Bachelor of Science
(B.Sc.- PCM)

Thermodynamics and Statistical Physics
(DBSPCO302T24)

Self-Learning Material
(SEM-III)

Jaipur National University
Centre for Distance and Online Education

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COURSE INTRODUCTION

The objectives of this course, thermodynamics and statistical physics in undergraduate programs are tailored to provide students with a solid foundation in these fundamental areas of physics. These objectives aim to develop both theoretical understanding and practical skills that are essential for further study and professional work in physics, engineering, and related fields. The course syllabus is divided in to 13 different units.

Introduce the basic concepts of thermodynamics, including systems, states, processes, and the zeroth, first, second, and third laws of thermodynamics.Familiarize students with the properties of substances, such as temperature, pressure, volume, entropy, enthalpy, and Gibbs free energy, and how to measure and calculate these properties.Study phase transitions and phase diagrams, including the critical point and triple point, and understand the behavior of substances during phase changes.Apply thermodynamic principles to real-world systems such as engines, refrigerators, and heat pumps, and understand the efficiency and limitations of these systems.Introduce the concepts of microstates and macrostates, and explain how macroscopic properties emerge from microscopic behavior.Teach the principles of probability and statistics as they apply to physical systems, including the use of probability distributions. Explain the different types of statistical ensembles (microcanonical, canonical, and grand canonical) and their use in describing systems in thermodynamic equilibrium. We hope you enjoy the course.

COURSE OUTCOMES

After the completion of the course, the students will be able to:

1. Understand the role of internal energy, enthalpy, temperature, pressure, andspecific volume thermodynamic properties.
2. Elucidate the basics of Carnot cycle, statistics and distributions.
3. Explain the fundamental differences between classical and quantum statistics andlearn about quantum statistical distribution laws.
4. Analyze important examples of ideal Bose systems and Fermi systems.
5. Compare the Thermodynamic functions of a completely and strongly DegenerateFermi Gas, Fermi Energy.
6. Draw the Clausius Clapeyron Equation and Herrin Festa equations.

ACKNOWLEDGEMENTS

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Chapter 1

Introduction of Thermodynamics

1.1. Introduction

At the outset it is imperative to know about the course title- The Thermodynamics. A branch of physics known as thermodynamics studies a system's work and energy. It all began in the 1800s when scientists learned how to build and run steam engines.

The atomic composition of matter, including its structure and other details, is not taken into consideration by thermodynamics. However, it only addresses the system's large-scale response, which is observable and quantifiable by experiment. The kinetic theory of gases explains interactions among molecules at small scales. The two methods work well together; some ideas are better understood in terms of thermodynamics, whereas kinetic theory gives more detail for certain ideas.

Thermodynamics is a perfect mathematical science describing the inter- relationship between heat and any other form of energy viz., electrical, mechanical, chemical, magnetic etc. The basic concept is the transformation of heat into mechanical work through any bulk material. Thermodynamics has innumerable applications in physics, chemistry & engineering sciences. While studying thermodynamics, you will learn about some basic terms like temperature, thermodynamic system, internal energy, thermal equilibrium and about certain thermodynamic processes such as isothermal and adiabatic processes etc. You will also know here about the concept of a system and its surroundings. In our day to day life we often come across the examples of isothermal and adiabatic processes. The melting of ice at zero degree centigrade temperature and that of sudden burst of a tyre are the practical examples of isothermal and adiabatic processes respectively. The understanding of the different thermodynamic process will help you to know the physics behind many such practical examples. There are three principal laws of thermodynamics besides the one called the zeroth law. The explanation of thermodynamic properties that helps in understanding and forecasting a physical system’s behaviour follows from each law.

1.2. System and Surroundings

A defined quantity of substance (like solid, liquid, or gas) surrounded by a closed surface is commonly referred to as a system. A system's most basic form is a gas within a cylindrical container with a moving piston. that can be heated by a burner. Here the system is the gas and the surroundings are piston and burner. When a system is completely uniform throughout such as a gas, mixture of gases, pure solid, a liquid or a solution you will say it is homogeneous system, but when it consists of two or more phases which are separated from one another by definite boundary surface it is said to be heterogeneous system e.g., a liquid and its vapor, two immiscible or partially miscible liquids. Anything which is outside this system and can exchange energy with it and has a direct bearing on its behaviors called its surrounding. The complete system and its surrounding together is called universe.

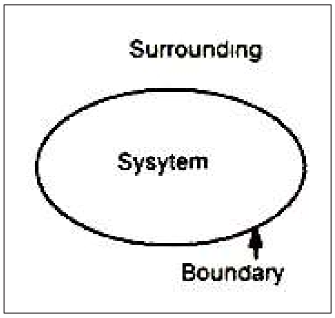


Figure 1.1

Further you can distinguish the system in three classes as discussed in the next article. The surface that separates the system from the surrounding area is called a boundary or wall. Interactions among the system and the surroundings may or may not be allowed by this wall or boundary.

1.3. Thermodynamic System

Four observable properties determine a system's thermodynamic state. Which are pressure (P), volume (V), and temperature (T) are these features. The systems can be classified into different groups according to the nature of their boundaries:

- **Open System:** An open system is one that is able to exchange matter and energy with its surroundings. An example of such a system is an air compressor, wherein air enters the system at low pressure and exits at high pressure, exchanging energy as well as matter with the surroundings.
- **Close system:** A closed system is one that can only exchange energy, not matter, with its surroundings. For example, heated gas inside a cylinder causes the piston to expand and move outward. The system's boundaries changes, but the matter (gas) within it doesn't.

- **Isolated system:** It is a thermally isolated system, so no exchange of heat or works permits with the surrounding. e.g., a beverages or any other liquid contained in a thermos flask.

1.4. Macroscopic and Microscopic System

The behavior of the system can be described in two different ways namely macroscopic and microscopic. Macroscopic properties can usually be directly experienced by our senses. These properties describe the gross characteristics of the system and can directly be measured in the laboratory. Macroscopic properties are not concerned with the structure of the system (chemical composition). Pressure, temperature, volume, internal energy, entropy etc. are few examples of these properties. A macroscopic system is one whose state can completely be described in terms of its macroscopic properties or coordinates.

Microscopic properties cannot be directly experienced by our sense of perception. These properties describe the internal structure (atoms & molecules) of the system and cannot be measured directly in the laboratory.

In fact the macroscopic & microscopic properties are simply the different ways of describing the same system so they are related to each other e.g., the pressure of a gas is related to the average rate of change of momentum due to all the molecular collisions taking place on a unit area. Higher is the rate of change of momentum, higher will be the pressure. Here the pressure is a macroscopic property, whereas the rate of change of momentum due to molecular collisions is a microscopic property. Similarly the temperature of a gas (macroscopic property) is related to the average kinetic energy of translational motion of its molecules which is microscopic.

1.5. Concept of Temperature and Heat

A body's temperature is an indicator of how hot or cold it is. In fact we distinguish hot bodies or cold bodies by our sense of touch. That is by touching we can roughly distinguish between a hot and a cold body.

Let us consider two bodies A and B kept in contact such that A is at higher temperature. After some time they both acquire the same temperature which is approximately in between the two temperatures. It means there is something which has been transferred from A to B. This something is called Heat. Thus heat is that physical entity which is transferred from one body to other because of a temperature difference between them. In reality, because of the temperature difference between two bodies, heat is a kind of energy that is exchanged between them.

We can explain it with a simple example of water level. If two vessels are filled with water up to the levels of different height and are inter connected, the water will always flow from the higher level to the lower level side. In the same way, when two bodies come into touch, heat flows from hot to cold.

There is a distinction between temperature of a body and the heat that it contains. In fact the heat that a body contains depends upon its mass as well as upon its temperature. For example the sparks from a blacksmith's hammer are white hot (at very high temperature) but they do not burn the hand since their mass is very small, therefore contain little heat. On the other hand a jug of hot water (at a much lower temperature than the spark) causes a severe burn because it contains more heat.

Hence, the flow of heat depends only on the temperature difference but the quantity of heat flown does not depend only on temperature difference but also depends on mass and specific heat of the body. For example, if a hot body and a cold body are put in mutual contact, heat flows from hot to a cold body until they attain a common temperature. It means the temperature of a hot body falls and that of cold body rises. But these temperature- changes are not necessarily equal because the masses (and also the specific heats) of the two bodies may be different.

1.6. Concept of Thermodynamic Equilibrium

In general, a system is considered to be in equilibrium when its attributes or state variables do not vary considerably with time over the interval of interest, that is, observation time. Thermal equilibrium is reached, if any two of the three variables—P, V, and T—remain steady over time in a homogeneous system as long as the external conditions don't change.
Different thermodynamical equilibrium take place, which are:

Mechanical Equilibrium: A system must be in mechanical equilibrium if there is no macroscopic movement within it (i.e., no imbalance pressures at work), nor should there be any change between it and its surroundings or with another system.

Thermal Equilibrium: This occurs when there's no exchange of heat among two systems that are in thermal contact with one another or with their surroundings. This is attained when the two systems or one system and its surrounding area are at the same temperature.

Chemical Equilibrium : A system must not undergo any chemical changes or allow any chemical constituents transfer from one area of the system to others. In other words, both the system's internal structure and chemical composition must remain unchanged for the system to be in a state of chemical equilibrium.

1.7. Zeroth Law of Thermodynamics

Let us analyse a situation in which two systems are separated by a diathermic (good conductor of heat) and adiabatic (bad conductor of heat) walls. Now Let us consider the systems A, B, C in which A and B are isolated from each other through an adiabatic wall and both are in contact with C through diathermic wall as is shown in fig.1.3. As time passes A and B will separately attain equilibrium with C. Now if the diathermic and adiabatic walls are interchanged, no further change in states of any of the three systems will occur.

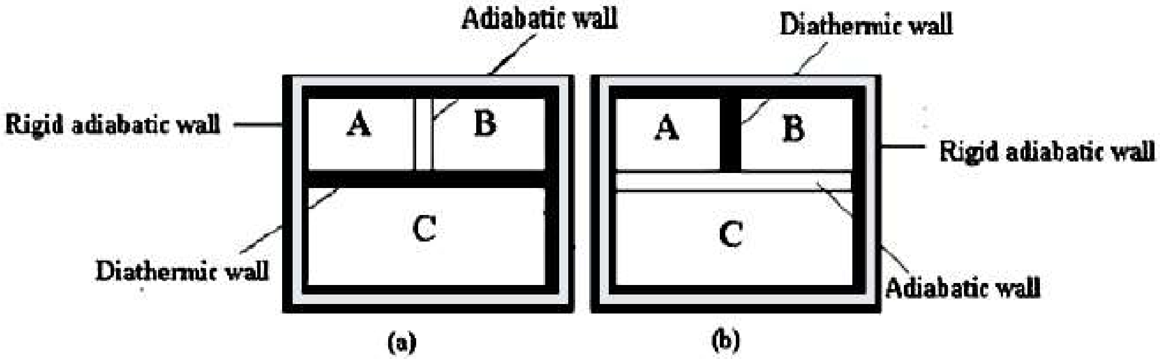


Figure 1.2

This indicates that system A and B themselves are in thermal equilibrium before the walls are interchanged. This experimental observation was first developed by R.H Fowler in 1931 and was named as Zeroth law of thermodynamics which can be stated as follows:

"If two systems are separately in thermal equilibrium with a third one, then they themselves are in thermal equilibrium with each other."

This law in a more general form, can be expressed as:

"If a system A is in thermal equilibrium with each of the several other systems B,C,D,E etc., separately then any pair among B,C,D,E etc., will be in mutual thermal equilibrium i.e., D and C or B and D or B and C are always in equilibrium.”

1.8. Concept of Temperature

Zeroth law permits us to assert that *all systems* in thermal equilibrium with each other have a common property. We call this common property as *temperature*. A feature of a system that determines the degree to which it is in a thermal equilibrium with other systems is its temperature. Equal temperatures imply thermal equilibrium; unequal temperatures imply its absence. Thus the zeroth law gives the concept of temperature.

Let us analyse the concept of temperature in mathematical terms. Let two systems A and B with coordinates (x_A, y_A) and (x_B, y_B) respectively, be in equilibrium as shown in Fig.1.3 (b). Now if we remove A from contact of B and change its state so that the new variables become (x_A', y_A') and again make contact with B to find that A is still in equilibrium with B, zeroth law tells us that the two states of A viz., (x_A, y_A) and (x_A', y_A') are in equilibrium.

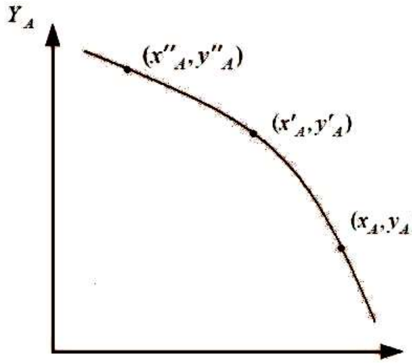


Fig 1.3

In this way we can find a number of states of A as (x_A, y_A), (x_A', y_A'), (x_A'', y_A'') etc., all of which are in thermal equilibrium with the same state (x_B, y_B) of B so that all these states of A are in thermal equilibrium with each other and thus, have the same temperature. Now if all these states of A are plotted on a x – y graph they will form a curve as shown in Fig. 1.4, the locus of all those points which represent states at same temperature is called an *isotherm*. All the points on an isotherm represent states in equilibrium with each other. A similar isotherm of *B*, all points of which are in thermal equilibrium with any of the states of isotherm A will be called a corresponding isotherm. A process in which all thermodynamic coordinates but the temperature are changed is called an isothermal process i.e., in an isothermal process the pressure or volume of the system may change but the temperature of the system does not change.

Let us now give the mathematical presentation of the concept of temperature. Suppose two systems A and B are in thermal equilibrium. At equilibrium both the systems assume fixed coordinates. Any change in the state of one system will change the state of the second in a restricted way. Hence equations of constraint for the two systems A and B in thermal equilibrium is based on the fact that coordinates of the one depend upon those of the other and thus is written in a combined way as:

$$f_{AB}\,(x_{A}, y_{A}, x_{B}, y_{B}) = 0 \qquad (1)$$

Similarly, when A is in thermal equilibrium with B and C separately, we may write

$$f_{AB}\,(x_{A}, y_{A}, x_{B}, y_{B}) = 0 \text{ and} \qquad (2)$$

$$f_{AC}\,(x_{A}, y_{A}, x_{C}, y_{C}) = 0 \qquad (3)$$

Functions f_{AB} and f_{AC} may be quite different from each other. However, from both these equations the common value of x_A can be obtained as.

$$x_{A} = f''_{AB}\,(y_{A}, x_{B}, y_{B}) \quad \text{and } x_{A} = f''_{AC}\,(y_{A}, x_{C}, y_{C})$$

which give

$$f''_{AB}\,(y_{A}, x_{A}, y_{A}) - f'_{AC}\,(y_{A}, x_{C}, y_{C}) = 0 \qquad (4)$$

But, from zeroth law, B and C should be in equilibrium. Thus we must have

$$f_{BC}\,(x_{B}, y_{B}, x_{C}, y_{C}) = 0 \qquad (5)$$

Equation (4) and (5) represent the same equilibrium conditions and thus they must agree with each other. Comparing with eq. (5) we must therefore, drop the variable y_A from eq. (4). (In a physical example the co-ordinate y_A will cancel out from two sides of equation). Thus eq. (4) takes the form

$$f''_{AB}\,(x_{B}, y_{B}) - f'_{AC}\,(x_{C}, y_{C}) = 0 \text{ or}$$

$$f''_{B}\,(x_{B}, y_{B}) = f''_{C}\,(x_{C}, y_{C}) = T \text{ (say)} \qquad (6)$$

subscripts A are also dropped as f'' are functions of B and C only. Eqs. (5) and (6) show that if B and C are in equilibrium, there exists a function f'' of the variables x and y for each one, having a common value T and we may write that for any system A in equilibrium with a reference system

$$f'(x, y) = T \qquad (7)$$

This common value T of all these functions is the empirical temperature. The next step is to define the difference of temperatures. Suppose that a contact between systems A and B produces a net energy transfer from A to B. In that instance, it will be claimed that A's starting state temperature was higher than B's. Thus, the order of temperature may be given by this definition. However, it does not give a scale of temperature which may enable us to define some unit for temperature by which different temperatures may be measured. Developing a proper scale of the temperature measurements is out of scope of the present unit. For further description on temperature measurements you may consult the book mentioned at serial number three in the list of suggested reading given in the last section of the unit.

