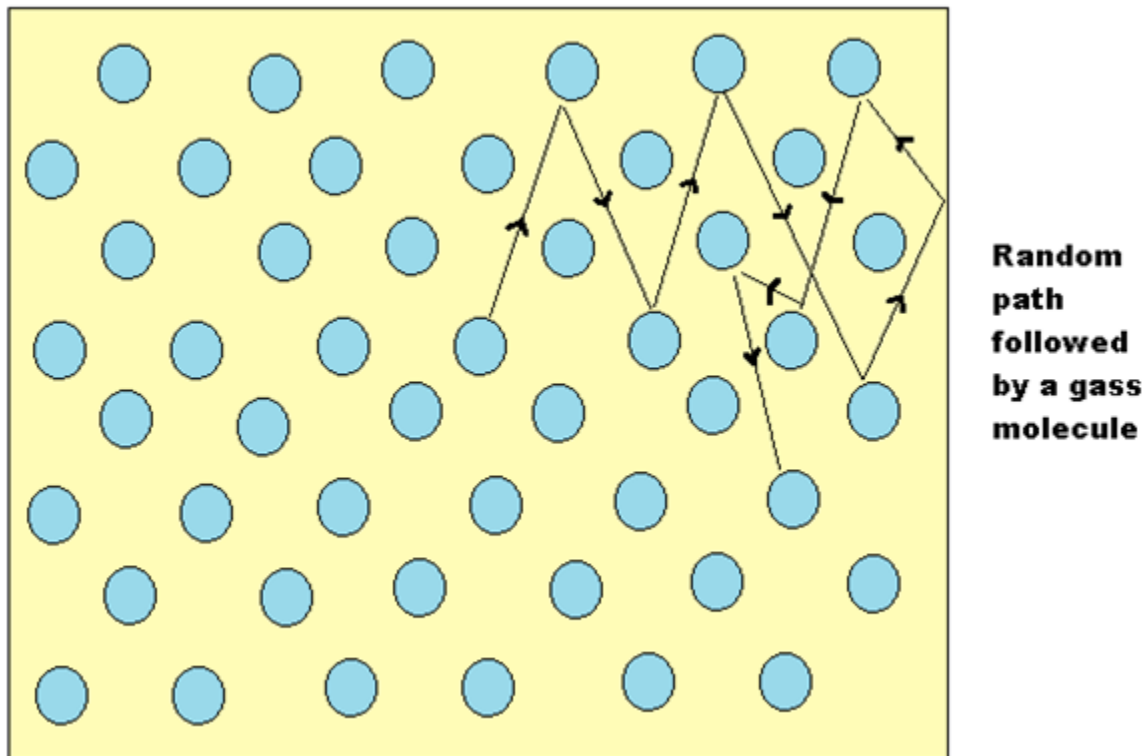
As its name says λ is the average distance travelled by any molecule between collisions, we expect λ to vary inversely with N/V, which is the number of molecules per unit volume or the density of molecules because if there are more molecules more are the chances of them colliding with each other hence reducing the mean free path, and also λ would be inversely proportional to the diameter d of the molecules, because if the molecules were point masses then they would never collide with each other, thus larger the molecule smaller the mean free path,

and it should be proportional to π times square of the diameter and not the diameter itself because we consider the circular cross-section and not the diameter itself.

8.9 TRANSPORT PHENOMENON IN GASES

Transport phenomena According to kinetic theory of gases, the molecules of a gas in a state of thermal agitation Therefore gas attains equilibrium state by transporting momentum, heat (thermal energy) and mass form one layer of gas to another layer giving rise to the viscosity, conductivity and diffusion respectively. This phenomena is called transport phenomena. The transport phenomena occur only in non-equilibrium state of a gas. Viscosity: Transport of momentum There is a relative motion of different layers of a non-equilibrium gas with respect to one another. The layer moving faster will impart momentum to the layer moving slower to bring about an equilibrium state. Thus the transport of momentum gives rise to phenomenon of viscosity. Consider a layer of gas AB moving with velocity V at a distance Z form O.
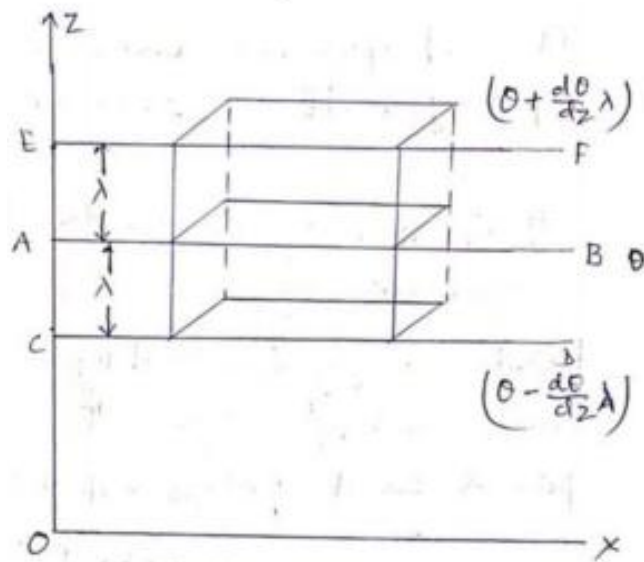
Velocity gradient $= \dfrac{dv}{dz}$

Consider two layers EF & CD just above and below AB respectively at a distance λ equal to mean free path of molecule.

Velocity of gas in the layer EF $= V + \dfrac{dv}{dz}\lambda$

Velocity of gas in layer CD $= V - \dfrac{dv}{dz}\lambda$

Let   n =Number of molecule per unit volume

   m = mass of each gas molecule

Due to thermal agitation the gas molecules are moving in all possible directions.

ie $\dfrac{1}{3}$ rd molecules moving in each three directions parallel to three co-ordinate axis.

So that average $\dfrac{1}{6}$ th of molecules more parallel to any one axis in one particular direction *ie +ve* or *− ve* direction.

Number of molecule passing downward from EF to CD per unit area per sec. $= \dfrac{nc}{6}$

Forward momentum lost per unit area per second by layer EF $= \dfrac{mnc}{6}\left(V + \dfrac{dv}{dz}\lambda\right)$.

Similarly

Forward momentum gained per unit area per sec. by layer EF $= \frac{mnc}{6}\left(V - \frac{dv}{dz}\lambda\right)$.

Net momentum lost by the layer EF per unit area per second

$$= \frac{mnc}{6}\left\{\left(V + \frac{dv}{dz}\lambda\right) - \left(V - \frac{dv}{dz}\lambda\right)\right\}.$$

$$= \frac{1}{3}mnc\,\lambda\,\frac{dv}{dz}.$$

Backward dragging force per unit area = Gain or loss in momentum per unit area
of layer AB

$$F = \frac{1}{3}mnc\,\lambda\,\frac{dv}{dz}$$

This must be equal to the viscous force or tangential force $\left(\eta\frac{dv}{dz}\right)$ per unit area

η = coefficient of viscosity

$$\eta\frac{dv}{dz} = \frac{1}{3}mnc\,\lambda\frac{dv}{dz}$$

$$\eta = \frac{1}{3}mnc\,\lambda, \qquad \eta = \frac{1}{3}\rho c\,\lambda$$

where $\rho = mn$ = Density of gas.

## Thermal Conductivity : Transport of thermal Energy

The different layers of gas may have different temperatures. The molecules will carry Kinetic energy (heat) from the regions of higher temperature to the region of lower temperature to bring on equilibrium state. Thus the transport of thermal energy gives rise to the phenomenon of thermal conductivity.

Let θ be the temperature of layer of gas AB

Temperature gradient $= \frac{d\theta}{dz}$ along oz

Temperature of layer EF at a distance λ above AB is $= \left(\theta + \frac{d\theta}{dz}\lambda\right)$

Temperature of layer CD at a distance λ below AB is $= \left(\theta - \frac{d\theta}{dz}\lambda\right)$
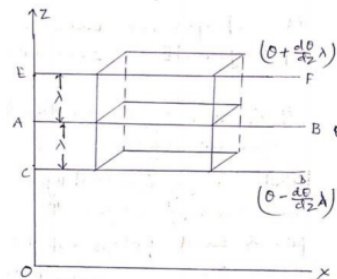
This means that the gas above the layer AB is at higher temperature than the gas below AB. Hence the molecules of gas coming from EF and passing downward across AB possesses more kinetic energy than the molecules coming from CD and passing upward across AB till the equilibrium is reached.

Let n = Number of molecules per unit volume

m = mass of each molecule

c = Average velocity of gas molecule Number of molecules crossing per unit area of layer AB upward or downward per second nc/6

Mass of gas molecule crossing per unit area of layer AB upward or downward per second $= \dfrac{mnc}{6}$

If C_v is the specific heat of gas at constant volume then

Heat energy carried by molecules in crossing unit area of layer AB in downward direction per second = Mass x Sp. Heat x temperature

$$= \dfrac{mnc}{6} C_v \left(\theta + \dfrac{d\theta}{dz}\lambda \right).$$

Similarly

Heat energy carried by molecules in crossing in unit area of layer AB in upward direction per second $= \dfrac{mnc}{6} C_v \left(\theta - \dfrac{d\theta}{dz}\lambda \right).$

Net transfer of heat energy per unit area of layer AB in downward direction per sec.

$$Q = \dfrac{mnc}{6} C_v \left\{ \left(\theta + \dfrac{d\theta}{dz}\lambda \right) - \left(\theta - \dfrac{d\theta}{dz}\lambda \right) \right\}.$$

$$Q = \dfrac{mnc}{6} C_v . 2\lambda \dfrac{d\theta}{dz}$$

$$Q = \dfrac{1}{3} mnC\lambda \ C_v \dfrac{d\theta}{dz}$$

$$Q = \dfrac{1}{3} \rho c\lambda \ C_v \dfrac{d\theta}{dz}$$

Where $mn = \rho$ = density of gas

The coefficient of thermal conductivity (K) of the gas is defined as the quantity of heat flows per unit area per second to maintain unit temperature gradient

$$ie \quad Q = K\dfrac{d\theta}{dz}$$

$$\therefore K\dfrac{d\theta}{dz} = \dfrac{1}{3}\rho c \lambda \ C_v \dfrac{d\theta}{dz}$$

$$K = \dfrac{1}{3}\rho c \lambda \ C_v$$

Effect of temperature of K :-

Coefficient of thermal conductivity $K = \frac{1}{3}mnC_v\lambda$

But Mean free path $\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n}$

$$K = \frac{1}{3}mnc\, C_v \frac{1}{\sqrt{2}\pi\sigma^2 n}$$

$$K = \frac{mc\, C_v}{3\sqrt{2}\pi\sigma^2}$$

But Average molecular speed, $C \propto \sqrt{T}$

$$\therefore K \propto \sqrt{T}$$

Thus the coefficient of thermal conductivity is directly proportional to square root of absolute temperature.

Diffusion : Transport of mass

The phenomenon of diffusion is due to the transport of mass from a region of higher concentration to a region of lower concentration to bring about an equilibrium.
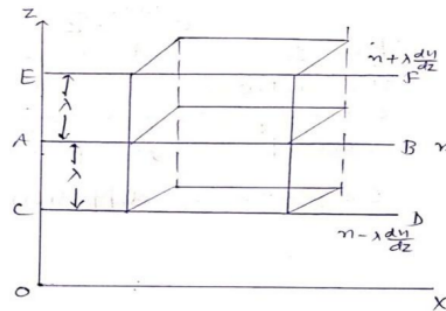
Let n be the concentration of layer of gas AB.

Concentration gradient = $\frac{dn}{dz}$ along oz

Consider two layer EF & CD just above and below AB respectively at a distance λ equal to mean free path

Concentration of layer EF = $n + \lambda\frac{dn}{dz}$

Concentration of layer CD = $n - \lambda\frac{dn}{dz}$

Number of molecules coming from layer EF and crossing AB in downward per unit area per second $= \frac{1}{6}c(n + \lambda\frac{dn}{dz})$

Number of molecules coming from layer EF and crossing AB in upward per unit area per second $= \frac{1}{6}c(n - \lambda\frac{dn}{dz})$

Net number of molecules crossing per unit area per second of layer AB in

downward direction $= \frac{1}{6} c \left\{ \left(n + \lambda \frac{dn}{dz} \right) - \left(n - \lambda \frac{dn}{dz} \right) \right\}$

$$= \frac{1}{3} c \lambda \frac{dn}{dz}$$

The coefficient of diffusion is defined as the ratio of the number of molec
crossing per unit area per sec. to the rate of change of concentration with dista

Coefficient of diffusion $D = \dfrac{\frac{1}{3} c \lambda \frac{dn}{dz}}{\frac{dn}{dz}}$

$$D = \frac{1}{3} c \lambda$$

Effect of temperature and pressure

Mean free path $\lambda = \dfrac{KT}{\sqrt{2} \pi \sigma^2 p}$ & $C = \sqrt{\dfrac{8KT}{\pi m}}$

$$\therefore D = \frac{1}{3} \frac{KT}{\sqrt{2} \pi \sigma^2 p} \sqrt{\frac{8KT}{\pi m}}$$

$$D = \frac{2}{3} \frac{1}{\sigma^2 p \sqrt{m}} \left(\frac{KT}{\pi} \right)^{3/2}$$

Thus the coefficient of diffusion is directly proportional to $T^{3/2}$ and inversely proportional to pressure P.

8.10 BROWNIAN'S MOTIONS

"Brownian motion refers to the random movement displayed by small particles that are suspended in fluids. It is commonly referred to as Brownian movement". This motion is a result of the collisions of the particles with other fast-moving particles in the fluid.