Self-Assessment

1. Explain the term ‘heat and temperature'.
2. Distinguish between isothermal and adiabatic process.
3. To represent isothermal and adiabatic process, draw P-V diagram.
4. “For a non-isolated system internal energy is zero” verify the statement.
5. The primary significance of the Zeroth Law of Thermodynamics?
   a) It defines the concept of temperature.
   b) It establishes the concept of entropy.
   c) It relates the work done by a system to the heat added to it.
   d) It introduces the concept of internal energy.
6. According to the Zeroth Law of Thermodynamics, which of the following is true?
   a) All systems in thermal equilibrium have the same internal energy.
   b) Thermal equilibrium is not transitive.
   c) Temperature is a transitive property.
   d) All systems in thermal equilibrium have the same pressure.
7. The Zeroth Law of Thermodynamics is essential for the construction of which of the following instruments?
   a) Barometer
   b) Thermometer
   c) Hygrometer
   d) Manometer
8. If system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, what can be said about systems A and C?
   a) A is not in equilibrium with C.
   b) A is in thermal equilibrium with C.
   c) A and C have the same internal energy.
   d) A and C have the same pressure.

9. Which of the following is an example of the Zeroth Law of Thermodynamics in action?

   a) Heating a pot of water on a stove until it boils.

   b) Mixing hot and cold water until a uniform temperature is achieved.

   c) Using a thermometer to measure the temperature of a substance.

   d) Compressing a gas in a piston.

10. What does the Zeroth Law of Thermodynamics imply about the nature of temperature?

    a) Total energy of the system is represented by temperature.

    b) Temperature is a property that can be transferred between systems.

    c) Temperature is a fundamental and measurable property that determines thermal equilibrium.

    d) Temperature is only relevant in systems with a net heat transfer.

Answers:

1. c) , a) ,c) ,b) ,b) ,c) ,c)

Chapter 2

First Law of Thermodynamics and its Application

2.1. Extensive and intensive Thermodynamic Variables

An intensive property is a bulk property, which means that it is a system's physical characteristic independent of the system's material's volume or the amount. Temperature, pressure, density, viscosity, hardness, refractive index, specific volume, emf, and so on are a few examples of intensive properties.

A physical quantity whose magnitude is cumulative through the system is called an extensive property. An additive property like this has a value that is proportionate to the system's size or mass content. Length, area, volume, mass, internal energy, entropy, electric charge, heat capacity, magnetization, and other properties are examples of extensive properties.

One such example of an intensive property is the ratio of two extensive properties of the same object or system. Density (M/V) or specific volume (V/M) is an example of an intensive variable. It is the ratio of an object's mass and volume, which are two extensive attributes.

2.2. Equation of State

It is an equation connect the physical variable to represent the state of the system. Stated differently, the established relationship among the properties or variables of thermodynamics is the equation of state. This equation explains a mathematical connection between two or more state functions of matter, such as its temperature, pressure, volume, and internal energy. With the above description of equation of state the Boyle's laws, Charles' law etc are all regarded as examples of equation of state. Some of the EOS are :

a. Ideal Gas Equation

For an ideal gas $PV = nRT$ (1)

where P,V and R are pressure, volume and universal gas constant ($R=8.314\ JK^{-1}mol^{-1}$), T defines the temperature in Kelvin, and n is the number of moles of the gas.

b. Vander-Waals Gas Equation

The EOS for real gases, can be expressed by van der Waals Equation which is

$$\left(P + \frac{a}{v}\right)(V - b) \ = RT$$

a and b are constants for a real gas.

There are many more equations of state that you may come across besides these two given above.

2.3. Thermodynamic Process

Any change in energy that takes place within a system—typically related to changes in pressure, volume, internal energy, temperature, or heat transfer—is said as a thermodynamic process.

In thermodynamics, there are several different kinds of processes which frequently occur (and in practical contexts). Each of them can be identified by a unique feature that allows to explain the energy and work changes related to the process. The descriptions of some of the important thermodynamic processes explained below.

- **Adiabatic process** Heat transport neither into nor out of the system occurs in this thermodynamic process. The quantity of heat does not alter for this process.i.e., during this process $\Delta Q = 0$
- **Isochoric process** In this thermodynamic process system's volume remains constant. This indicates that the no operation done on the system or by the system during this process. i.e., during this process $\Delta V = 0$
- **Isobaric process** In this process system's pressure remains constant. i.e., during this process $\Delta P = 0$
- **Isothermal process** In this process system's temperature remains constant. An excellent example would be if, during a process, there is a change in volume and pressure but no change in temperature or heat transfer. i.e., $\Delta T = 0$ during this procedure
- **Cyclic processes** These are a set of processes that bring the system to its initial state after certain heat-and-work exchange. For a cyclic process change in internal energy $\Delta U = 0$, and if this is put into the first law of thermodynamics which states $\Delta U = \Delta Q - \Delta W$, then for cyclic process $Q = W$. This suggests that the system's stored internal energy remains constant, but the net work done through this process must precisely

correspond to the total amount of energy transferred as heat.

- **Reversible process** Reversible processes are those whose direction can be changed with a very little adjustment to some of the system's properties.
- **Irreversible process** A process is considered to be irreversible, if even a minute alteration to any one of its features prohibits it from going in the opposite direction.
- **Quasi-static process** This procedure is designed to keep the system as close to an equilibrium condition as possible at all times or to be nearly static. Therefore, a series of states of equilibrium are closely represented by a quasi-static process. A quasi-static process is one that operates at an exceptionally sluggish speed.
- **Non-quasi-static process** The process is run in a way that ensures the system deviates from the state of equilibrium by only a certain amount at each instant. Fast operations tend to be non-quasistatic in nature.

2.4. Details of Quasi-static, Isothermal, Adiabatic Process

Quasi-static Process

The system may go through non-equilibrium stages as a result of a finite imbalanced force. A quasistatic process is one in which there is very little departure from thermodynamic equilibrium and every state that the system goes through can be viewed as a state of equilibrium. An ideal concept that is never strictly realized in reality is a quasistatic process. But in reality, a lot of processes resemble quasistatic processes with negligible error.

Isothermal Process

An isothermal process happens when a thermodynamic system goes through a process while keeping a constant temperature.

A completely conduction chamber is a requirement for an isothermal process, indicating that any heat generated or absorbed during the process must instantly exit the chamber or enter it from the outside. In this way the temperature will remain constant. But in practice we do not find a perfect conductor. Therefore, a perfect isothermal process cannot be obtained.

We can, however, obtain approximate isothermal process if the process is extremely slow. For example if a gas filled in a brass cylinder(good conductor of heat) is compressed very slowly with the help of a piston. The heat produced through compression has plenty of time to pass through the cylinder's walls and exit outside. As result, the temperature of the gas stays constant, indicating that it changes by zero throughout the process ($\Delta T = 0$). Similarly if the gas is slowly expanded it loses energy in doing work against the piston but an equal amount of heat comes in from outside. Again the temperature remains constant.

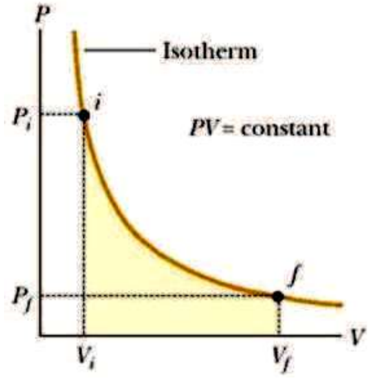


Fig 1.4

Graphically Isothermal Process can be represented by the curve as shown in Fig.1.5

An isothermal process is one in which the temperature stays constant during the process and the system is perfectly conducive to the surrounding. Consider a working substance with a volume given by point A in figure 1.4, at a specific temperature and pressure. The gas is now expanding and approaching point B on the curve in terms of volume.

The working substance has a drop in temperature and loses internal energy as a consequence of the decreased pressure. But the system is perfectly appropriate for the environment because it draws heat from it and keeps the temperature constant.

Thus, the temperature remains unchanged from i to *f*. An isothermal curve is denoted by curve i.‘. When the system goes from *f* to i, it transfers more heat to the surrounding air while maintaining the same temperature.

Since the working substance can absorb and emit heat, the substance's temperature remains constant during the isothermal process. An isothermal process equation is

$$PV = \text{constant} \qquad (1)$$

For an ideal gas undergoing isothermal process the change in internal is zero, i.e.,

$$(U_2 - U_1) = 0 \qquad (2)$$

Adiabatic Process

Adiabatic processes are those in which a thermodynamic system goes through an process without any heat being transferred into or out of the system.

An entirely insulated system is necessary for such a procedure to take place.

But such a system is not possible and hence a perfect adiabatic change is impossible.

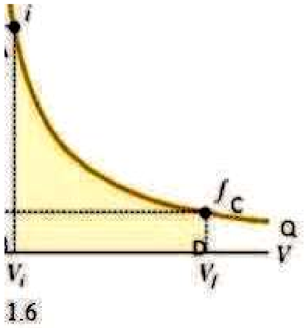


Fig. 1.5

We can however obtain approximate adiabatic process in a way that if the process is extremely rapid so that there is very little time for the heat to escape as it is suddenly compressed. The heat produced due to compression is added to its internal energy and its temperature rises. That is why the bicycle pump is heated when the air in it is suddenly compressed. Conversely if a gas is suddenly expanded the external work done by it is drawn from its internal energy and its temperature falls. A car's tire explodes due to the adiabatic, sudden expansion of air into the atmosphere, which cools the tire.

Other examples of adiabatic process are the expansion of steam in the cylinder of a steam engine and the compression of air in a diesel engine. The compression is so rapid that the behavior of the air is adiabatic.

Graphically adiabatic process can be represented as shown in Fig.1.5.

Provided that you know that an adiabatic procedure occurs when a system moves from an initial state (i) to a final state (‘f) without heat entering or leaving the system, So that

$\Delta Q = 0$

Thus when a system expands adiabatically then W (work done) is positive and its internal energy decreases eq.(1), W is in minus if system compresses adiabatically. Thus in case of compression, internal energy increases eq.(2).

$U_2 - U_1 = -W$ 1

$U_2 - U_1 = -(-W) = W$ 2

The equation of adiabatic process is

$P V^{\gamma} = \text{constant}$ 3

where $\gamma = C_p / C_v$.

2.5. First Law of Thermodynamics

First law of thermodynamics which places work and heat as the only way, the internal energy of a system of a body can be altered. It is a variant of the law of conservation of energy, which states that an isolated system's total energy never changes. However, a perfectly isolated system does not exist in practice. All systems exchange energy with their surroundings through one or other process no matter how well insulated they are. For example, hot tea or water in a thermos flask will only stay hot for a few hours and will reach to room temperature with the passage of time.

The conservation of energy concept used in a thermodynamic system is known as the first law of thermodynamics. Following is a description of this law:

If a quantity of heat dQ is supplied to a body, then in general it is used in three ways.

- Partially, it is used in raising the temperature of the body *i.e.*, increasing its internal kinetic energy dU_K.
- Partially, it is used in doing internal work against molecular attraction, *i.e.*, increasing the internal potential energy dUp.
- And rest is used in expanding the body against the external pressure *i.e.*, in doing external work dW.

So, above statement can be written as,

$$dQ = dU_K + dU_P + dW \qquad 1$$

This is the differential form of the first law of thermodynamics.

But,

$dU_K + dU_P = dU$ (where dU is the increase in total internal energy of the body)

$$\therefore dQ = dU + dW \text{ or} \qquad 2$$

$$\Delta Q = \Delta U + \Delta W \qquad 3$$

Therefore, amount of heat supplied to the system is divided in two parts which is external work done and increase in its internal energy. In equation (3) we should note that,

Equation (2) represents the differential form whereas eq. (3) stands for change in respective quantities.

1. ΔQ, ΔU and ΔW are to be measured in the same unit i.e., all the three either in joules or in calories.
2. If the heat is absorbed by the system ΔQ is positive and negative if rejected by the system. Similarly, ΔW is positive if work is done by the system and negative if work is done on the system.

a. Important features of first law of thermodynamics

The mathematical form of the first law contains three important features:

1. Heat is a form of energy.

2. Energy is conserved in a thermodynamic system process.
3. Every thermodynamic system in equilibrium state possesses internal energy and this internal energy is a function of its state i.e. temperature only.

2.6. Specific Capacity of Solids

A substance's specific heat capacity is the amount of heat it can hold per unit mass for each unit increase in temperature.

$$C = \frac{\Delta Q}{m\Delta T} \qquad (1)$$

The specific heat capacity C is given by the equation if a mass m of the substance absorbs an amount of heat ΔQ and its temperature rises by ΔT.

The same is true when temperature is lowered by taking heat from the substance. This definition applies to any form of the substance, solid, liquid or gas. In terms of mathematics, specific heat means the amount of heat required to increase the temperature by 1 degree for a substance of unit mass.. For pure water 1 calorie heat is required to raie its temperature by 1^oC

Thus, Sp. heat capacity of water = 1 cal/gm□C
= 1 kilo cal/kg□C
= 4.18×10^3 joule / kg□C (m 1 cal = 4.18 J)

This definition is sufficient for solids and liquids. Since gases can be compressed, a gas's specific heat can vary from zero to infinity. For example, if a gas is compressed, it increases temperature without absorbing any heat (Q = 0). Thus, specific heat

$$C = \frac{Q}{m\Delta T} = 0 \qquad (2)$$

On the contrary, gas is allowed to expand freely, without any increase in temperature (i. e. , when ΔT = 0) then

$$C = \frac{Q}{m\ X\ 0} = Infiniti \qquad (3)$$

Hence the specific heat of a gas is defined by considering any of the two (pressure or volume) as constant. Thus, a gas has two specific heats.

1. Cp, or specific heat at a constant pressure, is the quantity of heat required to increase a gas's temperature by one degree Celsius for every unit mass while retaining a constant pressure.

   It is expressed as $C_p = \left(\frac{\Delta Q}{\Delta T}\right)_p$ (4)

2. The specific heat at constant volume, or Cv, is the amount of heat needed to raise a gas's unit mass temperature by one degree Celsius while maintaining a constant volume.

   It is represented as: $C_V = \left(\frac{\Delta Q}{\Delta T}\right)_V$ (5)

   C_p is always greater than Cv. Let us see how?

Heat capacity of a gas is different under these two conditions. Suppose the heat is supplied to a gas and is allowed to expand at constant pressure. Then the supplied heat is used up in doing two things:

It does two different things: (i) it raises the gas's temperature, or internal energy; and (ii) it extends the gas against external pressure.

$\Delta Q = \Delta U + \Delta W$ or $\Delta Q = \Delta U + pdV$ (6)

However, whenever gas is heated at constant volume, all of the heat provided is utilized to raise its temperature without any work taking place ($\Delta W = P\Delta V = 0$). As a consequence, at constant pressure, more heat is required to increase the gas's temperature by 1°C than at constant volume. Hence Cp is always greater than the Cv or Cp > Cv.

2.7. Mayer's Law

Let us consider one gram-molecule (mole) of an ideal gas at pressure p, Kelvin temperature T and volume V. Let C_V and C_p be the molecular specific heats at constant volume and at constant pressure respectively.

Let the gas be heated at constant volume so that its temperature is raised by an infinitesimal amount dT. The heat supplied will be $C_v\, dT$. As the volume remains constant, the external work done is zero. The differential form of the first law of thermodynamics is written as equation (2.2)

$dQ = dU + dW,$

where dQ is the heat supplied, dU the increase in internal energy and dW the work done (all expressed in same units). Here $dQ = C_v\, dT$ and $dW = 0$, so that

$C_V\, dT = Du$ 2.9

Let the same gas be now heated at constant pressure p until the temperature is raised by the same amount of dT. The heat supplied will be $C_P\, dT$. Now, the gas would expand and external work against the pressure p would be done. If dV be the change in volume of the gas, the external work would be $p\, dV$. Thus, for this process, $dQ = C_p\, dT$ and $dW = p\, dV$. Hence, from the first law of thermodynamics, we have

$C_P\, dT = dU + p\, dV.$ 2.10

The temperature change is the same in both the cases. Since internal energy U depends only on the temperature for an ideal gas (Joule's law), the internal energy-change dU is same in both processes. Then, eliminating dU from eq. (2.9) and (2.10) we get

$(C_P - C_V)\, dT = p\, dV.$ 2.11

Now, ideal gas equation,

$pV = RT,$

where R is the universal gas constant.

Differentiating it, keeping p constant, we get

$p\, dV = R\, dT$

Putting this value of $p\, dV$ in eq. (2.11), we obtain $(C_P - C_V)\, dT = R\, dT$

or, $C_P - C_V = R$ 2.12

This relation was first obtained by Mayer in 1842 and is therefore called "Mayer's relation". It is perfectly true for an ideal gas and very nearly true for real gases at moderate pressures.

In Mayer's relation, R must be expressed in the same unit as C_P and C_V. Usually C_P and C_V are expressed in cal/(mole-K). Hence R must also be in calorie/(mole-K).

Since R = 8.31 joule/(mole-K) and 4.18 joule = 1 calorie, we have

$$R = \frac{8.31}{4.18} = 1.99\ calorie/(mole.K)$$

$C_P - C_V$ = 1.99 calorie/(mole-K) $\simeq$ 2 calorie/(mole-K).

2.8. Application of First or Ist Law of thermodynamics

In this section we will apply first law of thermodynamics to certain basic processes to get simple relations involving the internal energy, work done and heat.

a. Explanation of work in different Processes

i. Isochoric process

An isochoric process is one in which the system's volume stays unchanged. If volume remains constant then the work done □W (=pdV) by the system will be zero (dV = 0). But by the first law of thermodynamics we have,

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

Putting ΔW =0, we get,

$$\Delta U = \Delta Q$$

Hence, in an isochoric process, the heat taken or lost by the system is entirely used in increasing or decreasing the internal energy of the system.

ii. Isobaric process

The process, system's pressure remains constant known as isobaric process. The boiling of The term "isobaric process" refers to a systemic process where the system pressure is constant. Examples of isobaric processes are the boiling of water to steam and the freezing of water to ice.

Let *m* gm of water is converted into steam at constant pressure and temperature also. If V_l is the volume of the water in liquid state and V_v is the volume of water in vapour state, then work done by the system (in expanding from V_l to V_V against the constant pressure p) will be,

$$W = \int_{V_l}^{V_v} PdV$$

$$W = P\int_{V_l}^{V_v} dV$$

$$-P(V_l - V_l)$$

and heat absorbed by the mass *m* during the change of state is,

$Q = m\,L_v$

where L_v is latent heat of vaporization.

If ΔU be the change in its internal energy, then from the first law of thermodynamics,

$\Delta U = Q - W$

$\therefore \Delta U = mL - (V_v - V_l)$

It is the expression for change in internal energy of the system during vaporization (isobaric process). Similarly, we can determine the expression for the change in the internal energy of the system during freezing (isobaric process),

$\Delta U = mL - p(V_{ice} - V_l)$

Here L_i is the latent heat of fusion of ice.

iii. Isothermal Process

If the temperature of the system is constant the thermodynamic process is called isothermal process. The temperature remains constant only in the change of state *i.e.,* liquid to vapour or liquid to ice as in the case of isobaric process. So we may write $\Delta U = m\,L_v - p(V_V - V_l)$ and $\Delta U = m\,L_i - p(V_{ice} - V_l)$

iv. Adiabatic Process

An adiabatic process refers to one in which a system's total heat stays steady, indicating that no heat enters or exits the system. Heat can't escape from or enter the system as it is thermally separated from its surroundings. So for such a process heat $Q = 0$, and from the first law of thermodynamics, we have

$\Delta U = Q - \mathrm{W}$

$\Delta U = -\mathrm{W}$

Thus, in an adiabatic process amount of work done is equals to change in internal energy. If work is done by the system i.e., work done is positive, the internal energy is decreased. On the other hand if work is done on the system i.e., work done is negative, the internal energy is increased. When a gas is suddenly compressed (adiabatic process), the work done on the gas is added to its internal energy so that its temperature rises. That is why a bicycle pump becomes hot when air in it is compressed to fill in cycle tube. Similarly, when a gas is suddenly expanded, the work against the surroundings is done by drawing heat from its internal energy. A decrease in its internal energy decreases the temperature of the gas. That is why when a motor car tyre bursts, the tyre gets cooled because of sudden expansion of air adiabatically.

v. Free Expantion

Free expansions happens when a system expands in a way that neither energy enters nor exits the system (adiabatic process) and no work done by or on the system.

Let us imagine an adiabatic, adequately insulated vessel with rigid walls that are divided into two sections, one of which has been evacuated and other containing a gas. The gas burst into a vacuum and spreads freely when the partition is suddenly removed.

If U_i and U_f be the initial and final internal energies of the gas, then by the first law of thermodynamics,

$\Delta U = Q - \mathrm{W}$

But, $Q = 0,\ W = 0$

So, $\Delta\ \ U = 0$

i.e., $U_i - U_f = 0$

or $U_i = U_f$

Thus, in the free expansion, the initial and final internal energies remain the same.

vi. Cyclic Process

In a cyclic process, the system after passing from initial state to final state comes back to its initial state. So, in this process the net change in the internal energy of the system is zero ($\Delta U = 0$). Hence, by the first law of thermodynamics, $\Delta U = Q - \mathrm{W}$, we have

$\Delta U = 0$ so, $Q - W = 0$ or $Q = W$

It means, in the cyclic process the heat taken by the system is equal to the work done by the system. In differential form, we may write

$dQ = dW$

b. Poisson's Equation

Let us consider an ideal gas having a volume V, pressure P and Kelvin temperature T. Suppose it undergoes a small adiabatic expansion. In doing so, it does the necessary external work at the cost of its own internal energy which therefore decreases and hence its temperature falls.

Let dV be the infinitesimally small change in the volume of the gas at pressure p. Then the external work done by the gas in its expansion will be

$$dW = p\,dV \tag{1}$$

If dT be the fall in temperature of the gas, the heat lost by it will be $C_V dT$ where C_v is the gram-molecular specific heat at constant volume. Now, in an ideal gas the molecules do not attract each other, so that its internal energy is entirely the kinetic energy of the molecules which depends only on the temperature of the gas. Therefore, the decrease in the internal energy of the gas by dU is equal to the heat lost by it. Thus,

$$dU = C_V\,dT \tag{2}$$

Now, the first law of thermodynamics for an adiabatic process ($dQ = 0$) becomes

$$dU + dW = 0$$

Substituting the values of dU and dW from eq. (2) and eq. (3) we get

$$C_V dT + dV = 0 \tag{3}$$

Now, the ideal gas equation for one mole substance is $pV = RT$

where, R is the universal gas constant. This on differentiation gives $p\,dV + V\,dp = R\,dT$

$$dT = \frac{p\,dV + V\,dp}{R}$$

Substituting for dT in eq. (3), we get

$$Cv\left(\frac{p\,dV + V\,dp}{R}\right) + pdV = 0$$

$$Cv(p\,dV + V\,dp) + pRdV = 0$$

But $R = C_P - C_V$ (Mayer's relation).

$$\therefore C_V\,(p\,dV + V\,dp) + (C_P - C_V)\,p\,dV = 0$$

Or $C_V\,V\,dp + C_p\,p\,dV = 0$ Dividing by $C_V\,p\,V$, we obtain

$$\frac{dP}{P} + \frac{C_p}{C_v}\frac{dV}{V} = 0$$

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

where γ is the ratio of the gram-molecular specific heats of the gas ($\gamma = C_p/C_V$). Integrating the last expression, we have $\log P + \gamma \log V$ = a constant or $PV^{\gamma} = Constant$.

This relation is known as Poisson's law.

If P_i, V_i be the initial and P_f, V_f the final pressures and volumes of the gas respectively, then $P_i V_i^{\gamma} = P_f V_f^{\gamma} = Constant$.

2.9. Limitation of First Law of Thermodynamics

a. There is no constraint on the direction in which heat can flow: the first law clearly states the connection between the quantity of heat received and the quantity of work that a system can perform. On the other hand, it doesn't say if heat can move from a cold end to a hot end. For example, freezing the ice to a low temperature is extracting heat from it. Here is a little external work to be performed.

b. Does not indicate whether the reaction is feasible: The first law makes no inquiry of whether the process is feasible. For example, equilibrium must be achieved when an iron rod is heated at one end, this is possible only using energy.

c. It is practically impossible to transform all of the heat energy into an equivalent amount of work. Another law of thermodynamics, the second law, is required to get around these restrictions.

The direction of the heat flow and the possibility of the reaction are both predicted by the second law of thermodynamics. The second law also tells that certain amount of heat energy cannot be completely converted into equivalent amount of work.

Self-Assessment

1. What is the First Law of Thermodynamics, and how is it mathematically expressed?
2. Define an isothermal process and explain how the First Law of Thermodynamics applies to it.
3. What is an adiabatic process, and how does it differ from an isothermal process in terms of heat exchange?
4. Explain what an isobaric process is and provide an example.
5. Describe an isochoric process and its significance in thermodynamics.
6. The First Law of Thermodynamics is a statement of which principle?
   a) Momentum conservation
   b) Mass conservation
   c) Energy conservation
   d) Entropy conservation
7. In an isothermal process, the internal energy change (ΔU\Delta UΔU) of an ideal gas is:

a) Positive b) Negative
c) Zero d) Cannot be determined

8. During an adiabatic process, the heat exchanged (QQQ) with the surroundings is:
   a) Positive b) Negative
   c) Zero d) Infinite
9. Which of the following processes occurs at a constant pressure?
   a) Isothermal b) Adiabatic
   c) Isobaric d) Isochoric
10. In an isochoric process, the work done by the system (WWW) is:
    a) Positive b) Negative
    c) Zero d) Infinite
11. The First Law of Thermodynamics is mathematically expressed as:
    a) Q=ΔU+WQ = \Delta U + WQ=ΔU+W b) ΔU=Q−W\Delta U = Q - WΔU=Q−W
    c) Q=ΔU−WQ = \Delta U - WQ=ΔU−W
    d) ΔU=Q+W\Delta U = Q + WΔU=Q+W
12. During a cyclic process, the change in internal energy (ΔU\Delta UΔU) over one complete cycle is:
    a) Positive b) Negative
    c) Zero d) Cannot be determined
13. In an isobaric process, the work done by the system is given by:
    a) W=PΔVW = P \Delta VW=PΔV
    b) W=ΔP·VW = \Delta P \cdot VW=ΔP·V
    c) W=P·ΔTW = P \cdot \Delta TW=P·ΔT
    d) W=ΔP·ΔVW = \Delta P \cdot \Delta VW=ΔP·ΔV
14. Which of the following is true for an adiabatic process?
    a) Temperature remains constant b) No heat is exchanged with the surroundings
    c) Volume remains constant d) Pressure remains constant
15. In a thermodynamic process, if the heat added to the system is equal to the work done by the system, the change in internal energy (ΔU\Delta UΔU) is:
    a) Positive b) Negative
    c) Zero d) Infinite

Answers: **c), c), c), c) ,c), b), c), a), b), c)**

Chapter 3

Thermodynamics Process

3.1. Heat- Path Function

Transfer of energy from one part to the other part of a body by virtue of difference of temperature defines Heat. This heat transfer take by different processes namely conduction, convection and radiation, also the amount of heat (thermal energy) produced is always proportional to the amount of work done. Both are the transient phenomena and have same unit. The heat Q positive if is absorbed by the system or negative if rejected by the system.

It is path function. It indicates that as a system changes from state 1 to state 2, the quantity of heat (Q) delivered, depends on the system's path, or the intermediate stages it travels through. Henceforth it is an inexact differential and written as □Q

On integrating, we get

$$\int_{1A}^{2A} \delta Q = Q_{1A}^{2A}$$

Here, Q^2 define the transfer of heat during the given process between the process 1 and 2 along a path A.

3.2. Work – Path Function

The work can be done by system or it can be done on the system. Work done is positive when it is done by the system, negative when it is done on the system.

Suppose a system is state taken from state 1 to 2, by two different ways.

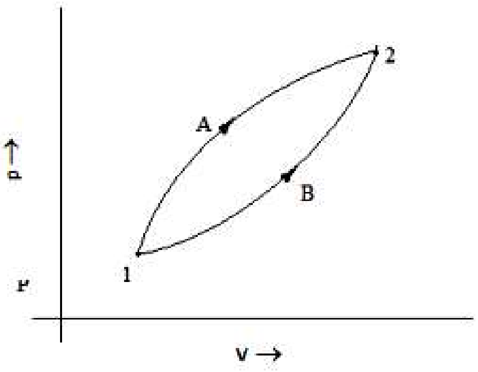


Fig: 3.1

A and B shown in Fig. (3.1). The processes are quasi-static.

The area under P-V plot gives the work done in that process. The graphic above illustrates how the regions under these curves vary, which in turn causes variations in the amounts of work completed.

For path A

$$W_A = \int_{1A}^{2A} \delta W = \int_{1A}^{2A} PdV$$

For path B

$$W_B = \int_{1B}^{2B} \delta Q = \int_{1B}^{2B} PdV$$

The values of W_A not equal to W_B. Consequently, work cannot be defined as the difference between a system property's values in the two states. Therefore, it is not correct to represent

$$W = \int_{W1}^{W2} \delta W = W_2 - W_1$$

It may be pointed out that it is meaningless to say "Work in a system or work of a system". Work cannot be compared to a system's pressure or temperature.

It terms of calculus δW is an in exact differential. In other words, W is not a system characteristic, and δW cannot be specified as the difference of two values that only rely on the initial and final states.

Heat and work are hence path functions that depend entirely on the process. These aren't point functions like temperature or pressure. The work required to get the system from state 1 to state 2 will differ based on the path chosen.