Brownian motion is named after the **Scottish Botanist Robert Brown**, who first observed that pollen grains move in random

directions when placed in water. An illustration describing the random movement of fluid particles (caused by the collisions between these particles)
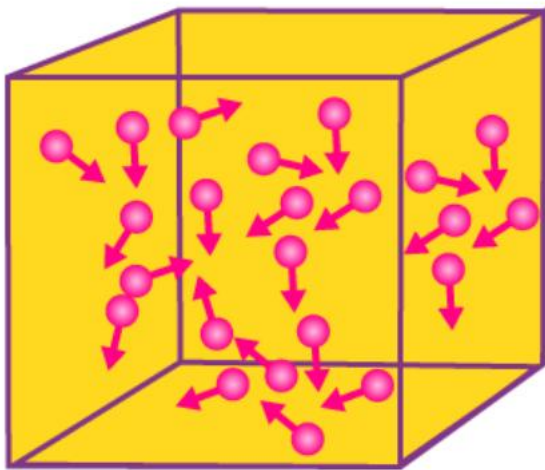
Brownian Movement

A particle changes its path when another particle collides with it. Further collisions cause the particle to follow a random, zig-zag motion. It involves a transfer or exchange of momentum/energy between the particles.
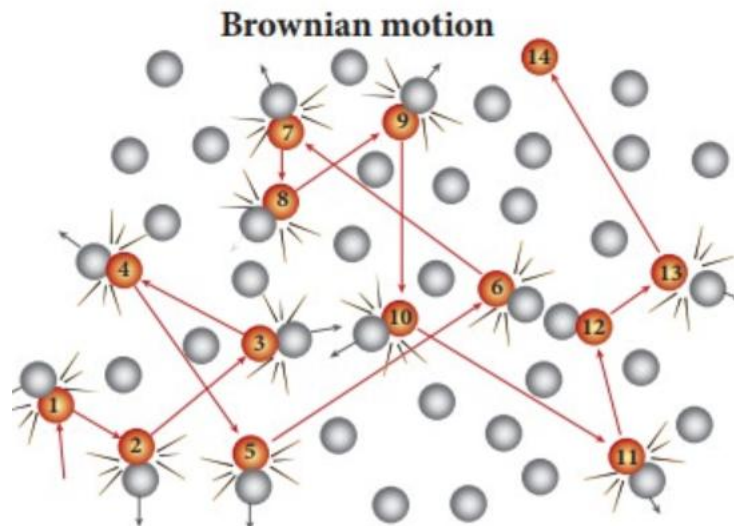
Brownian motion

Causes and Effects of Brownian Motion

Brownian motion describes randomness and chaos. It is one of the simplest models of randomness. The various causes and effects of this motion are listed in this subsection.

1. **What Causes Brownian Motion?**

- The **size of the particles is inversely proportional to the speed of the motion**, i.e. Small particles exhibit faster movements.

- This is because the transfer of momentum is inversely proportional to the mass of the particles. Lighter particles obtain greater speeds from collisions.

- The speed of the Brownian motion is inversely proportional to the <u>viscosity of the fluid</u>. The lower the viscosity of the fluid, the faster the Brownian movement.

- Viscosity is a quantity that expresses the magnitude of the internal friction in a liquid. It is the measure of the fluid's resistance to flow.

2. Effects of Brownian Motion

- **Brownian movement causes the particles in a fluid to be in constant motion.**

- This prevents particles from settling down, leading to the stability of colloidal solutions.

- A true solution can be distinguished from a colloid with the help of this motion.

Albert Einstein's paper on Brownian motion was vital evidence on the existence of atoms and molecules. The <u>kinetic theory of gases</u> which explains the pressure, temperature, and volume of gases is based on the Brownian motion model of particles.

8.11 SUMMARY

Kinetic theory of gases is **a theoretical model that describes the molecular composition of the gas in terms of a large number of submicroscopic particles which include atoms and molecules**. Further, the theory explains that gas pressure

arises due to particles colliding with each other and the walls of the container.

Postulates of the Kinetic Theory of Gases.

1 The molecules in a gas are small and very far apart. Most of the Volume which a gas occupies is empty space .

2 Gas molecules are in constant random motion. Just as many molecules are moving in one direction as in any other.

3 Molecules can collide with each other and with the walls of the container. Collisions with the walls account for the pressure of the gas.

4 When collisions occur, the molecules lose no kinetic energy; that is, the collisions are said to be **perfectly elastic**. The total kinetic energy of all the molecules remains constant unless there is some outside interference with the

5 The molecules exert no attractive or repulsive forces on one another except during the process of collision. Between collisions, they move in straight lines.

Kinetic Theory of Gases

Gas molecule

Container
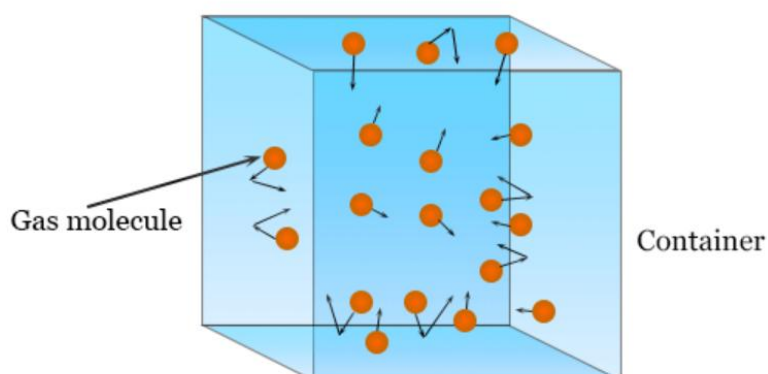
Ideal Gas Equation

$$PV = nRT$$

1. P is pressure measured in atmospheres.

2. V is volume measured in Liters

3. n is moles of gas present.

4. R is a constant that converts the units. It's value is 0.0821 atm·L/mol·K

5. T is temperature measured in Kelvin.

6. Simple algebra can be used to solve for any of these values.

$$P = \frac{nRT}{V} \quad V = \frac{nRT}{P} \quad n = \frac{PV}{RT} \quad T = \frac{PV}{nR} \quad R = \frac{nT}{PV}$$

8.12 TERMINAL QUESTIONS

1.   What is mean free path.

2.   Explain the concept of Brownian's motion.

3. Comparison of Ideal gas and Red gas.

4. Define Critical Constant.

5. Explain the transport Phenomenon in gages.

8.13 ANSWER AND SOLUTION OF TERMINAL QUESTION

1. Section 8.8

2. Section 8.6

3. Section 8.4

4. Section 8.7

5. Section 8.9

8.14 SUGGESTED READINGS

1. Thermal Physics : with Kinetic Theory, Thermodynamics : SC Garg.

2. Thermal Physics : R. Murugeshan, Er. Kiruthiga Siva Prasath.

3. Thermal Physics : C.B.P. Finn.

4. Heat Thermodynamics and Statistical Physics : Brij lal, Dr. N. Subrahmanyam, P.S. Hemne.

UNIT - 9   CONDUCTION AND CONVECTION

9.1   INTRODUCTION

The physical act of the transfer of thermal energy between two systems by the dissipation of heat is known as heat transfer. The three modes of heat transfer are conduction, convection and radiation.

Any matter which is made up of atoms and molecules has the ability to transfer heat. The atoms are in different types of motion at any time. The motion of molecules and atoms is responsible for heat or thermal energy and every matter has this thermal energy. The more the motion of molecules, more will be the heat energy. However, talking about heat transfer, it is nothing but the process of transfer of heat from a high-temperature body to a low temperature one.

According to thermodynamic systems, heat transfer is defined as **"The movement of heat across the border of the system due to a difference in temperature between the system and its surroundings**."

9.2   OBJECTIVES

After Studying this Unit, student should able to:

➢ Define Heat Transfer.

➢ Explain the concept of Modes of transfer of heat.

➢ Define Steady and Variable States.

➢ Explain the concept of Thermal Conductivity.

➢ Define Thermal Diffusivity.

9.3 MODES OF TRANSFER OF HEAT

In our everyday life, it has been observed that when a pan full of water is boiled on a flame, its temperature increases, but when the flame is turned off, it slowly cools down.

What are the different Modes of Heat Transfer?

This is because of the phenomenon of heat transfer taking place between the pan full of water and the flame. It has been established that heat transfer takes place from hotter objects to colder objects.

Modes of Heat Transfer
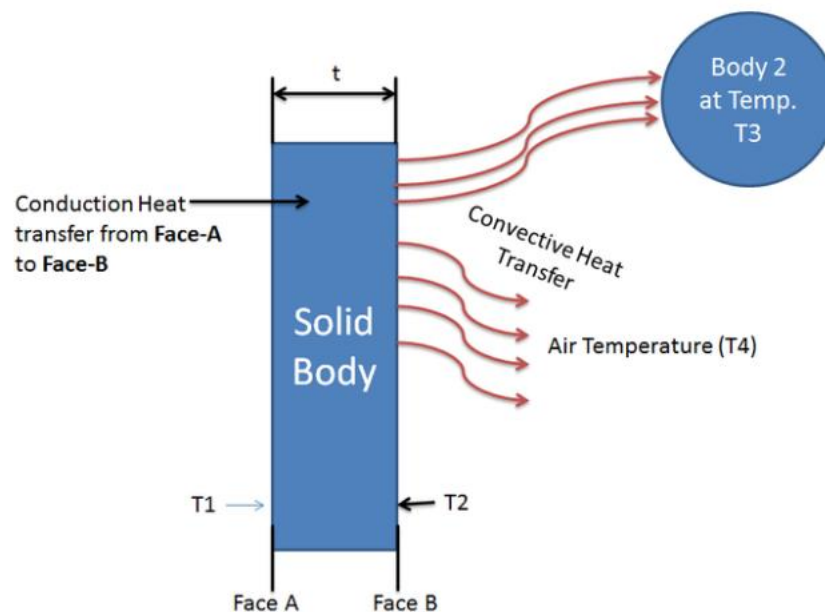
As shown above, A good example of heat transfer is when one side of a metal block (Face A) is heated. Heat is transferred from face A to face B through conduction. And when air is flowing over a hot surface. Convective heat transfer takes place through the air. Whereas radiation heat transfer takes place even if the body is in a vacuum.

Modes of Heat Transfer
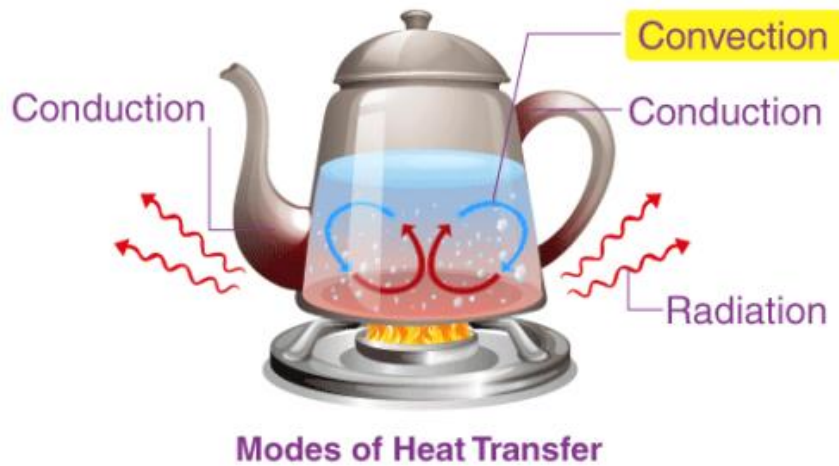
When there are objects which are at different temperatures or there is an object at a different temperature from the surroundings, then the transfer of heat takes place so that the object and the surrounding, both reach an equilibrium temperature.

There are three modes of heat transfer.

1. **Conduction**

2. **Convection**

3. **Radiation**

1. Conduction of Heat

Heat conduction is a process in which heat is transferred from the hotter part to the colder part in a body without involving any actual movement of the molecules of the body. Heat transfer takes place from one molecule to another molecule as a result of the vibratory motion of the molecules. Heat transfer through the process of

conduction occurs in substances which are in direct contact with each other. It generally takes place in solids.

Conduction example: When frying vegetables in a pan. Heat transfer takes place from flame to the pan and then to the vegetables.

Based on the conductivity of heat, substances can be classified as conductors and insulators. Substances that conduct heat easily are known as conductors and those that do not conduct heat are known as insulators.

2. Convection of Heat

In this process, heat is transferred in the liquid and gases from a region of higher temperature to a region of lower temperature. Convection heat transfer occurs partly due to the actual movement of molecules or due to the mass transfer.

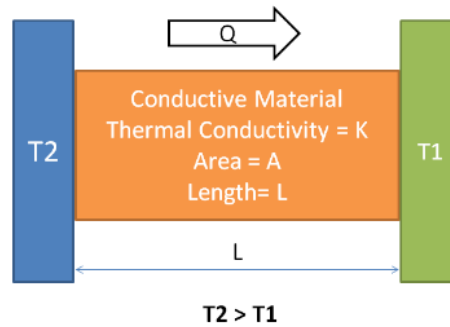For example. Heating of milk in a pan.

3. Radiation of Heat

It is the process in which heat is transferred from one body to another body without involving the molecules of the medium. Radiation heat transfer does not depend on the medium.

For example: In a microwave, the substances are heated directly without any heating medium.

Conductive Heat Transfer Calculation

The rate of heat transfer through conduction is governed by Fourier's law of heat conduction. The rate of conductive heat transfer is directly proportional to the contact area, material thermal conductivity, temperature difference, and inversely proportional to the thickness.

$$\text{Conductive Heat transfer } (Qc) = -\ K\ A\ dT\ /\ L$$

Where

Qc = Conductive heat transfer per unit time in watt

A = cross-section area in square meter

k = Material Thermal Conductivity

$dT = (T2\text{-}T1)$

L = Thickness or length of the part

Convection Heat Transfer Calculation

The rate of convective heat transfer is governed by Newton's law of cooling. It is directly proportional to heat transfer surface area, convective heat transfer coefficient, and temperature difference.

$$\textbf{Convection Heat transfer (Qv) = hc A dT}$$

where

Qv = Convective heat transfer per unit time in Watt

A = heat transfer area in square meter

hc= Convective Heat Transfer Coefficient (W/m² K)

dT = Temperature Difference

Convection Heat Transfer Types

Here are the two types of convective heat transfer:

1. Natural Convection
2. Forced Convection

1) Natural Convection

Natural convective heat transfer is caused by buoyancy forces. Buoyancy forces are generated due to the density and temperature variation of fluid. During natural convection hot fluid/air rises upward and is replaced by cooler fluid/air. Further, this fluid will also heat and rise. Gravity plays a very important role during natural convection.

2) Forced Convection

Forced convective heat transfer occurs when the flow of fluid/air is caused by an external force such as a fan or pump.