3.3. Comparison of Heat and Work

Some of the similarities between heat and work

1. Both work and heat are transient phenomena. Systems don't operate or generate heat. The unit of work is the same as the heat.
2. Heat transfer or work done can occur when a system changes.
3. The phenomena of heat and work are borderline. At the system's edge, they are observed.
4. The energy that crosses the system boundary is represented by heat and work.
5. Since heat and work are route functions, their differentials are inaccurate. The symbols δQ and δW stand for them, respectively.

3.4. Quasi-Static Process

A quasi-static defines that, a process in which the deviation from thermodynamic equilibrium is very small so that all states are considered as equilibrium states through which the system passes during the process.

The P-V plot under variable pressure and infinitesimal during compression from initial volume, Vi, to final volume, Vf, as shown in the diagram (Fig. 3.2). The shaded area indicates work done on the gas. Many processes actually resemble quasi-static processes in practice and can be treated as such with little or no error.

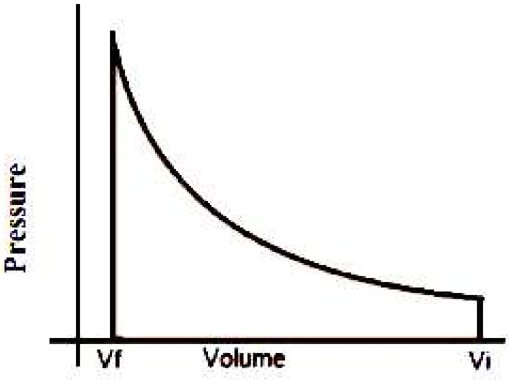


Fig 3.

Consider a gas expands in a closed cylinder with a frictionless piston. The pressure of gas inside the cylinder is higher than pressure of surrounding while the piston moved inwardly by apply weight on it. Small weights withdrawn steadily one at a time will cause the gas inside the cylinder to expand very slowly, making the process nearly static. However, expansion occurs quickly and is a non-equilibrium process if all the weights are removed at once. During this process, the system will never remain in equilibrium.

An ideal concept that may be applicable to all thermodynamic systems, including electric and magnetic systems, is a quasi-static process. It should be noted that the criteria for such a process require a very slow rate, that is impractical to attain in practice.

3.5. Wok Indicator Diagram

The work done in a quasi-static thermodynamic process (e.g., a slow change in volume of a gaseous system) can be easily obtained with the help of pressure P and volume V graph. Such plots are called Indicator diagrams. These diagrams can be drawn with the help of a device called the indicator which directly records the changes in the volume and pressure.

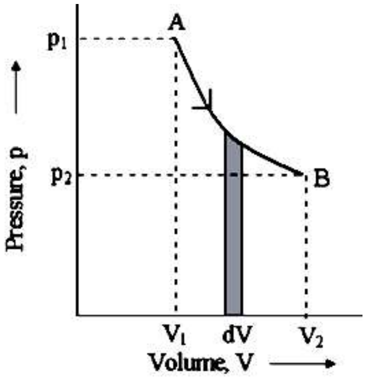
3.6. Thermodynamics Process

A change in the thermodynamic coordinates (pressure, volume, temperature etc.) of a thermodynamic system brings about a change in the state of the system and is called a thermodynamic process or simply a process.

3.7. Work Done during different Thermodynamic Process

a. Isothermal Process

If the change in pressure and volume of a gas (system) takes place in such a manner that its temperature remains the same throughout, it is called an isothermal process.



Let a gas be filled in a cylinder with a piston at room temperature under atmospheric pressure. If the piston be pushed down a little to compress the gas (i.e., the work is done on the gas) its internal energy will increase and its temperature will rise a little. If the temperature is to be maintained constant, the extra heat must at once be conducted to the surroundings. Similarly, if the gas is allowed to expand (push the piston up a little) i.e., work is done by the gas, its internal energy decreases and its temperature falls a little. Again to maintain its temperature constant, heat must at once be conducted to it from the surroundings.

Let 1 gm mole of a perfect gas is allowed to expand under isothermal conditions. Let its initial volume V_1 and pressure P_1 be represented by point A and its final volume V_2 and pressure P_2 by the point B on P-V indicator diagram (Fig. 3.3) keeping its temperature constant.

Let us consider a small increase dV in the volume of the gas at pressure P. Then, the work done by the gas,

$dW = p\,dV$ (shaded strip in the figure) (3.4)

Therefore, the total work done by the gas during the whole expansion from volume V_1 at A to volume V_2 at *B* will be

$$W = \sum dW = \int_{V1}^{V2} pdV = \text{Area under the curve AB}$$

Since, for a perfect gas pV = RT, where R is the gas constant for 1gm mole of the gas, then

$$p = R\frac{T}{V}$$

Putting the value of P in equation (3.5), we get

$$W = RT \int_{V1}^{V2} \frac{dV}{V} = RT \log_e \{\frac{V2}{V1}\}$$

$$W = 2.3026\ RT \log_{10} \{\frac{V2}{V1}\}$$

Since, the temperature remains constant and Boyle's law is obeyed, therefore

$$P_1V_1 = P_2V_2 \quad \text{or} \quad \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

Hence, equation (3.8) become

$$W = 2.3026\ RT \log_{10} \frac{P1}{P2}$$

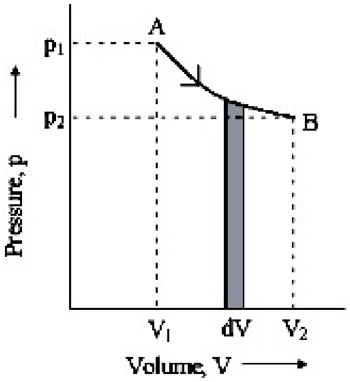
If we take 1 gm of the gas in place of 1 gm mole then the gas constant will be r and equation (3.8) and (3.10) then become,

$$W = 2.306rT \log_{10} (V_2/V_1)$$

$$W = 2.306rT \log_{10} (p_1 /p_2)$$

b. Adiabatic Process

Adiabatic means heat does not go out or come in the system. So adiabatic process implies a process in which heat is neither allowed to enter nor leave the system. Thus, it is a process which takes place in complete thermal isolation from the surroundings.Let, a gas be filled in a cylinder with a piston at the room temperature and atmospheric pressure. Also the cylinder and piston are perfectly insulated. If the piston be pushed a little to compress the gas i.e., the work is done on the gas, its internal energy will increase and its temperature will rise a little as the heat developed cannot possibly escape out to the surroundings. Similarly, if the gas be allowed to expand i.e., work is done by the gas, its internal energy decreases and its temperature falls a little. Again no heat can possibly enter the cylinder from outside.



Let 1 gm mole of a perfect gas be allowed to expand adiabatically from an initial volume V_1 to a final volume V_2, the pressure changing from P_1 to P_2 (P-V diagram shown in Fig. 3.4). Then, work done by the gas,

$$W = \int_{V1}^{V2} pdV$$

Since, for a perfect gas, in an adiabatic process,

$$pv^{\gamma} = K \text{ (constant)} \qquad \text{or}$$

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

Putting the value of *p* in equation (3.13), we get

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

$$= K \int_{V_1}^{V_2} \frac{dV}{V^{\gamma}}$$

$$= \left[\frac{V^{1-\gamma}}{1-\gamma}\right]_{V1}^{V2}$$

$$= \frac{K}{1-r} \left[V_2^{1-\gamma} - V_1^{1-\gamma}\right]$$

$$W = \frac{K}{\gamma-1} \left[\frac{K}{V_1^{1-\gamma}} - \frac{K}{V_2^{1-\gamma}}\right]$$

Also in adiabatic expansion, we have

$P_1V_1^{\gamma} = K = P_2V_2^{\gamma}$

Putting the value of K in equation (3.17), we have

$$W = \frac{1}{(\gamma-1)} \left[\frac{P_1V_1^{\gamma}}{V_1^{1-\gamma}} - \frac{P_2V_2^{\gamma}}{V_2^{1-\gamma}}\right]$$

or, $$W = \frac{1}{(\gamma-1)} [p_1V_1 - p_2V_2]$$

It can be shown that the work done by the gas during adiabatic expansion from volume V_1 at pressure p_1 to volume V_2 at pressure p_2 given by the area under the p-V curve for the gas i.e.,

$$W = \int_{V1}^{V2} pdV = \frac{1}{(\gamma-1)} (p_1V_1 - p_2V_2)$$

$$= \text{area under the curve AB}$$

Again, we have

$p_1V_1^{\gamma} = p_2V_2^{\gamma} = K$, so,

$V_1 = (K/p_1)^{1/\gamma}$ and $V_2 = (K/p_2)^{1/\gamma}$

Thus,

$$W = \frac{1}{(\gamma-1)}\left[p_1\left(\frac{K}{p_1}\right)^{1/\gamma} - p_2\left(\frac{K}{p_2}\right)^{1/\gamma}\right]$$

or $$W = \frac{(K)^{1/\gamma}}{(\gamma-1)}\left[(p_1)^{\gamma-1/\gamma} - (p_2)^{\gamma-1/\gamma}\right]$$

As the temperature of the gas changes from T_1 to T_2 and also we have $p_1V_1=RT_1$ and $p_2V_2=RT_2$ (where R is gas constant for 1 gm mole gas), substitution of these values in equation (3.18) results

$$W = \frac{R}{(\gamma-1)}(T_1 - T_2)$$

If we take 1gm of the gas in place of 1 gm mole then the gas constant will be r and eq.(3.21) becomes,

$$W = \frac{r}{(r-1)}(T_1 - T_2)$$

Since, in an adiabatic process, heat is not allowed to enter or leave the system, the external work W is done by the gas at the expense of its own internal energy and the work done becomes equal to decrease in internal energy of the gas.

c. Reversible process

In this process, if a process reversed in a way that leaves no alterations in the environment or in any of the bodies involved, and all changes that occur during the direct process are precisely duplicated in the opposite order and sense. A system should produce the same quantity of heat in the reverse process if, for instance, a certain amount of work is extracted from it and a system receives a given amount of heat in the direct process.

Conditions of Reversibility

A reversible process must satisfy following two conditions:

1. 1. There must be no dissipative forces at all, including electrical resistance, magnetic hysteresis, friction, viscosity, and inelasticity. Assume a gas is housed in a piston-equipped cylinder and is in touch with a source of constant temperature. The piston is loaded in such a way that the pressure it applies to the gas precisely balances the pressure the gas applies to it. As the piston's load decreases, the gas expands and

exerts external force to push the piston upward and reduce friction between the piston and the cylinder walls. This work requires heat, which is extracted from the source. The gas will compress if the piston's load is raised at this point. Now, the effort expended in raising the piston during the expansion is recovered. Conversely, greater effort needs to be made to minimise friction. Thus, expansion can't be reversed. In a similar vein, the process becomes irreversible due to additional dissipative effects including inelasticity and electrical resistance.

2. The process needs to be quasi-static. The gas expands and does some work in order to provide the piston with kinetic energy. More effort has to be done to supply the piston kinetic energy since this work cannot be recovered during the reverse operation. Therefore, the pressure of the gas on the piston must differ by an infinitesimal amount from the pressure the piston applies to the gas in order to cause the gas to expand reversibly. Provided that expansion or compression occurs indefinitely slowly, no kinetic energy will be generated. In reality, these requirements are never met. Therefore, a reversible process is only a theoretical idea.

d. Irreversible process

Any process which cannot be reversed called an irreversible process. Irreversible processes includes all practical processes like free expansion, Joule-Thomson expansion, electrical heating of a wire, diffusion of liquids and gasses, etc. Irreversible processes comprise all natural processes such as radiation, conduction, radioactive decay, etc.

Self-Assessment

1. What is the Second Law of Thermodynamics?
2. Define a quasi-static process and explain its significance in thermodynamics.
3. What is a work function in the context of thermodynamics?
4. Explain what is meant by a path function and give an example.
5. Describe a reversible process and its characteristics.
6. Which of the following statements is a correct interpretation of the Second Law of Thermodynamics?
   a) Energy is conserved.
   b) Isolated system’s entropy is always decreases.
   c) Heat cannot spontaneously flow from a colder body to a hotter body.
   d) The total energy of a system remains constant.

7. In a quasi-static process, the system:
    a) Is always in non-equilibrium.
    b) Changes state infinitely slowly.
    c) Experiences rapid state changes.
    d) Remains at constant volume.
8. Which is a thermodynamics quantity depends on path follows?
    a) Internal energy
    b) Enthalpy
    c) Work
    d) Temperature
9. A work function in thermodynamics typically refers to:
    a) The amount of heat required to raise the temperature of a substance.
    b) The energy required to remove an electron from a solid.
    c) The energy transferred by the system due to a force acting through a distance.
    d) The energy stored in chemical bonds.
10. Which of the following is true for a reversible process?
    a) It occurs instantaneously.
    b) It increases the entropy of the universe.
    c) It can be reversed without leaving any net change.
    d) It is the same as an adiabatic process.
11. An irreversible process is characterized by:
    a) Infinite slowness.
    b) No increase in entropy.
    c) Reaching equilibrium at every stage.
    d) Dissipative effects such as friction.
12. The entropy of an isolated system:
    a) Always remains constant.
    b) Always decreases.
    c) Always increases or remains constant.
    d) Can either increase or decrease depending on the process.
13. In a cyclic process, the change in entropy of the system over one complete cycle is:
    a) Positive
    b) Negative
    c) Zero
    d) Cannot be determined
14. Which of the following is an example of a path function in thermodynamics?
    a) Entropy
    b) Enthalpy
    c) Heat
    d) Pressure
15. The efficiency of a heat engine is fundamentally limited by:
    a) The First Law of Thermodynamics.
    b) The Second Law of Thermodynamics.
    c) The Zeroth Law of Thermodynamics.
    d) The Third Law of Thermodynamics.

Answers:

1. c), b), c), c), c), d), c), c), c), b)

Chapter 4

Heat Engine and Second Law of Thermodynamics

4.1. Heat Engine

Any cyclic device that continuously converts into mechanical work is called a heat engine. There are three main parts in a heat engine: a hot body called hot reservoir or source, working substance, and a cold reservoir or 'sink'.

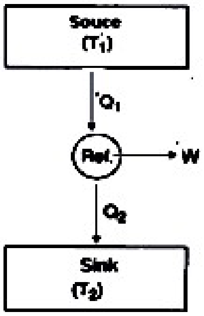


Fig: 4.1

A certain amount of heat is taken by the working substance from the source, part of it is converted into work, and the rest is rejected into the sink. Because the working substance returns to its initial state, this order of events is commonly referred as "cycle process". In Fig. 4.1, this is depicted schematically. Performing the same cycle repeatedly results in continual work accumulation at the cost of thermal energy.

Assume that the working substance absorbs heat Q1 from the source and reject heat Q2 into the sink. Consider that W indicates the total work performed. Q1-Q2 is the net the amount of heat absorbed by the substance; since its internal energy remain constant during the system's return to its initial state, the heat has actually been converted into work. Q1-Q2 = W is the result of applying the first law of thermodynamics to a single cycle.

Thermal Efficiency: It is the ratio of the work obtained to the heat taken from the source, that is

$$\eta = \frac{W}{Q1} = \frac{Q1-Q2}{Q1} \quad \text{or} \qquad (3.24)$$

$$\eta = 1 - \frac{Q2}{Q1}$$

Often the efficiency is expressed in percentage and then

$$\eta_{\%} = \left[1-\frac{Q_2}{Q_1}\right]\times 100$$

Based to this equation, the heat engine's efficiency will reach unity when Q2 = 0 (no heat is transferred to the sink). In reality, however, this is not possible. It suggests that not all of the heat that comes from the source can be utilized by the engine to produce work.

We cannot define the efficiency as W/Q_2, because in that case we shall have

$$\eta = \frac{W}{Q2} = \frac{Q1-Q2}{Q2} = \frac{Q1}{Q2}-1$$

so that the condition for the ideal value of efficiency (i.e., □ =1) would be $Q_1=2Q_2$ which is absurd.

4.2. Reversible Engine

The working substance of an engine goes through a cycle. It absorbs heat from a hot body, converts some of it in to work, and reject the remaining heat to a cold body before coming back to its initial condition. The surroundings and the hot and cold bodies experience changes during this cycle. This cycle is a "reversible cycle" and the engine is a "reversible engine" if it can be completed in reverse order with no changes to the environment and all of the component of engine completely return to their initial states. Such an engine can be realized if: (i) all of the engine components are friction-free; and (ii) the working substance's temperature and pressure are always fairly stable to their surroundings throughout the cycle, resulting in quasi-static operation for all of the cycle's operations.

All the above conditions are not possible in practice. So that reversible engine is a hypothetical phenomenon or an ideal conception.

4.3. Second Law of Thermodynamics

In accordance with the first law of thermodynamics, mechanical work and heat are equivalent when one is fully transformed into the other (W=Q). It is a thermodynamic system employing the conservation of energy principle.

However, the first law would not be broken if we suggested taking a specific amount of heat from a body and converting it completely into work. However, in real life, this is found to be impossible. If this were possible, we might utilize the heat from the ocean's water to move ships across it. Thus, the first law only states that energy is going to be conserved if a process occurs.

It doesn't indicate if the process will work or not. Similarly, whether heat moves from a hot body to a cold body or the other way around when two bodies with different temperatures come into touch does not break the first law. We know from observation that heat does not transfer from a cold to a hot body. Such experimental facts are supposed to be comprised into thermodynamics through the second law.

There are two statements for the second law of thermodynamics: -

A. Kelvin-Planck's statement

In case of a heat engine a working substance absorbed heat form source converts its some part in to work and rest I transfer to the cold body. There has never been an engine designed that operates in a cycle where all of the heat absorbed by the source is, transferred to work; some heat must be rejected to a cold body.

This experience led Kelvin and Planck to state the following:

"It is impossible to construct an reversible engine which operates in a cycle, which takes heat from from a hot body convert it completely into work, without rejecting any part to the sink."

B. Claussius statement

Within a refrigerator, a working substance absorbs heat from a cold body (sink), receives a net amount of work from an external agency (compressor), and reject heat to a hot body (source). Thus, it uses outside labor or energy to transfer heat from a cold body to a hot body. There has never been a refrigerator created that doesn't require an outside energy source to function. Clausius declare that:

"It is impossible to construct a device which operating in a cycle, will take heat from a cold body and reject it to a hot body without expenditure of work by an external energy source" . Stated differently, heat cannot naturally go from a colder body to a warmer one.

4.4. Equivalence of kelvin-Planck and Claussius statements

We can express that both the laws are equivalent.

To verify the equivalence of two statements, consider a a refrigerator R in fig 4.2 is able to transfer heat Q2 from a cold body to a hot body in the absence of an external energy source.

It is consequently against the Clausius statement. Let's say an engine E that is operating between the source and sink bodies absorbs heat Q1 from the hot body and reject a component of heat to sink and convert a part in to ($W = Q_1 - Q_2$),. The law is not broken by the engine E alone. However, when the engine E and the refrigerator R are coupled, they create a machine that takes heat Q1–Q2 from the hot body and convert it into work without rejecting any heat to the cold body. This clearly violates the Kelvin-Planck statement.

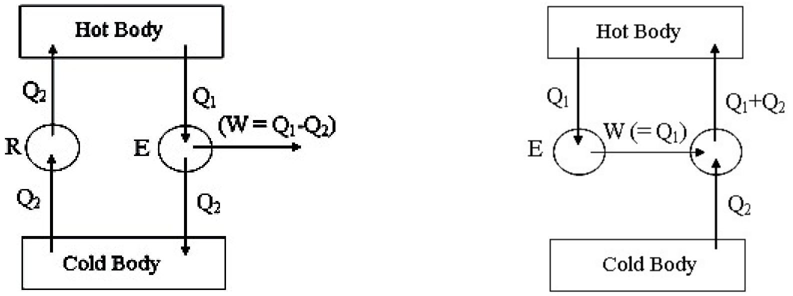


Fig : 4.2

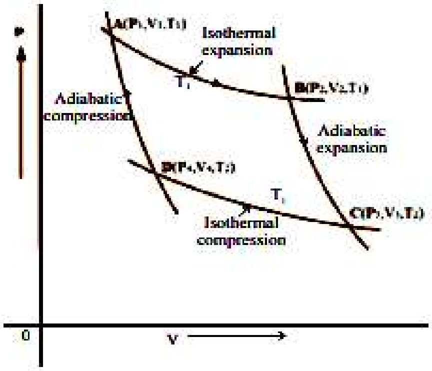
In the same way, suppose an engine E (Fig.4.2) that takes heat Q1 from a hot body and transforms it completely into work W(=Q1), without rejecting heat to the cold body. The Kelvin-Planck statement is violated. Suppose for the time being that a refrigerator R working between the the same hot and cold bodies takes heat Q2 from the cold body, experiences work W(=Q1) from a external agency, and outputs heat Q1+Q2 to the hot body. The law is not broken by the refrigerator R by itself. However, when combined, E and R create a device that, without the need for an outside energy source, transports a certain quantity of heat Q2 from a cold body to a hot one. This is clearly against the Clausius statement.

The first law of thermodynamics is reinforced by the second law. All that the first law tells us is that no devices can put out more energy than it takes in. It includes no mention of restrictions or prerequisites for the distribution of energy. But the second law accomplishes it. For instance, heat cannot naturally move from a colder to a hotter body or be entirely transferred as work by a substance. Though not prohibited by the first law, these phenomena are prohibited by the second law.

4.5. Carnot Cycle and Carnot Engine

Sadi Carnot, a French engineer, developed a theoretical reversible engine such that it operates between two reservoirs and operates with maximum possible efficiency. The cycle of processes adopted by this engine is called Carnot cycle. The Carnot cycle is a reversible cycle, this means that all the processes involved in it are reversible.

The Carnot cycle consists of two isothermal processes and two adiabatic processes. Fig.3.8 shows the Carnot cycle for a heat engine with ideal gas as its working substance.



The Carnot cycle has the following sequence of operations:

- Step 1□□2 : Reversible isothermal expansion of gas (P_1,V_1,T_1□P_2,V_2,T_1)

In this step, the gas absorbs heat (Q_1) from the reservoir at temperature T_1. Since the process is isothermal, there is no change in internal energy and so the temperature of the system.

From the first law of thermodynamics,

$$\delta Q = \delta U + \delta W$$

Putting $\delta U = 0$,we get,

$$\delta Q = \delta W + 0 \text{ or}$$

$$\delta W = \delta Q$$

$$W_{1\to 2} = Q_1 = \mu R T_1 \ln\left(\frac{V_2}{V_1}\right)$$

- Step 2□□3 : Reversible adiabatic expansion of gas (P_2,V_2,T_1□P_3,V_3,T_2)

In this step, the work is done by the gas adiabatically at the expense of internal energy which causes drop in temperature of system. From the first law of thermodynamics,

$$\delta Q = \delta U + \delta W$$

Putting $\delta Q = 0$,we get,

$$\delta U + \delta W = 0 \text{ or}$$

$$\delta W = -\delta U$$

$$W_{2\to 3} = \frac{\mu R(T_1 - T_2)}{\gamma - 1}$$

- Step 3□□4 : Reversible isothermal compression of gas (P_3,V_3,T_2□P_4,V_4,T_2)

In this step, the gas releases heat (Q_2) to the reservoir at temperature T_2. There is no change in internal energy and temperature of system as the process is isothermal. From the first law of thermodynamics.

$\delta Q = \delta U + \delta W$

Putting $\delta U = 0$,we get,

$\delta Q = \delta W + 0$ or

$\delta W = \delta Q$

$$W_{3\to4} = Q_2 = \mu RT_2 \ln\left(\frac{V_4}{V_3}\right)$$

$$= -\mu RT_2 \ln\left(\frac{V_3}{v_4}\right)$$

- Step 4□□1 : Reversible adiabatic compression of gas (P_4,V_4,T_2□P_1,V_1,T_1)

In this step, the work is done on the gas adiabatically. This leads to increase in internal energy of the system causing increase in temperature of system. From the first law of thermodynamics,

$\delta Q = \delta U + \delta W$

Putting $\delta Q = 0$,we get,

$\delta U + \delta W = 0$ or

4.6. Efficiency of carnot engine

The efficiency of heat engine is defined as ratio of net work done to the heat absorbed in one complete cycle. If the heat engine receives heat Q_1 and rejects heat Q_2 then efficiency is given by-

$$\eta = \frac{Wnet}{Q1} = \frac{Q1-Q2}{Q1} = 1 - \frac{Q2}{Q1}$$

Now, the total work done

$$W = W_{1\to2} + W_{2\to3} - W_{3\to4} - W_{4\to1}$$

$= W_{1\to2} + W_{3\to4}$ ($\because$ $W_{2\to3}$ and $W_{4\to1}$ are equal and opposite and hence they cancel each other).

$$= \mu RT_1 \ln\left(\frac{V_2}{V_1}\right) - \mu RT_2 \ln\left(\frac{V_3}{V_4}\right)$$

Therefore,

$$\eta = 1 - \left(\frac{T_2}{T_1}\right)\frac{\ln\left(\frac{V_3}{V_4}\right)}{\ln\left(\frac{V_2}{V_1}\right)}$$

Now Since 2→3 is an adiabatic process,

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

(3.34)

i.e., $\frac{V_2}{V_3} = \left[\frac{T_2}{T_1}\right]^{1/(\gamma-1)}$

Similarly, since step 4→ 1 is an adiabatic process

$$T_2 V_4^{\gamma-1} = T_1 V_1^{\gamma-1}$$

i.e., $\frac{V_1}{V_4} = \left[\frac{T_2}{T_1}\right]^{1/(\gamma-1)}$

From eqs. (3.35) and (3.36)

$$\frac{V_3}{V_4} = \frac{V_2}{V_1}$$

Using Eq. (3.33) in Eq. (3.37), we get

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

From relations (3.31) and (3.38), we have

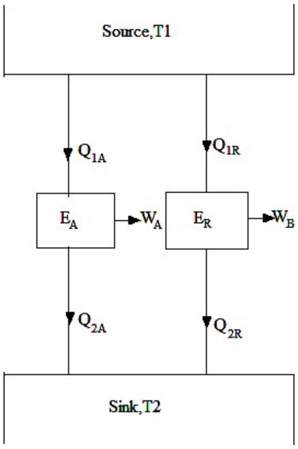
$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

i.e. in a Carnot cycle, the ratio of the amount of heat rejected to the sink to the heat received from the source is equal to the ratio of their respective temperatures.

In other words, the efficiency of a Carnot engine is unaffected by the kind of working substance; instead, it depends entirely on the temperature of the source and sink. The area in the indicator diagram (P V diagram) that the Carnot cycle covers represents the graphic efficiency of a Carnot engine.

4.7. Carnot Theorem

The second law of thermodynamics gives two important conclusions which can be taken together in the form of a theorem called Carnot's theorem. According to this theorem "The efficiency of a Carnot reversible engine is maximum and is independent of the nature of the working substance".



Or

"The efficiency of all reversible heat engines operating between the same two temperatures is the same and no irreversible heat engine working between the same two temperatures can have greater efficiency than Carnot's reversible heat engine".

To prove it, let us consider two heat engines E_A and E_R operating between a source at temperature T_1 and sink at temperature T_2 (Fig. 3.9). Let E_A be any heat engine and E_R be a reversible heat engine. Let us assume efficiency η_A of E_A is greater than efficiency η_R of E_R. In order to prove the Carnot theorem we have to contradict our assumption.

Let the rates of working of the engine E_A be Q_{1A} and that of E_R be Q_{1R} such that-

$Q_{1A}=Q_{1R}=Q_1$

As assumed, $\eta_A > \eta_R$

As we know that, $\eta = \frac{Wnet}{Q1}$

So we can write, $\frac{W_A}{Q_{1A}} > \frac{W_R}{Q_{1R}}$

Therefore, $W_A > W_R$ $(\because QA = Q_R)$A

Let us reverse E_R. Since E_R is a reversible heat engine, therefore, the magnitude of heat transferred and work done will remain the same but their directions will reverse (Fig. 3.10).

Since $W_A > W_R$ some part of W_A which is equal to W_R in magnitude can be fed to drive the reversed heat engine E_R. Since, $Q_{1A}=Q_{1R}=Q_1$, the heat discharged by E_R may be supplied to E_A thus the source may be eliminated. The net result is that E_A and E_R together constitute a heat engine which operating in a cycle produces a net work done W_A-W_R (Fig. 3.11) while exchanging heat with a single reservoir at temperature T_2, thus violating the Kelvin-Planck statement. Hence our assumption is wrong.

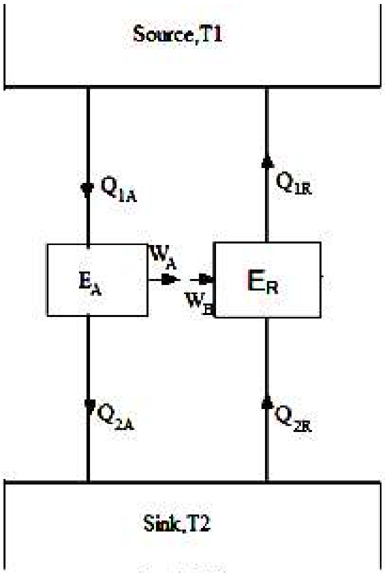


Fig. (3.10)

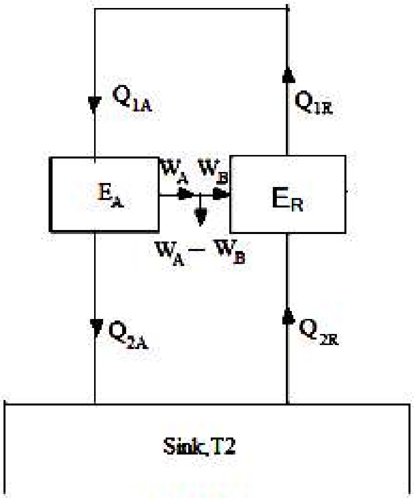


Fig. (3.11)

4.8. Carnot Engine as a Refrigerator

When a Carnot engine works in the reverse direction i.e., when it absorbs Q_2 amount of heat from the sink and work W is done on the working substance and finally Q_1 amount of heat is rejected to the source at higher temperature, the arrangement acts like a refrigerator.

The efficiency of a refrigerator is measured in terms of coefficient of performance.

The coefficient of performance k is defined as the ratio of the heat absorbed from the sink to the work done on the working substance by the external agent. i.e.,

$$k = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

Hence, the value of *k* may be greater than unity.

Self-Assessment

1. What is a heat engine and how does it work?
2. Describe the Carnot engine and its significance in thermodynamics.
3. What is Carnot's theorem?
4. Explain the working principle of a refrigerator.
5. How does the efficiency of a Carnot engine compare to that of a real heat engine?
6. A heat engine operates between two reservoirs at temperatures THT_HTH and TCT_CTC. According to the Second Law of Thermodynamics, which of the following statements is true?

   a) It is possible to convert all the heat energy from the hot reservoir into work.
   b) Some heat must be expelled to the cold reservoir.
   c) The efficiency of the heat engine is independent of the temperatures of the reservoirs.
   d) The engine can be 100% efficient.