9.4   STEADY AND VARIABLE STATES

During variable state, heat flow depends on `K, rho and c`, the specific heat capacity. But during steady state the heat flow depends only on thermal conductivity.
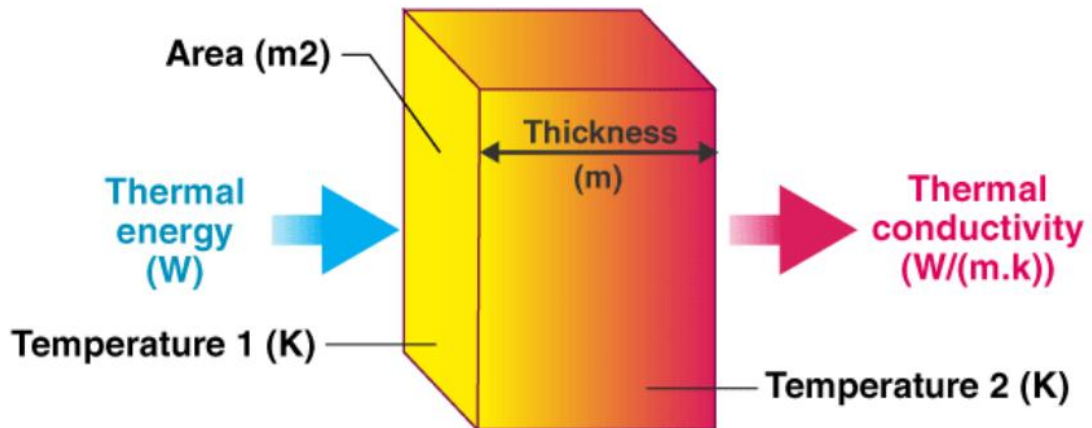
9.5 THERMAL CONDUCTIVITY

Thermal conductivity refers to the ability of a given material to conduct/transfer heat. It is generally denoted by the symbol 'k' but can also be denoted by 'λ' and 'κ'. The reciprocal of this quantity is known as thermal resistivity. Materials with high thermal conductivity are used in heat sinks whereas materials with low values of λ are used as thermal insulators.

Fourier's law of thermal conduction (also known as the law of heat conduction) states that the rate at which heat is transferred through a material is proportional to the negative of the temperature gradient and is also proportional to the area through which the heat flows. The differential form of this law can be expressed through the following equation:

$$\mathbf{q = -k.\nabla T}$$

Where ∇T refers to the temperature gradient, q denotes the thermal flux or heat flux, and k refers to the thermal conductivity of the material.

An illustration describing the thermal conductivity of a material in terms of the flow of heat through it is provided above. In this example, Temperature$_1$ is greater than Temperature$_2$. Therefore, the thermal conductivity can be obtained via the following equation:

**Heat Flux = -k * (Temperature$_2$ – Temperature$_1$)/Thickness**

Formula

Every substance has its own capacity to conduct heat. The thermal conductivity of a material is described by the following formula:

K = (QL)/(AΔT)

Where,

- K is the thermal conductivity in W/m.K

- Q is the amount of heat transferred through the material in Joules/second or Watts

- L is the distance between the two isothermal planes

- A is the area of the surface in square meters

- ΔT is the difference in temperature in Kelvin
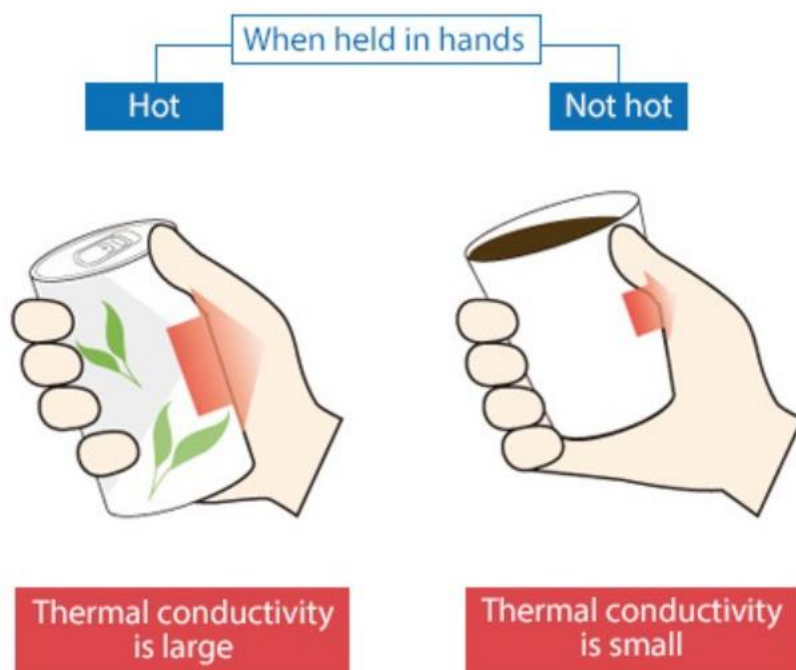
Measurement

There exist several methods of measuring the thermal conductivities of materials. These methods are broadly classified into two types of techniques – transient and steady-state techniques.

SI Unit

- Thermal conductivity is expressed in terms of the following dimensions: Temperature, Length, Mass, and Time.

- The SI unit of this quantity is watts per meter-Kelvin or $Wm^{-1}K^{-1}$.

- It is generally expressed in terms of power/ (length * temperature).

- These units describe the rate of conduction of heat through a material of unit thickness and for each Kelvin of temperature difference.

Steady-State Techniques

- These methods involve measurements where the temperature of the material in question does not change over a period of time.

- An advantage of these techniques is that the analysis is relatively straightforward since the temperature is constant.

- An important disadvantage of steady-state techniques is that they generally require a very well-engineered setup to perform the experiments.

- Examples of these techniques are the Searle's bar method for measuring the thermal conductivity of a good conductor and Lee's disc method.

Transient Techniques

- In these methods, the measurements are taken during the heating-up process.

- An important advantage of these methods is that the measurements can be taken relatively fast.

- One of the disadvantages of transient techniques is the difficulty in mathematically analyzing the data from the measurements.

- Some examples of these techniques include the transient plane source method, the transient line source method, and the laser flash method.

Thus, there exist various methods of measuring the thermal conductivity of materials, each with their own advantages and

disadvantages. It is important to note that it is easier to experimentally study the thermal properties of solids when compared to fluids.

Effect of Temperature on Thermal Conductivity

Temperature affects the thermal conductivities of metals and non-metals differently.

Metals

- The heat conductivity of metals is attributed to the presence of free electrons. It is somewhat proportional to the product of the absolute temperature and the electrical conductivity, as per the Wiedemann-Franz law.

- With an increase in temperature, the electrical conductivity of a pure metal decreases.

- This implies that the thermal conductivity of the pure metal shows little variance with an increase in temperature. However, a sharp decrease is observed when temperatures approach 0K.

- Alloys of metals do not show significant changes in electrical conductivity when the temperature is increased, implying that their heat conductivities increase with the increase in temperature.

- The peak value of heat conductivity in many pure metals can be found at temperatures ranging from 2K to 10K.

Non-Metals

- The thermal conductivities of non-metals are primarily attributed to lattice vibrations.

- The mean free path of the phonons does not reduce significantly when the temperatures are high, implying that the thermal conductivity of non-metals does not show significant change at higher temperatures.

- When the temperature is decreased to a point below the Debye temperature, the heat conductivity of a non-metal decreases along with its heat capacity.

Other Factors that Affect Thermal Conductivity

Temperature is not the only factor which causes a variance in thermal conductivity of a material. Some other important factors that influence the heat conductivity of substances are tabulated below.

Factor	Effect on Thermal Conductivity
The chemical phase	When the phase of a material changes, an abrupt

of the material	change in its heat conductivity may arise. For example, the thermal conductivity of ice changes from 2.18 $Wm^{-1}K^{-1}$ to 0.56 $Wm^{-1}K^{-1}$ when it melts into a liquid phase
Thermal Anisotropy	The differences in the coupling of phonons along a specific crystal axis causes some substances to exhibit different values of thermal conductivity along different crystal axes. The presence of thermal anisotropy implies that the direction in which the heat flows may not be the same as the temperature gradient's direction.
The electrical conductivity of the material	The Wiedemann-Franz law that provides a relation between electrical conductivity and thermal conductivity is only applicable to metals. The heat conductivity of non-metals is relatively unaffected by their electrical conductivities.
Influence of	The change in the thermal conductivity of a

magnetic fields	conductor when it is placed in a magnetic field is described by the Maggi-Righi-Leduc effect. The development of an orthogonal temperature gradient is observed when magnetic fields are applied.
Isotopic purity of the crystal	The effect of isotopic purity on heat conductivity can be observed in the following example: the thermal conductivity of type IIa diamond (98.9% concentration of carbon-12 isotope) is 10000 $Wm^{-1}K^{-1}$ whereas that of 99.9% enriched diamond is 41,000 $Wm^{-1}K^{-1}$

9.6 THERMAL DIFFUSIVITY

Thermal diffusivity is one of the important concepts in the heat transfer process. Thermal diffusivity is defined as the rate of temperature spread through a material. It is the measurement of heat transfer in a medium. It measures the heat transfer from the hot material to the cold.

Thermal diffusivity is denoted by the letter D or α (alpha).

SI unit of thermal diffusivity is m²/s.

The thermal diffusivity of a material is given by the thermal conductivity divided by the product of its density and specific heat capacity where the pressure is held constant.

$$\alpha = \frac{k}{\rho c_p}$$

Where,

k is the thermal conductivity

c_p is the specific heat capacity

ρ is density

ρc_p is the volumetric heat capacity

Thermal diffusivity can be defined as the ratio of heat that is let pass through the material to the heat per unit volume that is stored in the material.

Laser flash analysis or laser flash method, infrared thermography, and thermal wave interferometry are used to measure the thermal diffusivity of various materials.

Laser flash analysis involves heating a strip or cylindrical sample with a short energy pulse at one end and analyzing the temperature change

at another end of the sample. The laser flash technique for the measurement of thermal diffusivity was first explained in the year 1960 by Parker et al. of the U.S. Navy Radiological Defense Laboratory.

The thermal wave interferometry technique is used for thermal diffusivity measurements of coatings and thin slabs.

Thermal Diffusivity

Thermal diffusivity is a measure of how quickly heat spreads throughout an object or body. It is simply the rate at which heat diffuses through a material.

Thermal Diffusivity of Various Materials

Thermal diffusivity of different materials is given in the table below.

Material	Thermal diffusivity (mm²/s)

Gold	127
Silver	165.63
Aluminum	97
tin	40
iron	23
Quartz	1.4
Ice at zero degrees	1.02
Brick	0.52
Glass	0.34

We can observe that, material like silver has a high thermal diffusivity, while material like glass has a low thermal diffusivity. This means silver is a better diffuser of thermal energy than glass.

THERMAL CONDUCTIVITY

VERSUS

THERMAL DIFFUSIVITY

Thermal conductivity of a material is a measure of the ability of that material to conduct heat through it	Thermal diffusivity can be understood as the ability of a material to conduct heat relative to the heat stored per unit volume
$K(T) = \alpha(T)\rho(T)\, C_p(T)$	$\alpha(T) = K(T) / (\rho(T)\, C_p(T))$
Denoted by K	Denoted by α
SI unit is W/mK	SI unit is m2

9.7 TEMPERATURE GRADIENT

The rate of change of temperature with distance between two isothermal surfaces is called temperature gradient.

$$\text{Temperature Gradient} = \frac{change\ in\ temperature}{perpendicular\ distance} = -\frac{\Delta\theta}{\Delta x}$$

A temperature gradient is the gradual variance in temperature with distance. The slope of the gradient is consistent within a material. A gradient is established anytime two materials at different temperatures are in physical contact with each other. Units of measure of temperature gradients are degrees per unit distance, such as °F per inch or °C per meter.

Many temperature gradients exist naturally, while others are created. The largest temperature gradient on Earth is the Earth itself. The temperature of the Earth's core is estimated at about 9,000°F (5,000°C); it is 6,650°F (3,700°C) at the boundary between the core and the mantle, while the crust temperature is about 200°F (93°C). Each layer has a temperature gradient of a different slope, depending on the heat conductivity of the layer.

No temperature gradient exists between the Earth and the sun because there is not an atmosphere between them. Heat capacity is the ability for a material to hold heat. A vacuum has zero heat capacity.

Convection destroys a thermal gradient. In heating a pot of sauce, the liquid closest to the burner becomes the hottest. When stirred, the hot liquid mixes with cooler liquid, the heat becomes evenly distributed, and the temperature gradient is nullified.

If left unstirred, convective **heat transfer** will cause warm liquid to rise and cold to fall, and some circulation will occur, although it will not be as effective as active stirring. Over time, the **conduction** forces transferring heat from the bottom will establish equilibrium with the convective forces causing the water to circulate. If the heat source is low, circulation will be slow, a steep temperature gradient may exist, and the sauce may be burned on the bottom. If the heat is high, the sauce will boil, heat transfer by convection will be high, and the temperature gradient will be near zero.

Insulation is used to retard heat transfer by putting material with low heat conductivity next to the heat source. The insulation helps maintain the thermal gradient between the insulated object and ambient conditions. Coffee will stay warmer in a foam cup than in an **aluminum** cup because the foam conducts heat less readily. Likewise, the coffee drinker may burn a few fingers picking up the aluminum cup because the thermal gradient is near zero and the temperature of the outside of the cup is nearly the same as the inside of the cup.

To be stable, a thermal gradient must have a constant heat source and an available heat sink. Maintaining constant gradients is seldom important, except when conducting chemical reactions. Many industrial processes require careful heat control. The living cell also must maintain careful heat controls for optimum performance. While scientists understand how the human body as a whole maintains a temperature gradient between its core and the outside world, the options available to individual cells are less clear.

9.8   THERMAL RESISTANCE

Thermal resistance is a heat property and a measurement of a temperature difference by which an object or material resists a heat flow. Thermal resistance is the reciprocal of thermal conductance.