7. The efficiency of a Carnot engine depends on:
   a) The working substance used in the engine.
   b) The temperatures of the heat reservoirs.
   c) The pressure at which the engine operates.
   d) The volume change during the engine cycle.
8. Carnot's theorem states that:
   a) No real engine can be more efficient than a Carnot engine operating between the same two temperatures.
   b) The efficiency of all reversible engines is the same.
   c) The efficiency of an irreversible engine is higher than that of a reversible engine.
   d) The efficiency of a Carnot engine is always 100%.
9. Which of the following processes does not occur in a Carnot cycle?
   a) Isothermal expansion
   b) Adiabatic expansion
   c) Isothermal compression
   d) Isochoric heating
10. The maximum efficiency of a Carnot engine operating between two heat reservoirs depends on:
   e) The heat added to the system.
   f) The work done by the system.
   g) The temperature difference between the reservoirs.
   h) The specific heat capacity of the working substance.
11. In a heat engine, the work output is equal to:
   a) The heat input.
   b) The heat input minus the heat expelled to the cold reservoir.
   c) The heat expelled to the cold reservoir.
   d) The heat input plus the heat expelled to the cold reservoir.
12. Which of the following is true for a refrigerator?
   a) It transfers heat from a high-temperature region to a low-temperature region using work.

b) It transfers heat from a low-temperature region to a high-temperature region using work.
c) It converts all input work into heat.
d) It operates on the principle of spontaneous heat flow.

13. The Second Law of Thermodynamics implies that the efficiency of any real heat engine is:

a) Equal to the efficiency of a Carnot engine.
b) Greater than the efficiency of a Carnot engine.
c) Less than the efficiency of a Carnot engine.
d) Not related to the efficiency of a Carnot engine.

Chapter 5

Entropy

5.1 Concept of Entropy

Initially the thermodynamic state of a system was represented by only three variables named pressure, volume and temperature. In 1854, Rudolf Clausius while studying the thermodynamic systems realized that to represent the thermodynamic state of a system, in addition to these three variables we must have at least one more thermodynamical variable. This added quantity was named "Entropy". It was proved successfully that like pressure, volume and temperature the entropy is also a function of the state of the system.

The concept of entropy was introduced for many reasons. The changes in the state of a system can be represented in different ways e.g. the isothermal change (in which the temperature remains unchanged), the isobaric change (in which the pressure remains constant) and the isochoric change (in which the volume of the system remains constant). Now the real question arises that which quantity remains constant during an adiabatic change. It was established that the entropy remains constant in an adiabatic change in the system. The systems have a tendency to change from a more ordered state to a more disordered state. The perception of entropy expresses this in a better physical and mathematical form. The entropy of a substance is a real quantity, just like pressure, volume and temperature. Despite being an very important quantity, it can't be represented in some physical form. It, therefore, becomes very difficult to visualize it and to understand its exact nature. Entropy can be conveniently understood by studying its effect, properties and other aspects.

Let us consider a number of isothermals I_1, I, I_3,.... at temperatures T_1, T_2, T_3... respectively asrepresented in the P-V diagram (Fig. 5.1). let A_1 and A_2 are two adiabatic curves which cut the isothermal at points (a, b), (c, d), (e, f),   respectively. We can now imagine abdca to be a Carnot cycle, so that it works between temperatures T_1 and T_2, extracting heat Q_1 from the source and rejecting Q_2 to the sink, so that the efficiency of a Carnot engine completing the cycle abdca can be given by

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

or $$1-\frac{Q_2}{Q_1}=1-\frac{T_2}{T_1}$$

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

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

Similarly, for Carnot cycle cdfe, extracting heat Q_2 from the source at temperature T_2 and rejecting Q_3 to sink at T_3, then we have

$$\frac{Q_2}{T_2}=\frac{Q_3}{T_3}$$

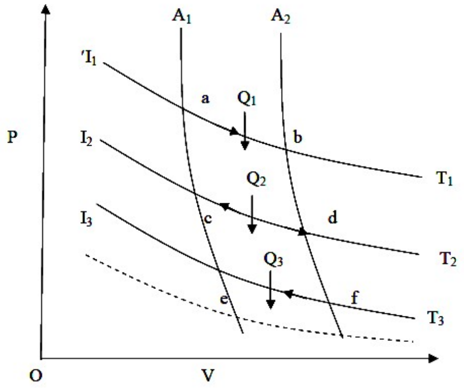


Fig: 5.1

Similar relations can be obtained for other mini Carnot cycles bound by adiabatics A_1 and A_2.Obviously, for all these Carnot cycles

$$\frac{Q_1}{T_1}=\frac{Q_2}{T_2}=\frac{Q_3}{T_3}=..........=\text{constant}$$

In going from one adiabatic to the other the system either absorbs heat or rejects it. If theexchange of heat is Q at temperature T, then generalizing relation (4.3), we can write-

$$\frac{Q}{T}=\text{constant}$$

This ratio is determined by two adiabatics, it can be regarded as some measure of the process.This constant ratio Q/T is given the name entropy of the system.

If S_1 and S_2 are the entropies corresponding to the adiabatic curves A_1 and A_2 respectively,then we can write

$$S_2 - S_1 = \frac{Q}{T} = \text{constant}$$

"If the adiabatics lie very close to each other and dQ is the quantity of heat absorbed or rejected at a temperature T in going from one adiabatic to the other", then change in entropy can be written as

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

In the above discussion, the changes from adiabatic A_1 to A_2 were considered isothermal butthis is not necessary. The only necessary condition is that the change should be reversible. In general, the change in entropy in passing from one adiabatic to another can be expressed as

$$\int_{S_1}^{S_2} dS = \Delta S = S_2 - S_1 = \int_A^B \frac{dQ}{T}$$

The expression $\int_A^B \frac{dQ}{T} = \int_{S_1}^{S_2} dS$ is a function of the thermodynamic coordinates of a system and refers to the value of the function at the final state minus the value at the initial state. Thisfunction is represented by the symbol S and is called entropy. Hence entropy of a system is a function of the thermo-dynamical coordinates defining the state of the system viz., thepressure, temperature, volume or internal energy and its change between the two states is equal to the integral of the quantity dQ/T between the states along any reversible path joining them. dS is an exact differential as it is differential of an actual function.

Since in an adiabatic change, no heat energy is given to or removed from the system i.e. there is no exchange of heat, dQ = 0, therefore, the change in entropy is

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

Thus, in an adiabatic process, the change in entropy of a system is zero or in other words, in the adiabatic processes, the entropy of a system remains constant. Due to this reason the adiabatic curves on the P-V diagram are called isentropics or constant entropy curves also.

It is, however, difficult to form physical conception of entropy as there is nothing physical to represent it and it cannot be felt like temperature or pressure. Now since

$$\text{change in entropy} = \frac{\text{Heat given or taken by the system}}{\text{Absolute temperature of the system}}$$

We conclude that dimensions of entropy are the same as the ratio of heat (or energy) and temperature. Its unit is joule/Kelvin (J/K).

5.2 Physical Significance of Entropy

The change in the entropy of a substance defined by the relation dS=dQ/T shows that the heat energy has the same dimensions as the product of entropy and absolute temperature. In earth's gravitational field the potential energy of a body is proportional to the product of its mass and the height above some zero level. A comparison indicates that if we regard heightas corresponding to temperature, then mass corresponds to entropy. Thus, entropy of a system is a quantity which bears to heat motion a similar relation as mass bears to linear motion.

5.3 Entropy changes in Reversible Process.

As shown in figure 2, let us investigate a completely reversible process: an ABCD Carnot cycle. The working substance absorbs a certain amount of heat Q1 at a constant temperature T1 of the source through the isothermal expansion from A to B. Entropy change is positive when the system absorbs heat Q1 at temperature T1.

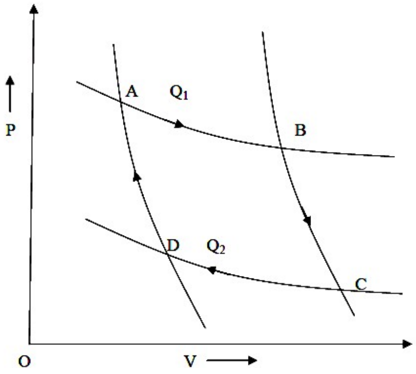


Fig: 5.2

Hence gain in entropy of working substance from A to B = Q_1/T_1

(Source loses this heat Q_1 at temperature T_1; therefore, its entropy decreases by Q_1/T_1

There is no change in entropy during the adiabatic expansion from B to C since heat is not absorbed or released. The working substance losses entropy from C to D = Q2/T2 (the sink gains this heat Q2 at temperature T2, therefore its entropy grows by Q2/T2) since the working substance gives out a certain amount of heat Q2 to the sink at a constant temperature T2.

Entropy remains unchanged during the adiabatic compression from D to B. Therefore, Q1/T1-Q2/T2 is an overall increase in working substance entropy over the whole cycle ABCDA.

But since in a complete reversible Carnot's cycle

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

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

It indicates that during a full cycle of a reversible process, the entire change in the working substance's entropy is zero. In the same way, the whole system's entropy change is also zero. Thus, in a reversible cycle, the system's entropy either stays constant or unchanged. i.e.

$$\oint dS = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = \sum \frac{Q}{T} = 0$$

where the integral sign with a circle refers to a complete cycle.

Hence we conclude that in a reversible cyclic process, the entropy change is zero. This is Clausius theorem.

5.4 Entropy changes in irreversible process

Let us suppose that the working substance in an engine performs an irreversible cycle of changes, absorbing an amount of heat Q_1 at a temperature T_1 from the source and rejecting the quantity of heat Q_2 at a temperature T_2 of the sink. Then the efficiency of this cycle is given by

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

According to Carnot's theorem, this efficiency is less than that of a reversible engine workingbetween the same two temperatures T_1 and T_2 for which

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

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

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

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

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

Considering the whole system, the source losses the entropy by an amount Q_1/T_1 and the sink gains the entropy Q_2/T_2 Therefore, the net change in entropy for the whole system is

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

which is clearly greater than zero or positive. Thus there is an increase in entropy of the system during an irreversible process.

As an example of irreversible process, consider the case of conduction or radiation. Suppose in a system, there are two objects A and B at temperatures T_1 and T_2 ($T_1 > T_2$) respectively. In conduction (or radiation) heat flows from the object of higher temperature to that of lower temperature. If an amount Q of heat is transferred then

Decrease in the entropy of object A = $\frac{Q}{T_1}$

Increase in the entropy of object B = $\frac{Q}{T_2}$

Therefore, the net increase in entropy = $\frac{Q}{T_2} - \frac{Q}{T_1} = Q(\frac{1}{T_2} - \frac{1}{T_1})$

Since $T_1 > T_2$, therefore the net increase in entropy is positive.

Now we may generalize the result and say that the entropy of a system increases in all irreversible processes. This is known as the 'Principle of increase of entropy'. In the processof equalization of temperature, entropy always increases.

5.5 Principle of Increase of Entropy

In the previous article, we have seen that in a reversible processes, the entropy remains unchanged while in an irreversible processes, it increases. Since, in general, most of the processes are not perfectly reversible, therefore, there is always an increase in the entropy always. If the processes occur in succession the entropy goes on increasing and tends to a maximum value. This is known as the principle of increase of entropy. It may be stated that the entropy of an isolated or self-contained system either increases or remains constant accordingly as the processes it undergoes are irreversible or reversible.

According to Clausius, the entropy of an isolated or self-contained system tends to a maximum value. Thus, the entropy of a system either increases or remains constant i.e. $dS \geq 0$

where, = sign stands for reversible processes and > sign for irreversible processes. Obviously,for the stability of a system its entropy must be maximum.

Since all physical events in the universe are irreversible, every action which takes place causes a certain amount of energy to be added to the universe in the form of heat through radiation, conduction, or friction. The additional energy is then unavailable for use in other processes.

This means that, due to irreversibility, all energy in the cosmos will eventually turn into heat energy and become unavailable for conversion into mechanical work; in other words, the universe's total energy will eventually approach zero.

It will be linked to a state of maximum entropy, wherein all temperature differences among the universe's bodies will be balanced via convection, among other factors. The uniformity of the universe's temperature would then prevent any heat flow, making it impossible for any heat engine to function in this state. This is often referred as concept of energy degradation and suggests that even total energy is conserved, it is changed into a form that can no longer be used for work.

With an increase in entropy, the thermal agitation and hence disorder of the molecules of substance increases i.e. growth of entropy implies a transition from order to disorder. Thusthe principle of increase of entropy is intimately connected with the less ordered state of affairs. As the temperature of a system is a measure of its degree of hotness, in a similar way, the entropy of a system is a measure of disorder in it. At absolute zero of temperature, the motion of the molecules of a substance ceases, the molecules become well arranged and the entropy becomes zero.

5.6 Temperature – Entropy diagram

The thermodynamic state of a substance can be determined by plotting the temperature as ordinate and entropy as abscissa. The resulting graph is known as temperature-entropy diagram and is used in the checking of efficient working of actual engines. The idea of T-S graph was first introduced by Gibbs.

If a thermodynamical system is given an infinitesimal amount of heat dQ , at temperature T then

$dQ = T\,dS$

where dS is the increase in the entropy of the system.

Therefore, in a process, total amount of heat given to the system is

$Q = \int T dS$

Obviously, the integral represents the area enclosed by the T-S diagram. Thus by finding the area of T-S diagram, we can find the amount of heat given to the system. The shape of the T-S graph depends upon the process.

An isothermal change is represented by a horizontal line parallel to the entropy axis while an adiabatic change is represented by a vertical line parallel to T-axis because in such a change S remains constant.

Let us study Carnot cycle represented by a temperature-entropy (T-S) diagram in figure (5.3).

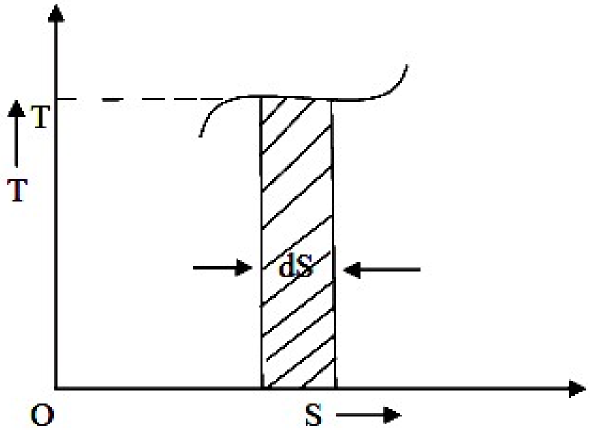


Fig: 5.3

As we know that Carnot's cycle consists of two isothermals and two adiabatics. The isothermals are represented by horizontal straight lines (parallel to entropy axis) and adiabatics by vertical straight lines (parallel to temperature axis) on a T-S diagram. In this way, in the figure, PQ represents the isothermal expansion at a constant temperature T_1 of the source, the vertical line QR is the adiabatic expansion during which there is no change in entropy but a fall of temperature from T_1 to T_2, the temperature of the sink. RS is the second isothermal representing compression at constant temperature T_2 and SP is the final adiabatic compression involving a rise of temperature from T_2 to T_1, entropy remaining the same.

The amount of heat energy absorbed in isothermal expansion PQ is given by the area under PQ, i.e. PQNM. In a similar way, the heat rejected in isothermal compression RS is given by the area SRNM.