Thermal resistance $= \dfrac{L}{(kA)}$, measured in KW^{-1},

L is the length of the material (measured on a path parallel to the heat flow) (m)

k is the thermal conductivity of the material (W/(Km))

A is the cross-sectional area (perpendicular to the path of heat flow) (m^2)

We can use thermal resistance **to estimate how hot a particular part might get under various loads based on how easily the heat is able to be transfered from one place to another**. For electronics the heat starts at the source, such as a semiconductor junction, and spreads to be eventually dissipated to ambient air.

Thermal resistance is considered the inverse of thermal conductivity. A materials thermal resistance can be measured by that materials ability to resist the flow of heat through it. Many materials with a high thermal resistance are known as insulators and are commonly used to keep or trap an area of hot or cold. For example, a Styrofoam cooler is used to keep drinks cold that are stored inside of it because it is slow to transfer the heat from its surroundings into the confined chilled area inside the cooler.

Thermal resistance is a key component in the engineering of thousands of products that are used every day around the globe.

Thermal Resistance
Heat Transfer by Conduction and Convection
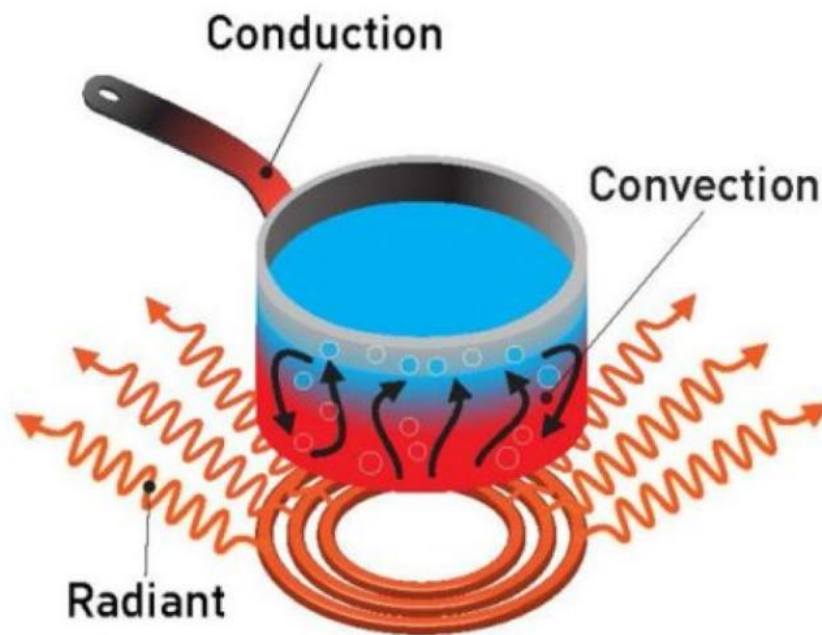
One of the most useful and widespread thermally resistive material is the concrete that is used during the construction of buildings and homes. A building can be easily compared to a Styrofoam cooler. The foundation and walls of a building are trapping the flow of the hot or cold air from the outdoors and maintaining a uniform temperature inside. Builders when constructing a home or building take into consideration the

thermal resistance properties of the materials that they are using to create the foundation. Building with materials that have a high thermal resistance can dramatically increase the energy savings and in turn the economic savings for the future owner of that home or building. This is the main factor that is contributing to the spike in research to discover the best combination of insulating materials that can be used during the construction of homes and buildings.

9.9 FOURIER EQUATION OF HEAT

Fourier's law states that the negative gradient of temperature and the time rate of heat transfer is proportional to the area at right angles of that gradient through which the heat flows. Fourier's law is the other name of the law of heat conduction.

Newton's law of cooling and Ohm's law are a discrete and electrical analog of Fourier's law.

Differential Form of Fourier's Law

Fourier's law differential form is as follows:

$$q = -k \nabla T$$

Where,

- q is the local heat flux density in $W.m^2$

- k is the conductivity of the material in $W.m^{-1}.K^{-1}$

- ∇T is the temperature gradient in $K.m^{-1}$

In one-dimensional form:

$$q_x = -k\frac{dT}{dx}$$

Integral form

$$\frac{\partial Q}{\partial t} = -k\oiint_S \nabla T \cdot dS$$

Where,

- $\frac{\partial Q}{\partial t}$

is the amount of heat transferred per unit time

- dS is the surface area element

When the same equation is given in the differential form, which is the basis of heat equation derivation:

$$\frac{Q}{\Delta t} = -kA\left(\frac{\Delta T}{\Delta x}\right)$$

Where,

- A is the area of the cross-sectional surface

- ΔT is the temperature difference between the endpoints

- Δx is the distance between two ends

Fourier's law in terms of conductance

$$\frac{\triangle Q}{\triangle t} = UA(-\triangle T)$$

Where,

- U is the conductance

Fourier's Law Derivation

The derivation of Fourier's law was explained with the help of an experiment which explained the *Rate of heat transfer through a plane layer is proportional to the temperature gradient across the layer and heat transfer area.*

$$Rate\ of\ heat\ conduction \propto \frac{(area)(temperature\ difference)}{thickness}$$

Let T_1 and T_2 be the temperature difference across a small distance Δx of area A. k is the **conductivity of the material**. Therefore, in one dimensional, the following is the equation used:

$$Q_{cond} = kA\frac{T_1 - T_2}{\Delta x} = -kA\frac{\Delta T}{\Delta x}$$

When $\Delta x \rightarrow 0$, the following is the equation in a reduced form to a differential form:

$$Q_{cond} = -kA\frac{\Delta T}{\Delta x}$$

The three-dimensional form the Fourier's law is given as:

$$\vec{q} = -k \nabla T$$

9.10 PERIODIC FLOW OF HEAT

❖ **Heat flow** is energy moving. It has the same units as power - **energy per unit time** .

❖ It means that during the given amount of time, during which heat is flowing, a certain amount of energy is transferred or moved from one place to another place
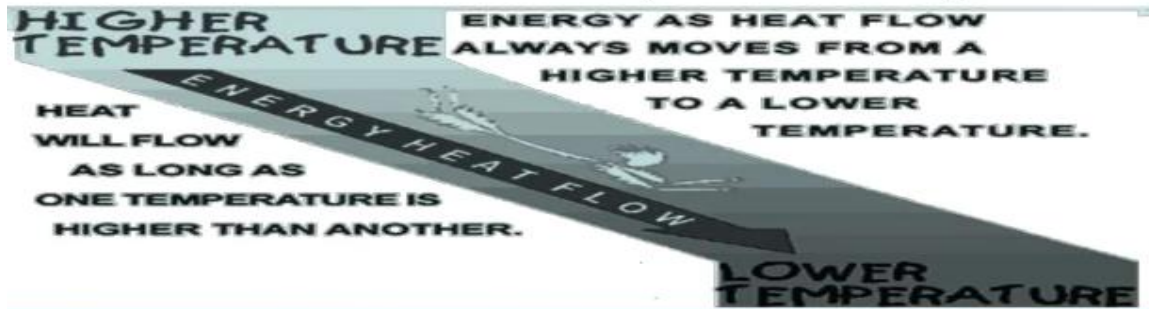
❖ Three easy things to know about the way heat flows:
1) There has to be a temperature difference. Energy only flows as heat if there is a temperature difference
2) Energy as heat flows from a higher temperature to a lower temperature.
3) The greater or larger the difference in temperature, the faster the energy flows.

❖ The science of how heat flows is called **heat transfer.**

❖ There are three ways heat transfer works: **conduction**, **convection**, and **radiation**.

❖ Heat flow depends on the **temperature difference**.
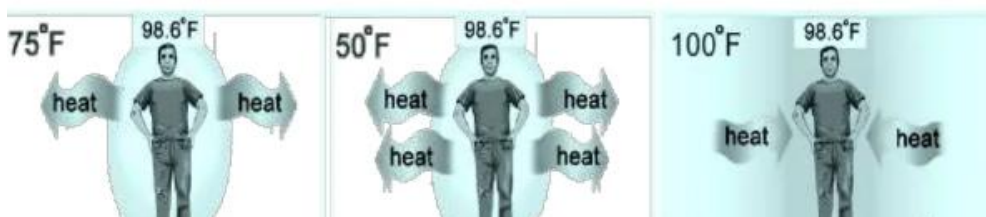
Periodic heat flow means that **heat flow is a continu- ous function of time and repeats itself at regular inter- vals**. A semi-infinite solid has only one bounding plane and extends to infinity in all other directions.

In nature the variation of climatic conditions produces a non-steady state. Diurnal variations produce an approximately repetitive 24-hour cycle of increasing and decreasing temperatures. The effect of this on a building is that in the hot period heat flows from the outdoors into the building, where some of it is stored, and at night during the cool period the heat flow is reversed: from the building to the outside. As this cycle is repetitive, it is described as periodic heat flow.

The diurnal variations of external and internal temperatures is a periodic cycle. In the morning, as the outdoor temperature increases, heat starts entering the outer surface of the wall. Each particle in the wall will absorb a certain amount of heat for every degree rise in temperature, depending on the specific heat of the wall material. Heat to the next particle will only be

transmitted after the temperature of the first particle is increased. Thus the corresponding increase in the internal temperature will be delayed.

The outdoor temperature reaches its peak and starts decreasing, before the inner surface temperature has reached the same level. From this moment the heat stored in the wall will be dissipated partly to the outside and only partly to the inside. As the out door air cools, an increasing proportion of this stored heat flows outwards, and when the wall temperature falls below the indoor temperature the direction of the heat flow is completely reversed.

The two quantities characteristic of this periodic change are the time lag (φ) and the decrement factor ($\grave{u}$). Decrement factor is the ratio of the maximum outer and inner surface temperature amplitudes taken from the daily mean.
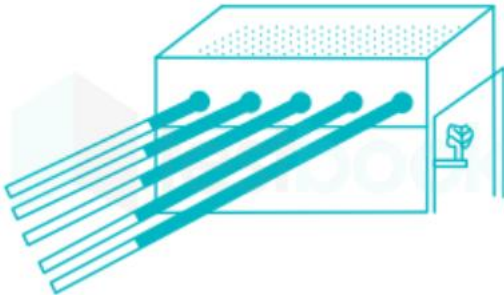
9.11 INGEN-HOUSE EXPERIMENT

- **Ingen-Housz experiment:** It states that the **thermal conductivities(K)** of different materials are **proportional to the square of the lengths (L)** of the melted wax on the rods of these materials in the steady-state.

Formula:

$$K = cL^2$$

where K = thermal conductivity and L = length of the rod

- In this experiment, here, several rods of different metals and of the equal area of cross-section and polish to ensure equal emissivity are coated with wax.

- One end of each of the rods is placed in an oil bath as shown in Fig above.

- Heat is transferred from the end introduced into the bath towards the other end exposed outside.

- This causes the melting of wax on the surface. At first, **heat is transferred quickly** and then it **slows down**.

- If $l_1, l_2, l_3,....$ are the lengths of the melted wax on the rods of different materials having a coefficient of thermal conductivities K_1, K_2, K_3, then

$$K_1 : K_2 : K_3 : = l_1^2 : l_2^2 : l_3^2$$

The correct relation is $K = cL^2$.

It is used to compare thermal conductivities of different materials. If l_1, l_2 and l_3 are the lengths of wax melted on rods as shown in the figure, then the ratio of thermal conductivities is $K_1 : K_2 : K_3 = l_1^2 : l_2^2 : l_3^2$
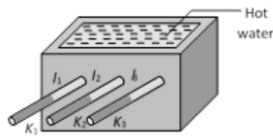

$\Rightarrow$ Thermal conductivity $(K) \propto (\text{Melted length } l)^2$

9.12 NATURAL AND FORCED CONVECTION

Natural convection- The convection occurring due to buoyant force with the distinction in densities caused by the distinction in temperature is called natural convection. The oceanic wind is an example of natural convection.

Forced convection- The external systems like pumps and fans create convection and is called forced convection. The geyser or water heater for heating of water and use of a fan in summer are some examples of forced convection.

Forced
convection

Natural
convection

AIR

AIR

hot egg

hot egg
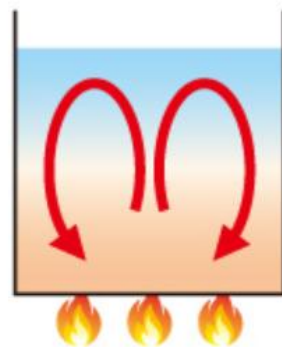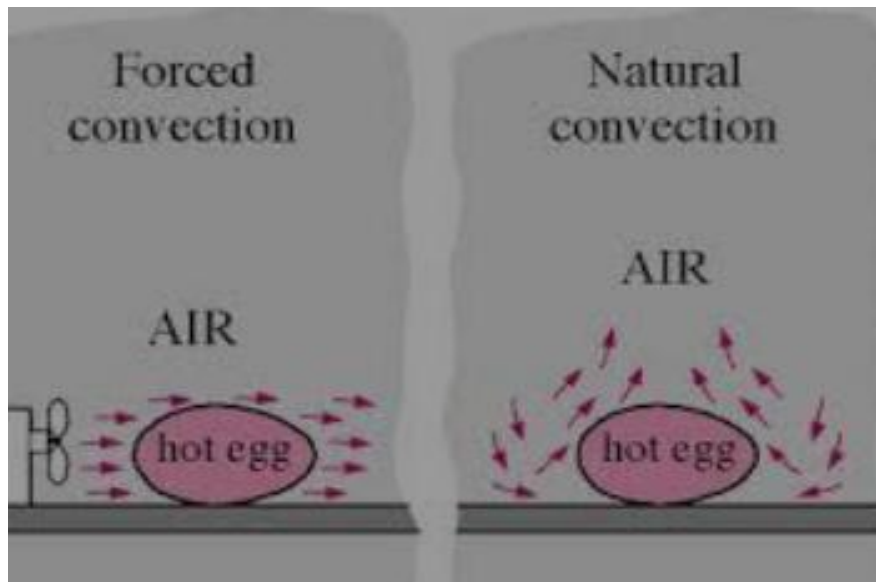
A flow is driven only by
temperature difference
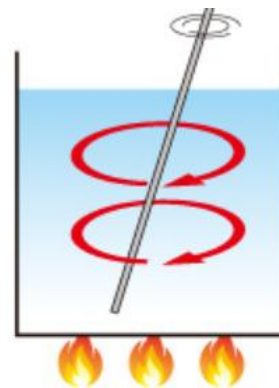
A flow is driven by an
external factor

(a) Natural convection

(b) Forced convection

Forced convection is a method of heat transfer in which external means influence the motion of the fluid. There, external sources such as pumping, fans, suction devices, etc. are useful in generating the fluid motion. This method is very valuable because it can efficiently transfer heat from a heated object. Some common examples of this mechanism include air conditioning, steam turbines, etc.

When considering the mechanism of forced convection, it is has a complicated mechanism than the natural way. That is because, in this method, we have to regulate two factors; fluid motion and heat conduction. These two factors have a strong connection since the fluid motion can enhance the heat transfer. Ex: higher the rate of motion of the fluid, higher the heat transfers.

What is the Difference Between Natural and Forced Convection?

Natural convection is a method of heat transfer in which the motion of the fluid is influenced by natural means. Forced convection is a method of heat transfer in which the motion of the fluid is influenced by external means. When considering the factors affecting the heat transfer, there are no external factors affecting the heat transfer in natural convection while external factors can cause heat transfer in forced convection.

The fluid motion in natural convection generates as a result of the change of the density of fluid when heated. However, the fluid motion in forced convection generates as a result of an external source such as pumping, fan, suction devices. Cooling

down a boiled egg when kept in the normal air, loss of cool of a cool drink can, etc. can be included as examples of natural convection, and air conditioning, steam turbines, etc. are examples of forced convection.


9.13 SUMMARY

Difference Between Conduction Convection and Radiation

Conduction	Convection	Radiation

In conduction, heat transfer occurs between objects by direct contact.	In convection, the heat transfer takes within the fluid.	In radiation, heat transfer occurs through electromagnetic waves without involving particles.
The heat transfer takes place due to the difference in temperature.	Heat transfer occurs due to the difference in density.	The heat transfer occurs in all objects with a temperature greater than 0 K.
Heat transfer in conduction is slow	Heat transfer in convection is faster.	Heat transfer in radiation is the fastest.
Heat transfer occurs through a heated solid object.	Heat transfer occurs through intermediate objects. For example, heat transfer between air and water.	Heat transfer occurs through electromagnetic waves.
It does not follow	It does not follow the	It follows the law of

the law of reflection and refraction.	law of reflection and refraction.	reflection and refraction.
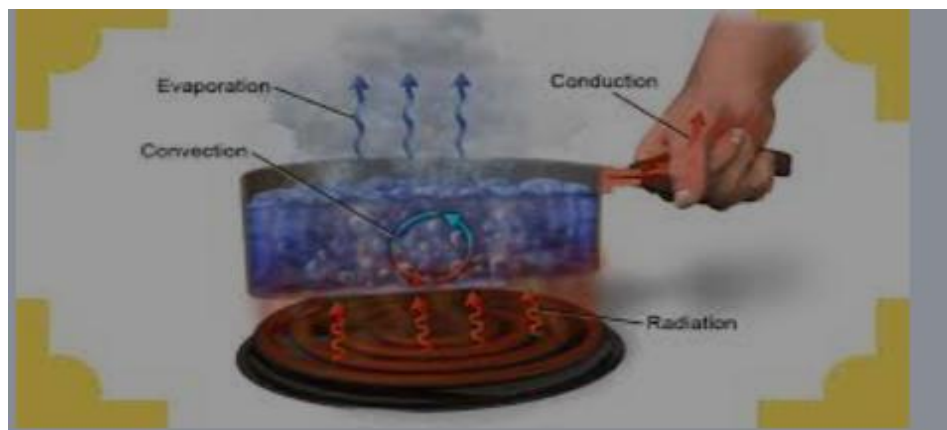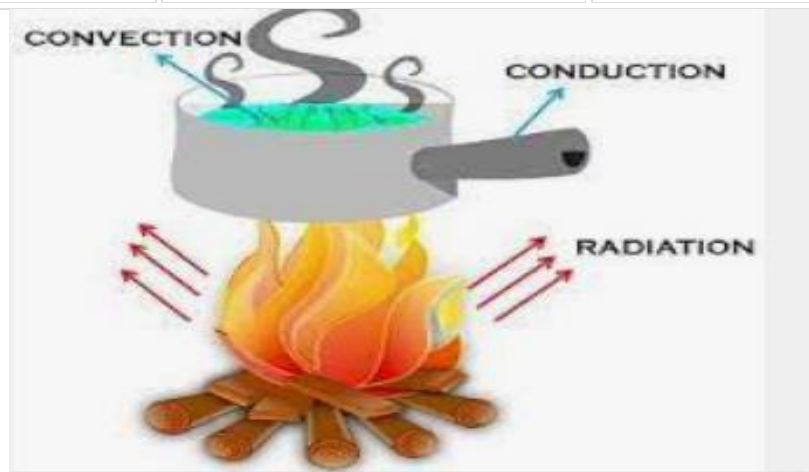
Heat transfer by conduction involves transfer of energy within a material without any motion of the material as a whole. The rate of heat transfer depends upon the temperature gradient and the thermal conductivity of the material. Thermal conductivity is a reasonably

straightforward concept when you are discussing heat loss through the walls of your house, and you can find tables which characterize the building materials and allow you to make reasonable calculations.

More fundamental questions arise when you examine the reasons for wide variations in thermal conductivity. Gases transfer heat by direct collisions between molecules, and as would be expected, their thermal conductivity is low compared to most solids since they are dilute media. Non-metallic solids transfer heat by lattice vibrations so that there is no net motion of the media as the energy propagates through. Such heat transfer is often described in terms of "phonons", quanta of lattice vibrations. Metals are much better thermal conductors than non-metals because the same mobile electrons which participate in electrical conduction also take part in the transfer of heat.

Conceptually, the thermal conductivity can be thought of as the container for the medium-dependent properties which relate the rate of heat loss per unit area to the rate of change of temperature.

$$\underbrace{\frac{\Delta Q}{\Delta t\, A}}_{\substack{\text{Power per} \\ \text{unit area} \\ \text{transported}}} = -\underbrace{\kappa}_{\substack{\text{Thermal} \\ \text{conductivity}}} \underbrace{\frac{\Delta T}{\Delta x}}_{\substack{\text{Temperature} \\ \text{gradient}}}$$

9.14 TERMINAL QUESTIONS

1. Explain the concept of Modes of Transfer of Heat.

2. Define steady and variable states.

3. Explain the concept of Thermal conductivity.

4. Define Thermal Diffusivity.

5. What is Temperature gradient.

9.15 ANSWER AND SOLUTION OF TERMINAL QUESTION

1. Section 9.3

2. Section 9.4

3. Section 9.5

4. Section 9.6

5. Section 9.7

9.16 SUGGESTED READINGS

1. Thermal Physics: with Kinetic Theory, Thermodynamics: SC Garg.

2. Thermal Physics: R. Murugeshan, Er. Kiruthiga Siva Prasath.

3. Thermal Physics: C.B.P. Finn.

4. Heat Thermodynamics and Statistical Physics: Brij lal, Dr. N. Subrahmanyam, P.S. Hemne.

UNIT – 10 RADIATION

10.1 INTRODUCTION

In physics, **radiation** is the emission or transmission of energy in the form of waves or particles through space or through a material medium. Radiation is often categorized as either *ionizing* or *non-ionizing* depending on the energy of the radiated particles. Ionizing radiation carries more than 10 eV, which is enough to ionize atoms and molecules and break chemical bonds. This is an important distinction due to the large difference in harmfulness to living organisms. A common source of ionizing radiation is radioactive materials that emit α, β, or γ radiation, consisting of helium nuclei, electrons or positrons, and photons, respectively. Other sources include X-rays from medical radiography examinations and muons, mesons, positrons, neutrons and other particles that constitute the secondary cosmic rays that are produced after primary cosmic rays interact with Earth's atmosphere.

10.2 OBJECTIVES

After studying this unit student should able to

Define radiant energy

Explain black body radiation

Understand the concept of Stefen Boltzman Law

Explain Wien's displacement Law

10.3 RADIANT ENERGY

Radiant energy is the physical energy resulting from electromagnetic radiation, usually observed as it radiates from a source into the surrounding environment.

Radiant energy sources include the entire electromagnetic radiation spectrum, including gamma rays, x-rays, radio frequencies, microwaves, light and heat. Often, *radiant energy* is used to describe the type of particle in question, but it is actually the energy carried by the particle. Radiant energy is not the photon itself, for example, but one can see the energy as light and feel it as heat as the photons it is associated with arrive on your skin.

Radiant energy travels in wave forms. Types of radiation with higher frequency are higher energy. As the source material is excited, the radiation of energy is increased. One can see this in effect with the turning up of a dimmer switch: As the power is increased, more light is emitted from the bulb, be it LED or incandescent. This effect is the result of more photons are radiating off in all directions.

Naturally occurring sources of radiant energy such as the sun can be converted into usable electricity with solar power or used as passive solar. Nuclear power plants use radiation to boil water driving steam turbines.

Radiant energy and its behaviors have been harnessed in many inventions from the light bulb to the large hadron collider.
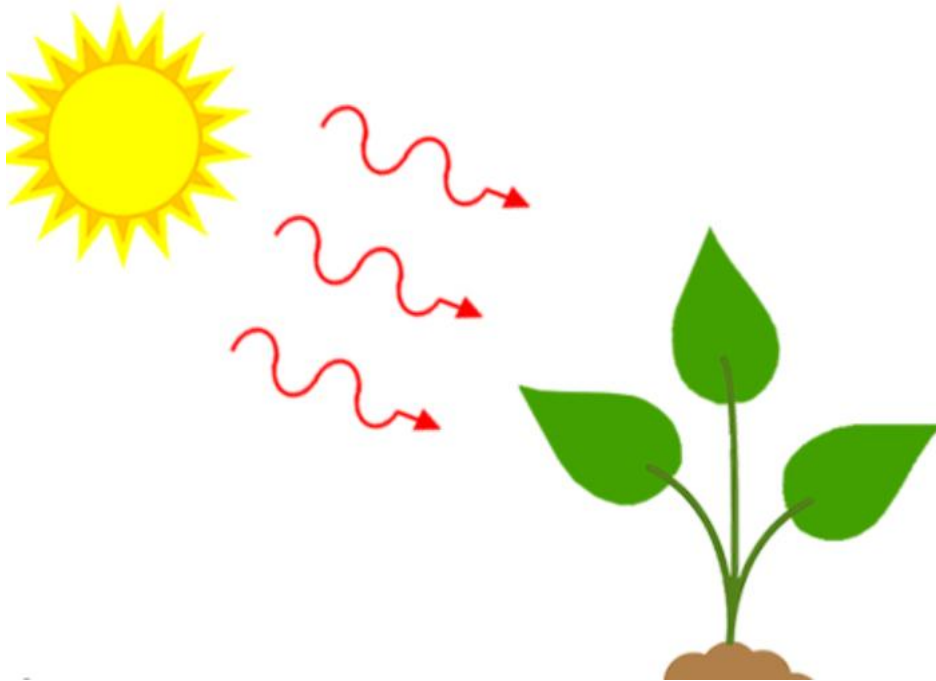
Radiant energy is the energy of electromagnetic waves.

Radiation is the emission of energy as electromagnetic waves.

Light energy is a type of radiant energy that can be seen by the human eye.

The Sun is the closest star to the planet Earth and radiates light energy.

What Causes Radiant Energy

Electromagnetic waves are made of oscillating electric and magnetic fields. The two fields oscillated in planes perpendicular to each other. The energy and the wave propagate in a direction perpendicular to the two planes. Since space is devoid of matter, electromagnetic waves do not require any medium to propagate. Oscillating fields involve the movement of charged particles; hence, radiant energy is considered kinetic energy. The frequency of oscillations gives the magnitude of radiant energy. The higher the frequency, the higher the energy. For example, infrared radiation has higher energy in the electromagnetic spectrum than

ultraviolet. According to wave-particle duality, electromagnetic radiation can also be considered particles. These particles are called photons and transmit energy in packets or quanta.

How Does Radiant Energy Work

Let us take the example of sunlight to understand how radiant energy works. Sun emits radiant energy in the form of light, traveling at a speed of 3×10^8 m/s. This energy travels through space and reaches Earth. The light radiation strikes our skin and excites the skin molecules. The molecules then start to vibrate rapidly, and we perceive the vibrations as heat.

Properties and Characteristics

- Caused by the motion of charged particles
- Transmitted by electromagnetic waves or particles knowns as photons
- Travels in a straight at the speed of light, which is 3×10^8 m/s
- Travels in solid, liquid, gas, and even in vacumn
- Can be transmitted, absorbed, and reflected
- High-frequency electromagnetic waves have higher radiant energy than low-frequency ones

Radiant Energy
Electromagnetic Spectrum
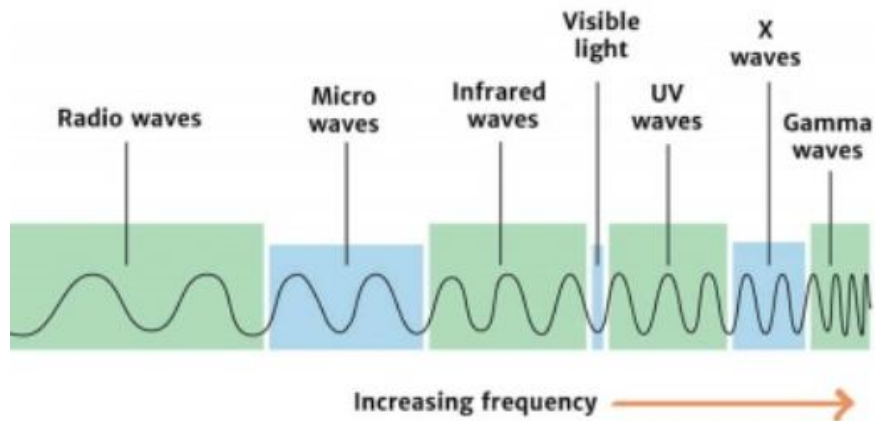
Radiant Energy Source

Here are some examples of objects emitting radiant energy.