Total heat absorbed = Area PQNM = $T_1 (S_2 - S_1)$

Heat energy converted into work = heat absorbed – heat rejected

= area PQNM – area SRNM = shaded area PQRS

= PS × SR = $(T_1 - T_2)(S_2 - S_1)$

$$\text{Therefore, efficiency of the engine } \eta = \frac{\text{Heat energy converted into work}}{\text{Total heat absorbed}}$$

$$= \frac{(T_1 - T_2)(S_2 - S_1)}{T_1(S_2 - S_1)} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

Thus, the T-S diagram gives an expression for efficiency of a Carnot's engine which only depends on the two working temperatures and not on the nature of the working substance.

5.7 Entropy of a perfect Gas

Let us calculate the entropy of a perfect gas. Let us consider 1 gm. of a perfect gas occupying a volume V at a pressure P and temperature T. Let a quantity of heat dQ be given to the gas, then by the first law of thermodynamics, we have

dQ = dU + dW

If C_v is the specific heat of the gas at constant volume, dT the rise in temperature, dV the change in volume then we can write

dU= C_v dT and dW = P dVUsing these values in equation we get-

dQ = C_v dT + P dVIf S is the entropy per unit mass of the gas, then

$$S = \int \frac{dQ}{T} = \int \frac{1}{T}(C_v dT + P\,dV)$$

$$= \int C_v \frac{dT}{T} + \int \frac{P}{T} dV$$

Now let us calculate the value of S in terms of temperature and volume. We know,

PV = rT or P/T = r/V, where r is the ordinary gas constant for unit mass of the gas. From equation, we get

$$S = \int C_v \frac{dT}{T} + \int \frac{r dV}{V}$$

$$= C_v \log_e T + r \log_e V + \text{constant}$$

$$S = C_v \log_e T + (C_p - C_v) \log_e V + \text{constant}$$

Where, r = $C_p - C_v$, Mayer's relation. C_p is the specific heat at constant pressure. Now let us calculate S in terms of temperature and pressure.

Again, PV = rT

Differentiating, we get

P dV + V dP = r dT

Or P dV = r dT- V dP

From equation, we get

$$S = \int C_v \frac{dT}{T} + \int \frac{P}{T} dV$$

$$= \int C_v \frac{dT}{T} + \int \frac{(r\,dT - V\,dP)}{T}$$

$$= \int C_v \frac{dT}{T} + \int r\left(\frac{dT}{T} - \frac{VdP}{rT}\right) = \int C_v \frac{dT}{T} + \int r\left(\frac{dT}{T} - \frac{dP}{P}\right) \qquad \text{(since } V/rT = 1/P\text{)}$$

$$= \int C_v \frac{dT}{T} + \int (C_p - C_v)\left(\frac{dT}{T} - \frac{dP}{P}\right) \qquad \text{(using } r = C_p - C_v\text{)}$$

$$= \int C_v \frac{dT}{T} + \int (C_p - C_v)\frac{dT}{T} + \int (C_p - C_v)\frac{dP}{P}$$

$$= \int C_v \frac{dT}{T} + \int C_p \frac{dT}{T} - \int C_v \frac{dT}{T} + \int (C_p - C_v)\frac{dP}{P}$$

$$S = \int \left\{C_p \frac{dT}{T} + (C_p\_C_v)\frac{dP}{P}\right\}$$

$$S = C_p \log_e T + (C_p - C_v) \log_e P + \text{constant}$$

Now let us calculate S in terms of pressure and volume.

$$PV = rT \quad \text{or} \quad T = \frac{PV}{r}$$

Differentiating above, we get

$$dT = \frac{P.dV + V.dP}{r}$$

Putting the value of dT, we get

$$S = \int \left[C_v \frac{PdV + VdP}{rT} + \frac{P\,dV}{T}\right]$$

$$= \int \left[C_v \frac{PdV + VdP}{PV} + \frac{P\,dV.r}{PV}\right] \qquad \text{(putting the value of T)}$$

$$= \int \left[C_v\left(\frac{dV}{V} + \frac{dP}{P}\right) + (C_p - C_v)\frac{dV}{V}\right]$$

$$S = \int \left[C_v \frac{dP}{P} + C_p \frac{dV}{V}\right]$$

$$S = C_v \log_e P + C_p \log_e V + \text{constant}$$

In the above calculations, we have assumed the entropy of the gas to be zero at zero temperature. In actual practice, however, we are concerned with a change in entropy of the gas, when the gas changes from a state of pressure P_1, volume V_1 and temperature T_1 to another of P_2, V_2 and T_2 respectively. This can be obtained by integrating relation between the limits T_1 and T_2. If we denote the change in entropy by $(S_2\text{-}S_1)$, then assumes the form, respectively, as

$$S_2\text{-}S_1 = C_v \log_e \frac{T_2}{T_1} + (C_p - C_v) \log_e \frac{V_2}{V_1}$$

$$S_2\text{-}S_1 = C_p \log_e \frac{T_2}{T_1} + (C_p\text{-} C_v) \log_e \frac{P_2}{P_1}$$

$$S_2\text{-}S_1 = C_v \log_e \frac{P_2}{P_1} + C_p \log_e \frac{V_2}{V_1}$$

All the above relations stand for unit mass of the gas. If the entropy S and the change in entropy (S_2-S_1) for m gms. of the gas is required, it can be obtained by multiplying these relations from by the given mass m.

5.8 Thermodynamic or Kelvin Scale of Temperature

We know that the efficiency of a reversible Carnot's engine depends only upon the two temperatures between which it works and is independent of the properties of the working substance. Thus there is a property which absolutely depends on temperature and on nothing else. Hence, if we define a temperature scale using this property of working of Carnot's engine, it is an absolute scale of temperature because it does not depend upon the particular property of any substance as in the case of other thermometric scales. Lord Kelvin workedout the theory of such an absolute scale called the Kelvin's work or thermodynamical scale and showed that it agrees with the ideal gas scale.

Presume that a reversible engine absorbs a certain amount of heat Q1 at temperature θ1 and rejects a certain amount of heat Q2 at temperature θ2, then the engine's efficiency depends on these two temperatures.

$$\eta = 1\text{-} \frac{Q_2}{Q_1} = f(\theta_1, \theta_2)$$

$$\frac{Q_1}{Q_2} = \frac{1}{1-f(\theta_1,\theta_2)} = F(\theta_1, \theta_2)$$

where F is some other function of θ_1 and θ_2.

Likewise, when the reversible engine operates between two temperatures, let's say θ2 and θ3 (where θ2>θ3), it will absorb heat from Q2 and reject heat from Q3.

$$\frac{Q_2}{Q_3} = \frac{1}{1-f(\theta_2,\theta_3)} = F(\theta_2, \theta_3)$$

Also, if it works between temperatures θ_1 and θ_3 ($\theta_1>\theta_3$), then

$$\frac{Q_1}{Q_3} = F(\theta_1, \theta_3)$$

Multiplying equations

$$\frac{Q_1}{Q_2} \times \frac{Q_2}{Q_3} = \frac{Q_1}{Q_3} = F(\theta_1, \theta_2) x\, F(\theta_2, \theta_3)$$

Comparing it with equation we have

$$F(\theta_1, \theta_3) = F(\theta_1, \theta_2) x\, F(\theta_2, \theta_3)$$

We refer this a functional equation. Since θ2 is absent from the left side, function F need to be selected in a such a way that no θ2 term present in the right hend side as well. This is possible if

$$F(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)} \text{ and } F(\theta_2, \theta_3) = \frac{\phi(\theta_2)}{\phi(\theta_3)}$$

where ϕ is another unknown function of temperature.

Equation (4.22) then gives

$$F(\theta_1, \theta_3) = \frac{\phi(\theta_1)}{\phi(\theta_2)} x \frac{\phi(\theta_2)}{\phi(\theta_3)} = \frac{\phi(\theta_1)}{\phi(\theta_3)}$$

Equation (4.19) gives

$$\frac{Q_1}{Q_2} = F(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)}$$

Since $\theta_1 > \theta_2$ and $Q_1 > Q_2$, the function $\phi(\theta_1) > \phi(\theta_2)$. Temperature can be determined by function˥(θ), which is a linear function of θ. Considering that˥(θ) shows a temperature on a new scale of τ (some multiple of θ), then

$$\frac{Q_1}{Q_2} = \frac{\tau_1}{\tau_2}$$

Equation defines the Kelvin's absolute thermodynamic scale of temperature. The ratio of the heat absorbed and rejected by a Carnot reversible engine working between any two temperatures on this scale is equal to the ratio of any two temperatures.

Now equation (4.23) can also be written as

$$\frac{Q_1 - Q_2}{Q_1} = \frac{\tau_1 - \tau_2}{\tau_1}$$

Since $(Q_1 - Q_2)$ represents the work done W per cycle by the reversible engine operating between the two temperature τ_1 and τ_2, temperatures are measured in terms of work and hence this scale is also known as work scale of temperature.

5.9 Absolute Scale of Temperature

We know that

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{\tau_2}{\tau_1}$$

If $\tau_2 = 0$, then efficiency

$$\eta = 1 - \frac{0}{\tau_1} = 0$$

Thus, for the efficiency to be unit i.e., $\eta = 1$, $\tau_2 = 0$

This temperature of the sink at which the efficiency of the reversible engine becomes unity is called the absolute zero of temperature. This is the thermodynamic definition of absolute zerotemperature.

From equation (4.25), it is clear that at the absolute zero of temperature ($\tau_2 = 0$), $Q_2 = 0$, therefore, $W = Q_1$. Therefore, the entire amount of heat absorbed by the reversible engine is converted into work and thus, the efficiency of the engine becomes unity. The temperature onthis scale can never be negative i.e. $\tau < 0$ is not possible. This is because if the temperature of the sink is a negative quantity (say –m) on this scale, then from equation (4.25),

$$\eta = 1 + \frac{m}{\tau}$$

The efficiency will be more than unity ($\eta > 1$) which is impossible. Because in this situation, the engine will be producing more work than the amount of heat received. This can never be true as it will be a violation of the second law of thermodynamics. Thus, negative temperatures are not possible on the absolute scale of temperature. That is why $\tau = 0$ is the lowest possible temperature and is called the absolute zero temperature.

5.10 Third Law of Thermodynamics: Unattainability of Absolute Zero.

It can be easily understood why the efficiency of an engine cannot be unity i.e. 100%. For this to happen we must have a sink at absolute zero temperature. But nature does not provide us with a sink at absolute zero. This temperature is neither available nor easily attainable. Therefore, 100% efficiency of an engine is not possible and thus absolute zero is also unattainable.

Self-Assessment

1. Explain entropy. Give its general concept and physical significance. Prove that the

entropyof a system increases in an irreversible process.

2. Give the definition of entropy. Prove that the entropy of a system remains constant in areversible process.
3. "The entropy of a substance is a unique function of its state," explain
4. Prove that the dimensions of entropy are the same as the ratio of heat and temperature.
5. Show that in a reversible cyclic process, the entropy change is zero.
6. The change in entropy of the universe in a reversible process is
7. (i) infinite (ii) zero (iii) 1 (iv) 100
8. The change in entropy of the working substance in a cyclic process is
    (i) 1
    (ii) infinite
    (iii) zero
    (iv) none of these
9. In an irreversible process, the entropy of the universe
    (i) remains constant
    (ii) decreases
    (iii) increases
    (iv) none of these
10. In a complete Carnot cycle, the change in the entropy of the universe is
    (i) Infinite
    (ii) Negative
    (iii) Positive
    (iv) zero
11. Entropy remains constant in
    (i) isothermal process
    (ii) adiabatic process
    (iii) cyclic process
    (iv) isobaric process
12. The area of the Carnot cycle on a T-S diagram represents
    (i) heat rejected to the sink
    (ii) work done in a cycle
    (iii)heat absorbed from the source
    (iv)efficiency of the engine

Chapter 6

Thermodynamics Potential

6.1 Thermodynamic Potentials

A scalar quantity which is used to represent a system's thermodynamic state is known as a thermodynamic potential. In 1886, Pierre Duhem introduced the idea of thermodynamic potentials. Four common thermodynamic potentials are: Internal energy (*U*), Gibbs energy (*G*), Enthalpy (*H*), Helmholtz free energy (*F*).

Thermodynamic potentials are of practical importance in studying the equilibrium conditions of a thermodynamic system. Any thermodynamic state of a system can be defined by the selection of thermodynamics variables, like P, V, T and S. Any two of these four variables can change on their own, and when they do, it makes the other variables known. Thus, there are only two independent variables and the others may be considered as their functions. Taking two of the four state variables P,V,T and S at a time, there are six variable pairs, i.e., (P,V), (P,T), (P,S), (V,T), (V,S), (T,S) corresponding to each pair, we can write a thermodynamic relation.

There exists certain relation between these thermodynamic variables. The first and second law of thermodynamics provide two relations given as

$dQ = dU + PdV$

and $dQ = TdS$ Therefore, $TdS = dU + PdV$or, $dU = TdS - PdV$

As change in internal energy of the system can be expressed in terms of four thermodynamic variables. However, for the complete knowledge of the system, some other quantities are required which hare based on different thermodynamics processes. For this purpose we introduce some thermodynamics functions depends on any of the two thermodynamic variable (P, V, T and S) known as thermodynamic potentials or the thermodynamic functions. There are four principal thermodynamic potentials and we shall discuss them one by one.

a. Internal Energy

The internal energy U of the system is a thermodynamic variable which characterises the system. This is also called the intrinsic energy or internal energy. The path followed between the two states has no impact on how the internal energy varies as the system changes between them.

The internal energy of a system is defined as the equation

$dU = dQ - dW$

where $dW = PdV$ is the external work done while $dQ = TdS$

$dU = TdS - PdV$ ... (6.1)

For an adiabatic process

$dQ = 0$

$dU = -PdV$

i.e., the work done by the system in an adiabatic process is at the expense of its internalenergy.

For an isochoric adiabatic process

$dV = 0$ and $dQ = 0$ $dU = 0$ or $U =$ constant

i.e., the internal energy of system remains constant in an isochoric adiabatic process.

b. Enthalpy

Enthalpy is an extensive thermodynamical property and is of particular significance. It is defined as

$H = U + PV$

For an infinitesimal reversible change, we get

$dH = dU + PdV + VdP$

$dH = TdS - PdV + PdV + VdP$ (Equation 6.1)

$dH = TdS + VdP$ ... (6.3)

(a) For reversible isobaric process

$dP = 0$

$dH = TdS = dQ$

i.e., Amount of heat absorbs is equal to change in enthalpy, as in case of isobaric process.

For an isobaric adiabatic process

$dP = 0$ and $dQ = 0$

$dH = 0$ or $H =$ Constant

i.e., enthalpy remains constant in a reversible isobaric adiabatic process.

c. Helmholtz Free Energy

The Helmholtz free energy is also called as ‘Helmholtz function' or ‘Thermodynamic Potential at constant volume' and It is defined by the equation

$F = U - TS.$

Since U, T and S and F are perfect differential. When a system experiences an infinitesimal reversible change from initial equilibrium to final equilibrium state, the Helmholtz free energy changes by an amount given by differentiating the above relation as

$dF = dU - TdS - SdT$

But $dU = TdS - PdV$, as shown in the earlier case.

$dF = (TdS - PdV) - TdS - SdT$

$dF = -SdT - PdV$ ... (6.2)

Equation represent the variation in Helmholtz free energy in an infinitesimal reversible process.