- Sun

- Stars

- Bulb

- Laser

- Space heater

- Hot stove

- Microwave oven

- X-ray machine

- Campfire

- Plants convert radiant energy from the sun into chemical energy, producing food through photosynthesis

- An induction stove converts electrical energy to radiant energy, which is used for cooking

- Solar cells harvest sunlight by converting it into electricity

- A campfire emits heat and keeps us warm at night

- Cell phones utilize radiant energy to function

- An x-ray machine generates x-rays that are used to detect fractures in our bones

10.4 BLACK BODY RADIATION

Black-body radiation is the thermal electromagnetic radiation within, or surrounding, a body in thermodynamic equilibrium with its environment, emitted by a black body (an idealized opaque, non-reflective body). It has a specific, continuous spectrum of wavelengths, inversely related to intensity, that depend only on the body's temperature, which is assumed, for the sake of calculations and theory, to be uniform and constant.
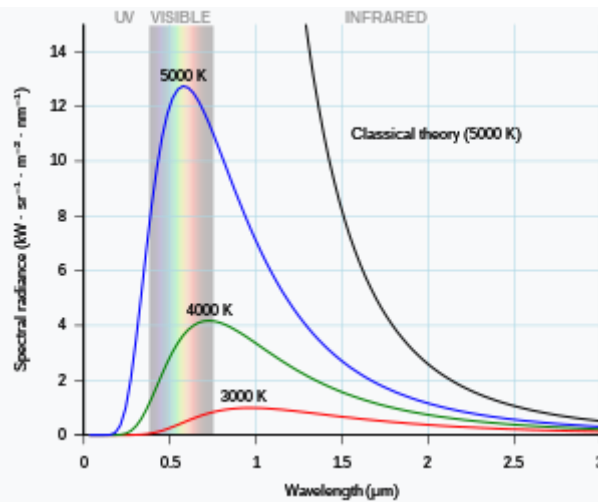
As the temperature of a black body decreases, its intensity also decreases and its peak moves to longer wavelengths. Shown for comparison is the classical Rayleigh–Jeans law and its ultraviolet catastrophe.

A perfectly insulated enclosure which is in thermal equilibrium internally contains black-body radiation, and will emit it through a hole made in its wall, provided the hole is small enough to have a negligible effect upon the equilibrium.

The thermal radiation spontaneously emitted by many ordinary objects can be approximated as black-body radiation.

Of particular importance, although planets and stars (including the Earth and Sun) are neither in thermal equilibrium with their surroundings nor perfect black bodies, black-body radiation is still a good first approximation for the energy they emit. The sun's radiation, after being filtered by the earth's atmosphere, thus characterises "daylight", which humans (also most other animals) have evolved to use for vision.

A black body at room temperature (23 °C (296 K; 73 °F)) radiates mostly in the infrared spectrum, which cannot be perceived by the human eye,[6] but can be sensed by some reptiles. As the object increases in temperature to about 500 °C (773 K; 932 °F), the emission spectrum gets stronger and extends into the human visual range, and the object appears dull red. As its temperature increases further, it emits more and more orange, yellow, green, and blue light (and ultimately beyond violet, ultraviolet).

Tungsten filament lights have a continuous black body spectrum with a cooler colour temperature, around 2,700 K (2,430 °C; 4,400 °F), which also emits considerable energy in the infrared range. Modern-day fluorescent and LED lights, which are more efficient, do not have a continuous black body emission spectrum, rather emitting directly, or using combinations of phosphors that emit multiple narrow spectrums.
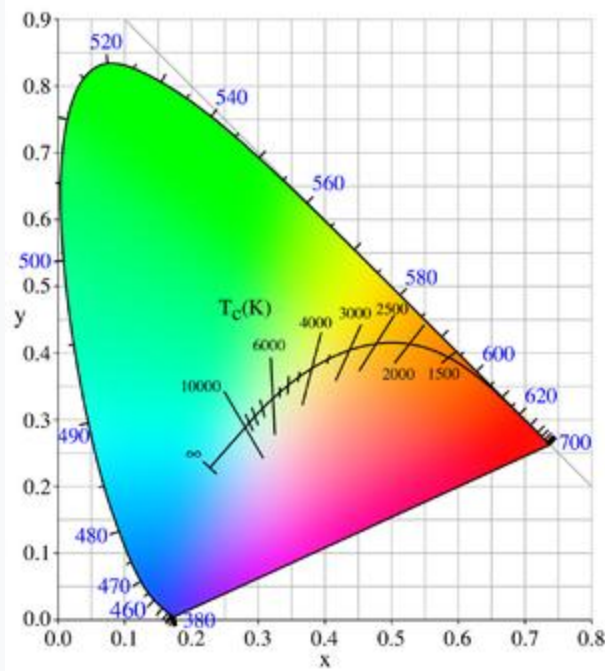
The color ([chromaticity](#)) of black-body radiation scales inversely with the temperature of the black body; the [locus](#) of such colors, shown here in [CIE 1931 *x,y* space](#), is known as the [Planckian locus](#).

[Black holes](#) are near-perfect black bodies in the sense that they absorb all the radiation that falls on them. It has been proposed that they emit black-body radiation (called [Hawking radiation](#)) with a temperature that depends on the mass of the black hole.

The term *black body* was introduced by [Gustav Kirchhoff](#) in 1860. Black-body radiation is also called [thermal radiation](#), *cavity radiation*, *complete radiation* or *temperature radiation*.

Characteristics of Blackbody Radiation

The characteristics of the blackbody radiation are explained with the help of the following laws:

- Wien's displacement law
- Planck's law
- Stefan-Boltzmann law

Wien's Displacement Law

Wien's displacement law states that

The blackbody radiation curve for different temperature peaks at a wavelength is inversely proportional to the temperature.

Planck's Law

Using Planck's law of blackbody radiation, the spectral density of the emission is determined for each wavelength at a particular temperature.

Stefan-Boltzmann Law

The Stefan-Boltzmann law explains the relationship between total energy emitted and the absolute temperature.

The radiation emitted by the blackbody is known as blackbody radiation. To stay in thermal equilibrium, a black body must emit radiation at the

same rate as it absorbs, so it must also be a good emitter.

What is a black body?

It is an ideal body that absorbs all incident electromagnetic waves or radiation, regardless of the angle of incidence or frequency. As it absorbs all colours of light, it is named as black "body".

10.5 WHITE RADIATION

White radiation is **believed due to the collision of the accelerated electrons with the atomic nuclei of the target atoms**. If all of the kinetic energy carried by an electron is converted into radiation, the energy of the X-ray photon would be given by. $E_{max} = h\nu_{max} = eV$.

Some kind of the collisions occurring between the thermionic electrons and the target is caused by the emission of a continuous spectrum of x rays. This is known as white radiation or otherwise called Bremsstrahlung. White radiation has been considered to be occurring due to the collision of the accelerated electrons with the atomic nuclei of the target atoms. As we all know that white light is having characteristic components of a wide range of wavelengths. Because of this, the white X-

rays are referred to as this because they have a continuous and white range of wavelengths in their composition. This term is also helpful in white noise where the noise has characteristic components of complete frequency range.

Note:

X-ray imaging develops pictures of the interior of our body. The images represent the parts of our body in a variety of shades of black and white. This is due to different tissues absorbing varying amounts of radiation. Calcium in bones is able to absorb x-rays the most. This is why bones are looking white

10.6 REFLECTIVITY, ABSORPTIVITY AND TRANSMITIVITY

When thermal radiation falls onto an object,

- The radiation will be absorbed by the surface of the object, causing its temperature to change
- The radiation will be reflected from the surface of the body, causing no temperature change
- The radiation will pass completely through the object, causing no temperature change

Absorptivity (α) is a measure of how much of the radiation is absorbed by the body.

Reflectivity (ρ) is a measure of how much is radiation is reflected.

Transmissivity (τ) is a measure of how much radiation passes through the object.

Each of these parameters is a number **that ranges from 0 to 1**.

For any given wavelength (λ), $\alpha + \rho + \tau = 1$.

10.7 KRICHHOFF'S LAW FOR RADIATION

Kirchhoff's law of thermal radiation states that the emissive power to the coefficient of absorption is constant for all the substances at a given temperature. We can say that at a given temperature, the emissivity of a substance is equal to the coefficient of   absorption.

Formula   used:

$$\frac{E}{a} = \text{constant} = E_b$$

In heat transfer, Kirchhoff's thermal radiation law refers to the wavelength-specific radiative emission and absorption by a body in thermodynamic equilibrium. Kirchhoff's law states that: For a body made up of any arbitrary material, the emitting and the absorbing thermal electromagnetic radiation, the ratio of its emissive power to its coefficient of absorption is equal to a universal function. That universal function describes the emissive power of a perfect black body.

Explanation   of   Kirchhoff's thermal   radiation   law:

If E is the emissive power of a substance and aa is the coefficient of absorption, then by Kirchhoff's law of radiation,

$$\frac{E}{a} = \text{constant} = E_b$$

Or we can say, $a = e$

Theoretical proof of Kirchhoff's law of thermal radiation:

We will consider two bodies A and B being suspended in a constant temperature enclosure. A is a normal material body and B is a perfectly black body. After some interval of time both A and B will attain the same temperature as that of the enclosure. Prevost heat exchange theory states that every body will emit and absorb thermal radiations.

Constant temperature enclosure
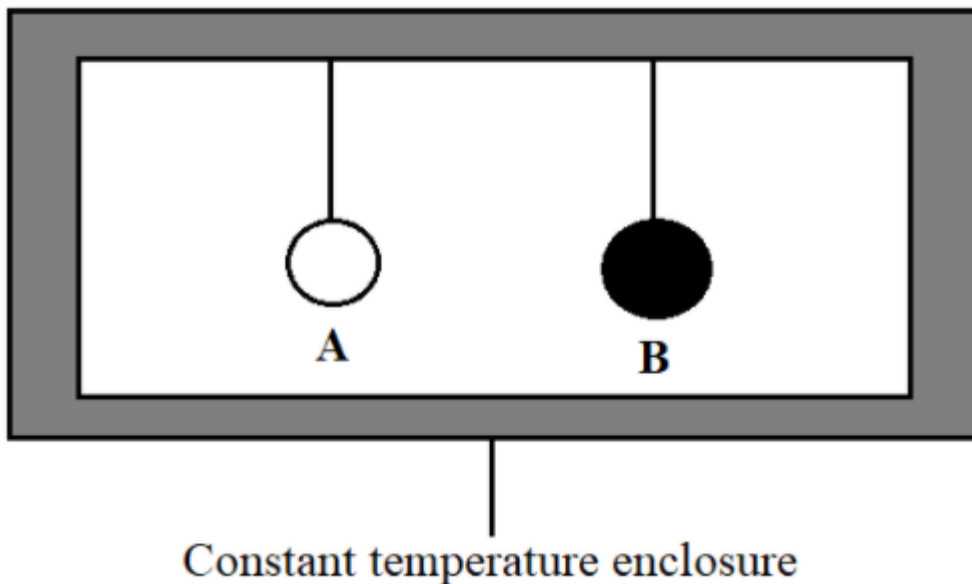
Let E be the emissive power of A and aa be its coefficient of absorption.

Let E_b be the emissive power of B. Let Q be the radiant heat incident per

unit time area of each body.

Heat absorbed by body A per unit time per unit area $= aQ$

Heat emitted by body A per unit time per unit area =

E_b

As the temperature remains constant, heat absorbed will be equal to the

heat emitted

$E_b = Q$

Perfectly black body will absorb the entire heat incident on it

Heat absorbed by body B per unit time per unit area $= Q$

Heat emitted by body B per unit time per unit area = E_b

As the temperature remains constant, heat absorbed will be equal to the heat emitted

$$E_b = Q$$

From above equations, we get

$$\frac{E}{E_b} = \frac{aQ}{Q}$$

$$\frac{E}{E_b} = a$$

But, $\dfrac{E}{E_b} = e = \text{coefficient of emission}$

Therefore, a=e

Thus, the coefficient of emission is equal to the coefficient of absorption.

This proves Kirchhoff's thermal radiation law theoretically.

Note: Students should keep in mind that Emissivity is a measure of how strongly a body interacts with thermal radiation. Always remember, a high emissivity of material comes together with a high absorptance. Emissivity of a black body is 1.

10.8 STEFEN BOLTZMAN LAW

Stefan's law states that the rate of emission of radiant energy by unit area of perfectly black-body is directly proportional to the fourth power of its absolute temperature. In symbolic form

$$E \propto T^4$$

or
$$E = \sigma T^4$$

where σ is a constant and is called **Stefan's constant**.

The law in the above form refers to the emission only and not the net loss of heat by body after exchange with the surroundings. It simply deals with the amount of heat emitted by the body by virtue of its temperature irrespective of what it receives from the surroundings. The law can be extended to represent the net loss of heat and ay be enunciated as follows:

A black-body at absolute temperature T surrounded by black-body at absolute temperature T_0 not only loses an amount of energy σT^4 but also gains σT_0^4, thus the amount of heat lost by the former per unit time is given by

$$E = \sigma\left(T^4 - T_0^4\right)$$

The law is known as Stefan Boltzmann's law as Boltzmann had deduced it thermodynamically.

Thermodynamic Proof:

Let us consider a cylindrical enclosure ABCD of uniform cross-section with perfectly reflecting walls and provided with a perfectly reflecting piston P. Let it be filed with diffuse radiations of density u at uniform temperature T.
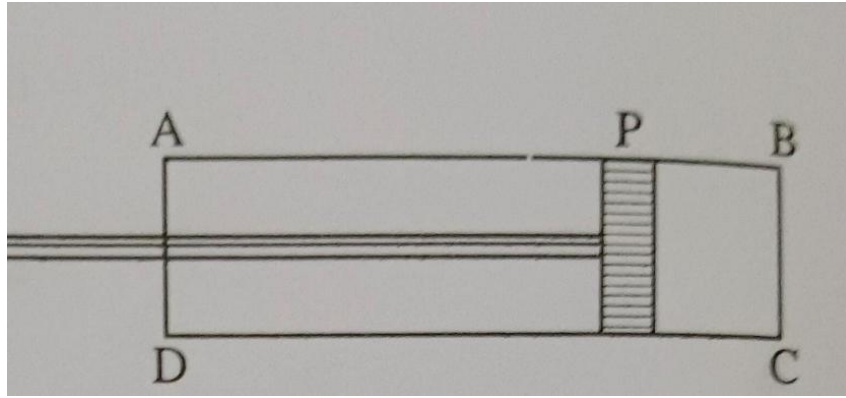
Figure :1

If V be the volume of the enclosure; then the total internal energy of radiation inside the enclosure is given by

$$U = uV.$$ .... (1)

Let a small amount of heat dQ flow in the enclosure from outside and at the same time let the piston move out so that the volume changes by a small amount dV. In this process the temperature and as a result the energy density u changes by an infinitesimal amount. If dU is the change in internal energy of radiation and dW is the external work done by radiation in the expansion of volume by an amount dV, then by the first law of thermodynamics

$$dQ = dU + dW.$$

But $U = uV$ and $dW = pdV$, p being the pressure of radiation

$$dQ = d(uV) + p\,dV.$$

But the pressure of diffuse radiation $p = \frac{u}{3}$, therefore,

$$dQ = d\,(uV) + \frac{1}{3}u\,dV$$

$$= u \, dV + V \, du + \frac{1}{3} u \, dV$$

$$= V \, du + \frac{4}{3} u \, dV.$$

$$\ldots\ldots\ldots\ldots (2)$$

If dS is the change in entropy of the radiation, then from second law of thermodynamics, we have

$$dS = \frac{dQ}{T}.$$

$$\ldots\ldots\ldots (3)$$

Substituting value of dQ from (2) in (3), we have

$$dS = \frac{V}{T} \, du + \frac{4u}{3T} \, dV.$$

$$\ldots\ldots\ldots (4)$$

From this expression it is clear that S in function of two independent variables u and V, i.e.,

$$S = f(u, V)$$

$$dS = \frac{\partial S}{\partial u} \, du + \frac{\partial S}{\partial V} \, dV \qquad \ldots\ldots (5)$$

$$\ldots$$

Comparing (4) and (5), we get

$$\frac{\partial S}{\partial u} = \frac{V}{T} \quad and \quad \frac{\partial S}{\partial V} = \frac{4u}{3T}.$$

$$\ldots\ldots\ldots (6)$$

As dS is a perfect differential, we have

$$\frac{\partial^2 S}{\partial u\, \partial V} = \frac{\partial^2 S}{\partial V\, \partial u}$$

$$\frac{\partial}{\partial u}\left(\frac{\partial S}{\partial v}\right) = \frac{\partial}{\partial v}\left(\frac{\partial S}{\partial u}\right).$$

.... (7)

Substituting the value of $\frac{\partial S}{\partial v}$ and $\frac{\partial S}{\partial u}$ from (6) in (7), we get

$$\frac{\partial}{\partial u}\left(\frac{4u}{3T}\right) = \frac{\partial}{\partial v}\left(\frac{V}{T}\right).$$

.... (8)

As T is independent of V and is a function of u only, on

differentiating (8), we get

$$\frac{4}{3}\cdot\frac{1}{T} - \frac{4}{3}\cdot\frac{u}{T^2}\cdot\frac{\partial T}{\partial u} = \frac{1}{T}.$$

or $\qquad\qquad \frac{4}{3}\cdot\frac{1}{T} = \frac{4}{3}\cdot\frac{u}{T^2}\cdot\frac{\partial T}{\partial u}$

or $\qquad\qquad \frac{\partial u}{u} = 4\frac{\partial T}{T}.$

Integrating, we have

log u = 4 log T + log A, log A being constant of integration

which gives $\qquad\qquad u = AT^4.$

.... (9)

Now it can be shown that the total rate of emission of radiant energy

per unit area is related to the energy density by the relation

$$E = \frac{1}{4}uc$$

where c is the velocity of light.

□ $E = \frac{1}{4}AcT^4$ or $E = \sigma T^4$. ………..

(10)

where , σ is a constant called Stefan's constant. The value of Stefan's constant in C.G.S. system is 5.672×10^{-5} erg. cm^{-2} sec^{-1} $(K)^{-4}$ and in M.K.S. system it is 5.672×10^{-8} joule m^{-2} sec^{-1} $(K)^{-4}$.

Note: For low temperature difference, Newton's law of cooling is just an approximation of Stefan Boltzmann law.

10.9 NEWTON'S LAW OF COOLING

Newton's law of cooling describes the rate at which an exposed body changes temperature through radiation which is approximately proportional to the difference between the object's temperature and its surroundings, provided the difference is small.

Definition: According to Newton's law of cooling, the rate of loss of heat from a body is directly proportional to the difference in the temperature of the body and its surroundings.

Newton's law of cooling is given by, $dT/dt = k(T_t - T_s)$

Where,

- T_t = temperature of the body at time t and
- T_s = temperature of the surrounding,
- k = Positive constant that depends on the area and nature of the surface of the body under consideration.

Greater the difference in temperature between the system and surrounding, more rapidly the heat is transferred i.e. more rapidly the body temperature of body changes. Newton's law of cooling formula is expressed by,

$T(t) = T_s + (T_o - T_s) e^{-kt}$

Where,

- t = time,
- T(t) = temperature of the given body at time t,
- T_s = surrounding temperature,
- T_o = initial temperature of the body,
- k = constant.

Limitations of Newton's Law of Cooling

- The difference in temperature between the body and surroundings must be small

- The loss of heat from the body should be by radiation only

- The major limitation of Newton's law of cooling is that the temperature of surroundings must remain constant during the cooling of the body

10.10 PLANK'S LAW FOR RADIATIONS

Planck found an empirical formula to explain the experimentally observed distribution of energy in the spectrum of a black-body. The formula may be deduced using the following postulates:

1. A black body radiation chamber if filed up not only with radiation, but also with simple harmonic oscillators or resonators of the molecular dimensions; which cannot have any value of energy; but only energies given by

$$E = n\,hv$$

where v is the frequency of the oscillator, h is the Planck's constant and n is a number that can take only integral values, i.e.

$$n = 0, 1, 2, 3 \dots$$

2. The oscillators cannot radiate or absorb energy continuously; but an oscillator of frequency v can only radiate or absorb energy in units or quanta of magnitude hv. This assumption is the most revolutionary in character. In simple words this states that the exchange of energy between radiation and matter cannot take place continuously; but is limited to discrete set of values 0, hv, 2hv ……. nhv, i.e., in multiples of some small unit, called the **quantum**.

The average energy of a Planck's oscillator is given by

$$\bar{\varepsilon} = \frac{hv}{e^{hv/kT}-1} \qquad \dots\dots$$

(1)

The number of resonators per unit volume in the frequency range v and v + dv is given by

$$N = \frac{8\pi \, v^2}{c^3} \, dv \qquad\qquad \text{........ (2)}$$

The **energy density** belonging to range dv can be obtained by multiplying the average energy of Planck's oscillator by the number of resonators per unit volume, in the frequency range v and v + dv, i.e.

$$E_v \, dv = \frac{8\pi \, v^2}{c^3} \cdot \frac{hv}{e^{hv/kT} - 1} \, dv$$

$$= \frac{8\pi \, hv^2}{c^3} \cdot \frac{hv}{e^{hv/kT} - 1} \, dv$$

where E_v dv is the energy density, i.e., total energy per unit volume belonging to the range dv.

The above law was found by Planck empirically and after his name is called **Planck's radiation law**.

The energy density E_λ dλ belonging to range dλ can be obtained by using the relation $v = \frac{c}{\lambda}$ and hence $|dv| = \left| -\frac{c}{\lambda^2} d\lambda \right|$, i.e.

$$E_\lambda \, d\lambda = \frac{8\pi h}{c^3} \cdot \left(\frac{c}{\lambda} \right)^3 \cdot \left(\frac{1}{e^{hc/\lambda kT} - 1} \right) \left(-\frac{c}{\lambda^2} d\lambda \right)$$

$$= \frac{8\pi \, hc}{\lambda^5} \cdot \frac{1}{e^{ch/\lambda kT} - 1} \, d\lambda \, .$$

which gives the energy density for wavelength range λ and λ + dλ in the spectrum of a black body.

10.11 EXPERIMENTAL VERIFICATION OF PLANCK'S RADIATION LAW

The Planck's radiation law has been verified by numerous experiments. Here we shall give the experimental verification due to Lummer and Pringsheim. They used a special radiating chamber in which the conditions of "black-body radiation" of "full radiation" were practically fulfilled.

The spectrum of the black-body radiation was produced by refraction through a flour-spar prism, flour-spar being very transparent to the infrared radiations. It was necessary to apply corrections in order to covert the prismatic spectrum to the normal one. This was done by means of the known dispersion curve of flour-spar.

A concave mirror was used to obtain an image of the slit. This image was focused on a Lummer Kurlbaum linear spectrum bolometer which was used to measure the radiant energy or distribution of energy. This bolometer was enclosed in an air-tight case in order to diminish the absorption effects due to water vapour and carbon-dioxide. The distribution of energy in the spectrum for various temperatures between 621 K and 1646 K was obtained and the curves were plotted. It was found that the distribution of energy in

the spectrum of a black-body, as found by Planck's radiation law, was in perfect agreement with the experiments.
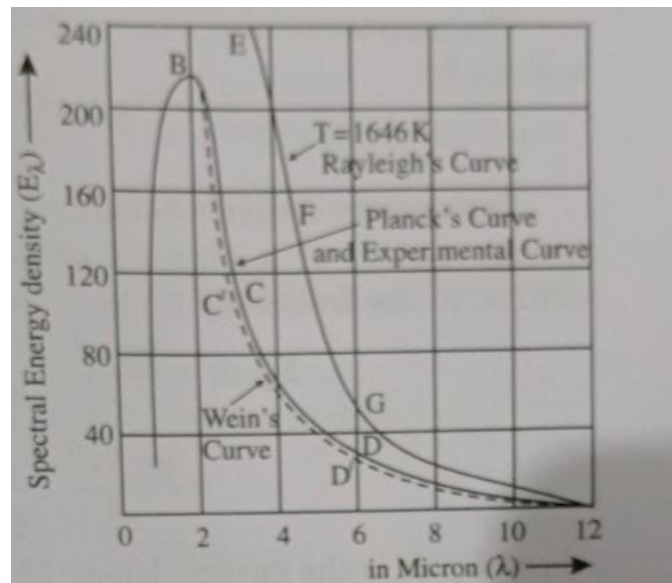

Figure :2

Fig. 2 represents the distribution of energy in the spectrum of black-body at 1646 K.

The ordinate represents the energy density per unit range of wavelength, while the abscissa represents the wavelength. In fig. 2, the curve ABCD is due to experiments and Planck's radiation formula, curve ABC'D; is due to Wein's radiation formula and the curve EFG is due to Rayleigh's radiation formula.

It is clear from the figure that the Planck's radiation formula is an perfect agreement with the experiments. The curve obtained by **Wein's law** agree with experimental curve only **at law wavelengths**

while the curve obtained by **Rayleigh-Jean's law** agrees with experimental curve only at large wavelengths.

10.12 WIEN'S DISPLACEMENT LAW

It states that the product of the wavelength corresponding to maximum energy λ_m and the absolute temperature T is constant i.e.

$$\lambda_m T = \text{constant.}$$

This constant is called **Wien's displacement constant** and has a value 0.2896 cm K = 0.2896×10^{-2} mK.

According to this law λ_m decreases with increase in temperature as we have already shown in fig. 9.

Deduction : Let us imagine a spherical enclosure of perfectly reflecting walls and capable of expanding. Let it be filled with diffuse radiations of energy density u at a uniform temperature T.

If V is the volume of the enclosure, then total internal energy of radiations is given by

$$U = rV$$

Let us now suppose that the walls of the enclosure move outward slowly with uniform velocity so that the radiation inside it expands adiabatically. If dV is the change in volume of the enclosure, the

work done by the pressure of radiation on the walls of the enclosure

= pdV which is drawn from internal energy of radiation. If dU is the

decrease in internal energy, then from first law of thermodynamics,

we have

$dU + pdV = dQ = 0$

.... (1)

Since dQ = 0 as the change is

adiabatic

We know $\qquad p = \dfrac{1}{3}u.$

Substituting values of p and U in (1), we get

$$d(uV) + \frac{1}{3}u\,dV = 0$$

or $\qquad udV + Vdu + \dfrac{1}{3}u\,dV = 0$

or $\qquad \dfrac{4}{3}u\,dV = -V\,du$

or $\qquad \dfrac{4}{3}\cdot\dfrac{dV}{V} = -\dfrac{du}{u}.$

.... (2)

Integrating we get

$$\frac{4}{3}\log V = -\log u + constant$$

or $\qquad \log V^{4/3} + \log u = constant.$

or $\qquad \log V^{4/3}\,u = constant.$

But $\qquad$ u = AT^4, where A is constant.

☐ $\qquad$ V$^{4/3}$ T^4 = constant.

or $\qquad$ V$^{1/3}$ T = constant.

…………….. (3)

Let us now find a change in wavelength suffered by a ray on reflection at the moving walls of the enclosure due to Doppler's effect. Let AO be a ray of wavelength λ incident at an angle θ on the wall as shown in fig. 10. Let a particular wave crest will be reflected along OC. If OC = λ then a the reflected wave crest reaches C, the next will reach at O in time T, T being time period of wave motion. During this second wave crest will be OBD. Then increase in wavelength due to one reflection is

$$= OB + BN = O'B + BN = O'N = OO' \cos \theta$$

$$= 2OM \cos \theta . = 2vT \cos \theta$$

$$= \frac{2v\lambda}{c} \cos \theta$$

………….. (4)

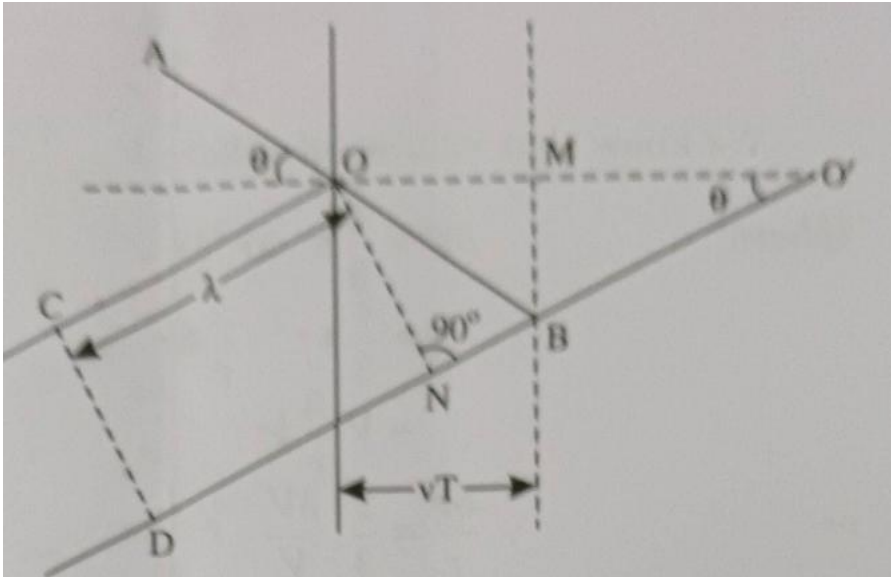Since $\qquad$ $T = \frac{\lambda}{c}$, c being velocity of radiation

Fig. 3

In order to calculate the number of reflections per second, let us consider a ray striking the wall of the sphere at M and reflected along MN making an angle θ with the normal.
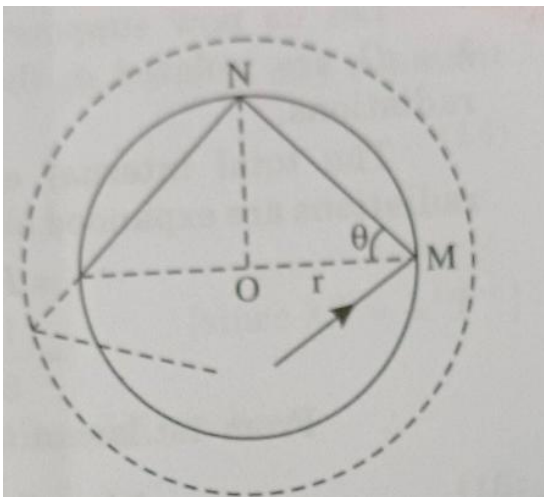

Figure :4

This distance traversed by the beam before it suffers the next reflection = MN = 2r cos θ.

Therefore, the time between two successive reflections

$$= \frac{2r \cos \theta}{c}.$$

☐   The number of reflections per sec.

$$= \frac{c}{2r \cos \theta}.$$

If δr is the increase in radius in time δt, then the number

of reflections in time δt.

$$= \frac{c}{2r \cos \theta} \delta t$$

$$= \frac{c}{2r \cos \theta} . \frac{\delta r}{v}.$$

.... (5)

The change in wavelength in time δt

$\delta \lambda =$ change in wavelength in one reflection $\times$ number of

reflections in time δt using (4) and (5)

☐ $$\delta \lambda = \frac{2v\lambda}{c} \cos \theta \times \frac{c}{2r \cos \theta} . \frac{\delta r}{v}$$

$$= \lambda \frac{\delta r}{r}$$

☐ $$\frac{\delta \lambda}{\lambda} = \frac{\delta r}{r}.$$

.... (6)

We know that volume of sphere $V = \frac{4}{3} \pi r^3$, so that the change

in volume of sphere,

$$\delta V = \frac{4}{3} \pi . 3r^2 \delta r$$

$$= \frac{4}{3}\pi r^2 \cdot \frac{3}{r}\delta r$$

$$= V\frac{3}{r}\delta r$$

or
$$\frac{\delta r}{r} = \frac{1}{3} \cdot \frac{\delta V}{V}$$

……………… (7)

Substituting this in eqn. (6), we get

$$\frac{\delta \lambda}{\lambda} = \frac{1}{3} \cdot \frac{\delta V}{V}$$

………………. (8)

Integrating, we get

$$log\,\lambda = \frac{1}{3}log\,V + log\,K, \quad where\,log\,K\,is\,a\,constant.$$

It gives $\quad \lambda = KV^{1/3}$

or
$$V^{1/3} = \frac{\lambda}{K}.$$

………………… (9)

Substituting this in eqn. (3), we get

$$\frac{\lambda}{K} \cdot T = constant.$$

or $\quad\quad \lambda T = constant.$

………………. (10)

It is the usual form of Wien's displacement law. According to this, if the radiation of a particular wavelength at a certain temperature is

adiabatically altered to another wavelength, the temperature changes inversely.

THE RAYLEIGH-JEANS LAW OF SPECTRAL DISTRIBUTION OF ENERGY

The number of modes of vibration per unit volume in the frequency range v and $v + dv$ is

$$N_v\, dv = \frac{8\pi\, v^2}{c^3}\, dv$$

……………

(1)

Rayleigh and Jeans assumed that the law of equipartition of energy is applicable to radiation also i.e., they considered average energy of an oscillator, (i.e., per mode of vibration) as

$$\bar{\varepsilon} = kT \quad (classical\ result)$$

The energy density (i.e., energy per unit volume) within frequency v and v + dv is given by

u_v dv = Number of modes of vibration per unit volume in the frequency range v and v + dv × Average energy per mode of vibration

$$N_v\, dv = \frac{8\pi\, v^2\, dv}{c^3}\, . kT.$$

……………… (2)

This is **Rayleigh-Jean's law in terms of frequency**.

In terms of wavelength

$$u_\lambda \, d\lambda = \frac{8\pi}{c^3} \cdot \left(\frac{c}{\lambda}\right)^2 \left(\frac{-c}{\lambda^2} d\lambda\right) . kT$$

$$= \frac{8\pi \, kT}{\lambda^4} . d\lambda$$

…………….. (3)

This is **Rayeigh-Jean's law in terms of wavelength**. This law explains the experimental measurement of the energy distribution at long wavelengths fairly well; but it fails for short wavelengths.

WEIN'S LAW AND RAYLEIGH-JEAN'S LAW IN RELATION TO PLANCK'S LAW

Planck's formula is given by

$$E_\lambda \, d\lambda = \frac{8\pi \, hc}{\lambda^5} \cdot \frac{1}{e^{hc/\lambda kT} - 1} \, d\lambda$$

For shorter wavelength $e^{hc/\lambda kT}$ becomes large compared to unity and hence the Planck's law reduces to

$$E_\lambda \, d\lambda = \frac{8\pi \, hc}{\lambda^5} \cdot \frac{1}{e^{hc/\lambda kT} - 1} \, d\lambda = \frac{8\pi \, hc}{\lambda^5} \cdot e^{hc/\lambda kT} - 1 \, d\lambda$$

Which is **Wein's law**.

For longer wavelengths $e^{hc/\lambda kT}$ may be approximated to $\left(1 + \frac{hc}{\lambda kT}\right)$ and hence Planck's law reduces to

$$E_\lambda \, d\lambda = \frac{8\pi \, hc}{\lambda^5} \cdot \frac{1}{1 + (hc/\lambda kT) - 1} \, d\lambda$$

$$= \frac{8\pi \, hc}{\lambda^5} \cdot \frac{1}{hc/\lambda kT} \, d\lambda$$

$$= \frac{8\pi \, hc}{\lambda^5} \cdot \frac{\lambda kT}{hc} \, d\lambda = \frac{8\pi \, kT}{\lambda^4} \, d\lambda$$

which is **Rayleigh Jean's law**.

Thus, we see that Wein's law holds good for shorter wavelengths while the Rayleigh Jein's law for longer wavelengths.

10.13 SPECTRAL DISTRIBUTION OF BLACK-BODY RADIATION

Lummer and Pringsheim investigated the distribution of energy among the radiations emitted by a black-body at different temperatures.

The experimental arrangement of Lummer and Pringsheim is shown in fig. 8. Their black-body was an electrically heated chamber with a small aperture whose temperature was measured by a thermocouple.
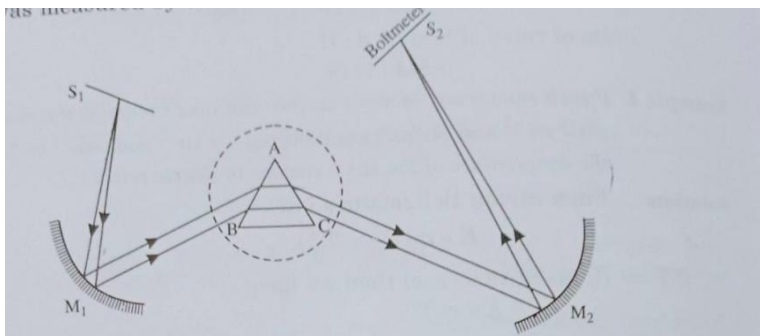
Figure : 5

The radiations from the black body pass through the slit S_1 and fall on the reflector M_1. After being reflected, the parallel beams of radiation fall on a rock-salt or fluorspar prism ABC placed on the turn table of the spectrometer. The emergent light is focused by the reflector (concave mirror) M_2 on a line bolometer placed behind the slit S_2. The bolometer is connected to a sensitive galvanometer. The turn table is rotated slowly so that different parts of the radiation spectrum successively fall on the bolometer and the corresponding deflections in galvanometer connected in the bolometer circuit are read. The intensity of each line is proportional to the deflection in the galvanometer. Then a curve (Fig. 9) is drawn between intensity and the wavelength.
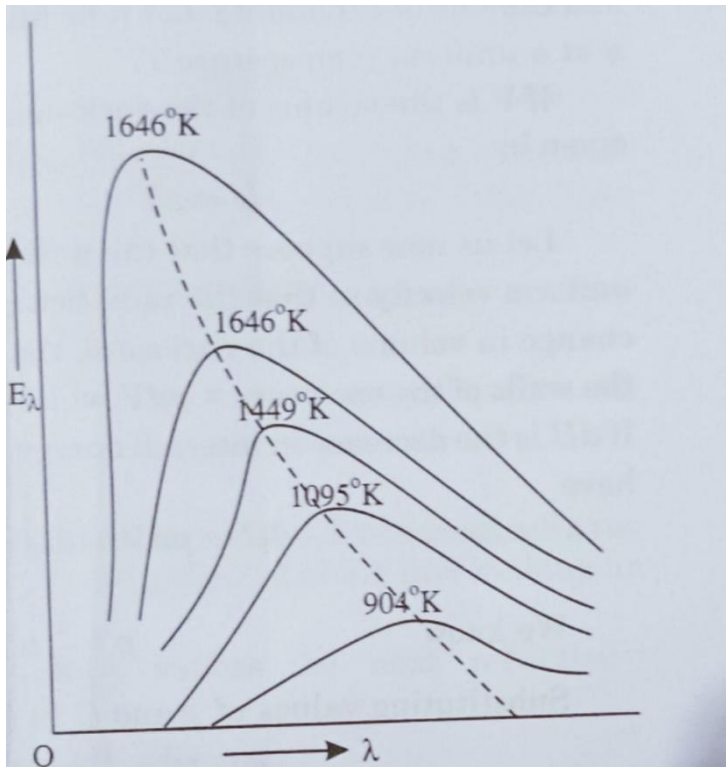
Figure : 6

Then the body is heated to different temperatures and the heated to drawn for various temperatures.

Result: The curves show:

(i)   The energy is not uniformly distributed in the radiation spectrum of a black-body.

(ii) At a given temperature, the intensity of radiation increases with increase of wavelength and becomes maximum at a particular wavelength. By further increasing the wavelength, intensity of heat radiations decreases.

(iii) An increase in temperature causes a decrease in λ_m where λ_m is the wavelength for which the energy emitted is maximum. Thus, λ_m is inversely proportional to absolute temperature i.e.,

$$\lambda_m \propto \frac{1}{T}$$

or $\qquad\qquad\qquad\qquad\qquad \lambda_m T = constant.$

This is known as **Wien's displacement law**.

(iv) An increase in temperature causes an increase in energy emission for all wavelengths.

(v) The area under each curve represents the total energy emitted by the body at a particular temperature for the range of the wavelengths considered. This area increases with increase in temperature. It is found that area is directly proportional to the fourth power of absolute temperature i.e. $E \propto T^4$ which is **Stefan's law**.

10.14 SUMMARY

Radiant heat is present in some or other form in our daily lives. Thermal radiations are referred to as radiant heat. Thermal radiation is generated by the emission of electromagnetic waves. These waves carry away the energy from the emitting body. Radiation takes place through a vacuum or

transparent medium which can be either solid or liquid. Thermal radiation is the result of the random motion of molecules in matter. The movement of charged electrons and protons is responsible for the emission of electromagnetic radiation. Let us know more about radiation heat transfer.

Radiation heat transfer is measured by a device known as thermocouple. A thermocouple is used for measuring the temperature. In this device sometimes, error takes place while measuring the temperature through radiation heat transfer.

Radiation Equation

As temperature rises, the wavelength in the spectra of the radiation emitted decreases and shorter wavelengths radiations are emitted. ***Thermal radiation can be calculated by Stefan-Boltzmann law:***

$$P = e \cdot \sigma \cdot A \cdot (T_r - T_c)^4$$

Where,

- P is the net power of radiation
- A is the area of radiation
- T_r is the radiator temperature
- T_c is the surrounding temperature
- e is emissivity and σ is Stefan's constant ($\sigma = 5.67 \times 10^{-8} Wm^{-2}K^{-4}$

Radiation Example

Following are the examples of radiation:

- Microwave radiation emitted in the oven is an example of radiation.

- UV rays coming from the sun is an example of radiation.

- The release of alpha particles during the decaying of Uranium-238 into Thorium-234 is an example of radiation.

Unit of Heat Transfer

SI system	Joule
MKS system	cal
Rate of transfer of heat	KW

10.15 TERMINAL QUESTIONS

1. Explain Kirchhoff's law for radiation.

2 Explain Stefen Boltzman Law.

3.Discuss Wien's displacement Law.

4.Define radiant energy.

10.16 ANSWER AND SOLUTION OF TERMINAL QUESTION

1.Section 10.7

2. Section 10.8

3. Section 10.12

4.Section 10.3

10.17 SUGGESTED READINGS

1.   Thermal Physics: with Kinetic Theory, Thermodynamics: SC

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2.   Thermal Physics: R. Murugeshan, Er. Kiruthiga Siva Prasath.

3.   Thermal Physics: C.B.P. Finn.

4.   Heat Thermodynamics and Statistical Physics: Brij lal, Dr. N.

Subrahmanyam, P.S. Hemne.