For Reversible isothermal process

$dT = 0$

$dF = -PdV$ or $PdV = -dF$

thus, decrease in Helmholtz free energy equal to the work done in a reversible isothermal process

For isothermal isochoric process

$dT = 0$ and $dV = 0$

$dF = 0$ or $F = \text{Constant}$

i.e., during isothermal isochoric process, Helmholtz free energy remains constant.

d. Gibb’s Free Energy

This is also known as ‘Gibb's Function' or ‘Thermodynamic Potential at constant pressure'.It is defined as

$G = H - TS$

For an infinitesimal reversible process

$dG = dH - TdS - SdT$

But $dH = TdS + VdP$

$dG = VdP - SdT$ ... (6.4)

For an isothermal isobaric process

$dT = 0$ and $dP = 0$

$dG = 0$ or $G = \text{Constant}$

Thus, Gibbs free energy remains constant in an isothermal isobaric process.

6.2 Relations of Thermodynamics potential and variables

Because the thermodynamic variables S, T, P, and V may be derived from the four numbers U(S,V), F(T,V), H(S, P), and G (P, T) through their differentiations with regard to the independent variables linked to them, they are known as thermodynamic potentials. Now let's extract them.

a. Thermodynamic Potential U (S, V)

Taking partial derivatives of the intrinsic energy equation (6.1) with respect to variable S, and V, we get

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

These are the relation connecting the internal energy U with the thermodynamic variable S, V, T and P.

Now since dU is perfect differential, we must have

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S$$

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

This is the first thermodynamic relation of Maxwell.

b. Thermodynamic Potential F (T, V)

Taking the partial derivatives of F from equation (6.2), we have

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

Since dF is a perfect differential, we have

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

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

This is the second thermodynamic relation of Maxwell.

c. Thermodynamic Potential H (S, P)

The partial derivatives of H from equation (6.3) are

$$\left(\frac{\partial H}{\partial S}\right)_P = T \text{ and } \left(\frac{\partial H}{\partial P}\right)_S = V$$

Since dH is a perfect differential, we have

$$\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_S$$

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

This is the third thermodynamic relation of Maxwell

d. Thermodynamic Potential G (P, T)

The partial derivatives of G from equation (6.4) are

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

Since dG is a perfect differential, we have

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P$$

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

This is fourth thermodynamic relation of Maxwell.

Thus, the thermodynamical variables S, T, P and V can be written by using equation(6.5), (6.7), (6.9) and (6.11) as

$$S = -\left(\frac{\partial G}{\partial T}\right)_P = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_S = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$V = \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T$$

These equations (6.13) give the value of thermodynamic variables in terms of thermodynamicpotentials.

6.3 Applications pf Thermodynamics Potentials and Maxwell’s Equation

a. Clausius-Clapeyron Latent Heat Equation

Maxwell's second thermodynamic relation is written as:

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

Multiplying both sides by T, we have

$$T\left(\frac{\partial S}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$ But, $T\partial s = \partial Q$ (from second law of thermodynamics). Hence

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

Hear $\left(\frac{\partial Q}{\partial V}\right)_T$ represents the quantity of heat absorbed or liberated per unit change in volume at constant temperature. This mean that at constant temperature the heat absorbed or liberated bring out simply a change in the volume of the substance. Therefore, the quantity of heat which is absorbed or released at constant temperature must be latent heat, and the explanation for the volume change must be a change in condition. Let L be the latent heat when a substance with a unit mass changes its volume from V1 to V2 at constant temperature.

$\partial Q = L$ and $\partial V = V_2 - V_1$

Substituting these values in the above expression

$$\left(\frac{L}{V_2 - V_1}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\frac{L}{V_2 - V_1} = T\frac{dP}{dT}$$

$$\frac{dP}{dT} = \frac{L}{T\,(V_2 - V_1)}$$

This is the Clausius-Clapeyron latent heat equation.

b. Joule Thompson Effect

When a gas under a constant pressure is made to pass through an insulated porous-plug to a region of lower constant pressure, it suffers a change in temperature. This is called the 'Joule - Thomson or Joule-Kelvin effect'. The process is called the 'throttling process'. The change in temperature is proportional to the pressure-difference between the two sides of the plug. At ordinary temperature, all gases, expect hydrogen and helium, show a cooling effect while hydrogen and heliumshow a heating effect.

Let us consider 1 mole of gas. Let $P_1$and V_1 be its pressure and volume before passing and P_2 and V_2 the pressure and volume after passing through the porous plug. The net external work done by the gas in passing through the plug is then P_2V_2 - P_1V_1. Since there is no heat-exchange between the gas and its surroundings, this work must come from the internal energy of the gas. Thus, if U_1 and U_2 be the internal energies of the gas before and after passing through the plug, we have from the firstlaw of thermodynamics

$U_1 - U_2 = P_2V_2 - P_1V_1$

Or $U_1 + P_1V_1 = U_2 + P_2V_2$

$U + PV = \text{constant}$

The quantity $(U + PV)$ which remains constant during a throttling process, is called the enthalpy (H)of the gas. Thus, we may write

$dH = d(U + PV) = 0 dU + PdV + VdP = 0$

But $dU + PdV = dQ$ and $dQ = TdS$ (first and second law respectively). Therefore,

$TdS + VdP = 0$ …(1)

Let as assume that the entropy S is the function of variables P and T. Since dS is a perfect differential,we have

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Substituting this value of dS in equation (1), we get

$$T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP + VdP = 0$$

(2)

But $dQ = TdS$. Therefore, $T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P$ where C_P is the specific heat at constant pressure.

Maxwell's fourth relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

Therefore equation (2) becomes

$$C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP + VdP = 0$$

$$C_P dT = \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP$$

$$\frac{dT}{dP} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

Since, the enthalpy H remains constant during throttling process, $\frac{dT}{dP}$ as $\left(\frac{\partial T}{\partial P}\right)_H$ which is called the Joule-Thomson coefficient μ. Thus,

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \qquad (4)$$

Integrating it, we get the temperature-change for finite drop in pressure from P_1 to P_2 as

$$\Delta T = \frac{1}{C_P}\int_{P_1}^{P_2}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]dP$$

For ideal Gas:

For 1 mole of a perfect gas, the equation of state is PV=RT. Differentiating it with respect to T, taking P constant, we have

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$T\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}T = V$$

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = 0$$

Substituting this value for Joule-Thomson coefficient, we get

$\mu = 0$ …(3)

Thus, the Joule-Thomson effect for a perfect gas μ is zero.

For Real Gas:

For a van der Waals' gas, we have

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Differentiating it with respect to T, taking P constant, we have

$$\left(P + \frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P - \frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P (V - b) = R$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\left(P+\frac{a}{V^2}\right)-\frac{2a}{V^3}(V-b)}$$

$$= \frac{R}{\frac{RT}{V-b}-\frac{2a}{V^3}(V-b)} = \frac{R(V-b)}{RT-\frac{2a}{V^3}(V-b)^2}$$

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{RT(V-b)}{RT-\frac{2a}{V^3}(V-b)^2} - V$$

$$= \frac{-RTb+\frac{2a}{V^2}(V-b)^2}{RT-\frac{2a}{V^3}(V-b)^2}$$

$$= \frac{2aV(V-b)^2-RTV^3b}{RTV^3-2a(V-b)^2}$$

Since, a and b are very small quantities, we replace $2aV(V - b)^2$ by $2aV^3$ in the numerator and ignore $2a(V - b)^2$ in comparison with RTV^3 in the denominator. Then, we get

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{2aV^3 - RTV^3 b}{RTV^3}$$

$$= \frac{2a}{RT} - b \qquad (5)$$

Substituting this result in equations (4) and (5), we get

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right]$$

$$\Delta T = \frac{1}{C_P}\int_{P_1}^{P_2}\left[\frac{2a}{RT} - b\right]dP = \frac{\frac{2a}{RT} - b}{C_P}(P_2 - P_1).$$

$$\Delta T = -\frac{\frac{2a}{RT} - b}{C_P}(P_2 - P_1)$$

The pressure is lower on the emergent side of the porous plug ($P_2 < P_1$). Hence, we may write as

This expression shows the Joule-Thomson effect for real gas.

6.4 Cooling due to adiabatic demagnetization

In 1926, Debye and Giauque showed theoretically that the temperatures considerably below 1K could be obtained by the process known as adiabatic demagnetization of a paramagnetic salt (i.e., those substances for which the magnetic susceptibility χ is small, but positive).

Experimental Method

There is liquid helium around vessel A, in which the paramagnetic specimen (salt) is suspended. Under low pressure, liquid helium placed in Dewar flask D is boiled. Liquid hydrogen in a Dewar flask D2 is positioned around it. The helium gas and salt are in contact. As shown in figure 6.1, a magnetic field of approximately 30,000 Gauss is applied.

The specimen (salt) gets magnetized when the magnetic field is switched on. In order to guarantee that the sample is thermally isolated, hydrogen gas is initially introduced into A and then pumped out using a high vacuum pump. This reduces the heat generated by magnetization. The sample monitors the temperature in the intervening period. The magnetic field is switched off at this point. The substance undergoes adiabatic demagnetization, which reduces its temperature. By wrapping a coaxial solenoid coil around tube A and measuring the material's self-inductance and thus its susceptibility at the start and finish of the experiment, the temperature of the specimen is determined. The phenomena is called Magneto-Caloric effect.

In 1994, Haas used a double sulfate of potassium and aluminum to produce temperatures as high as 0.002 K. Klerk, Stenland, and Gorter used a powder mixture of aluminium and chromium alum crystals and lowered the temperature to 0.0014 K.

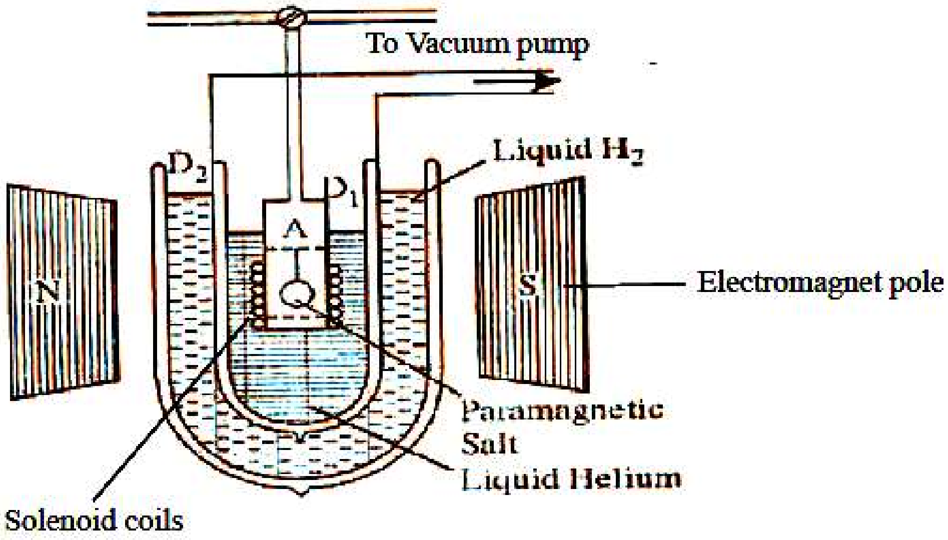


Fig : 6.1

Theory

Then a paramagnetic material placed in a magnetizing field (H), so that its magnetic dipoles align in parallel to magnetizing filed. Becouse of alignment of dipole a magnetic moment produced per unit volume, which is called intensity of magnetization (I). I is inversely proportional to the temperature T of the paramagnetic material and directly proportional to the magnetizing field H, based on Curie's law.

Thus

$$I \propto \frac{H}{T}$$

$$I = C\left(\frac{H}{T}\right) \qquad (1)$$

where C is Curie constant of paramagnetic substance.

If V is the volume of I mole of the substance then intensity of magnetization of I mole of paramagnetic substance M = IV

$$M = CV\left(\frac{H}{T}\right) \qquad (2)$$

Let 1 mole of paramagnetic substance is placed in magnetizing field.

H. Then its thermodynamic behaviour the substance can be expressed in terms of thermodynamic quantities P, V, T and S. In thermodynamic system, increment in in pressure P decreases the volume V. correspondingly increase in H results in increase in M. by replacing P by –H and V by M in Maxwell's third thermodynamic relation

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

(3)

We have $$\left(\frac{\partial T}{\partial H}\right)_S = -\left(\frac{\partial M}{\partial S}\right)_H$$

or, $$\left(\frac{\partial T}{\partial H}\right)_S = \frac{-\left(\frac{\partial M}{\partial T}\right)_H}{\left(\frac{\partial S}{\partial T}\right)_H}$$

Multiplying numerator and denominator by T, we get

$$\left(\frac{\partial T}{\partial H}\right)_S = \frac{-T\left(\frac{\partial M}{\partial T}\right)_H}{T\left(\frac{\partial S}{\partial T}\right)_H}$$

$$\left(\frac{\partial T}{\partial H}\right)_S = \frac{-T\left(\frac{\partial M}{\partial T}\right)_H}{\left(\frac{\partial Q}{\partial T}\right)_H} \qquad (T\partial S = \partial Q)$$

(4)

$$\left(\frac{\partial T}{\partial H}\right)_S = -\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H$$

(5)

Where

$$\left(\frac{\partial Q}{\partial T}\right)_H = C_H,$$

(6)

the specific heat of the substance at constant magnetic field H. Since the process is carried out adiabatically (S = constant), we may write for infinitesimalchange,

$$dT = -\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H dH$$

(7)

When field changes from H_1 -> H_2, temperature change represented by

$$\Delta T = -\frac{T}{C_H}\int_{H_1}^{H_2}\left(\frac{\partial M}{\partial T}\right)_H dH$$

(8)

Differentiating equation (2) with respect to T at constant H, we get

$$\left(\frac{\partial M}{\partial T}\right)_H = -\frac{CVH}{T^2} \tag{9}$$

Substituting this value in equation (8), we have

$$\Delta T = -\frac{T}{C_H}\int_{H_1}^{H_2}\left(-\frac{CVH}{T^2}\right)dH$$

$$\Delta T = \frac{CV}{C_H T}\int_{H_1}^{H_2} HdH$$

$$\Delta T = \frac{CV}{2C_H T}\left(H_2^2 - H_1^2\right) \tag{10}$$

Changes in magnetic field from $H_1 = H$ to $H_2 = 0$, its effect on temperature

$$\Delta T = \frac{CV}{2C_H T}H^2 \tag{11}$$

The following conclusions can be drawn from the equation (11)

The temperature of paramagnetic material changes as the magnetizing field is reduced. Greater is the initial field H and lower is the initial temperature T, greater is the temperature fall ΔT.

It is to be noted that here CV is the Curie constant per mole. If 1 gm of paramagnetic substance is taken, then CV would stand for Curie constant per gm.

6.5 Phase Transitions

Whenever system parameters like pressure and temperature alter, a phenomenon known as a phase transition takes place where there is an abrupt change between thermodynamics phases. The presence of singularities (non-analyticities) in functions that represent physical variables is the theoretical description of a phase transition, which can be defined as a sudden change in macroscopic attributes. An illustration of this is the melting of ice, when the system has to be supplied with latent heat, allowing the entropy to increase significantly. The amount of water changes quickly when it boils and transforms into vapor. From a physics viewpoint, the conflict between the system's (internal) energy E and entropy S, which together define its free energy F = E − TS, is what allows a phase transition to occur.

One of the two terms predominates based on the value of the external factors (such as T), with the first term (E) favoring order and the second (S) favoring disorder. Phase shifts can be broadly divided into two types based on the degree of singularity in physical quantities, as per the standard classification. The transition is of first order when there is a discontinuity in the free energy F's first-order derivative. When there is a discontinuity or divergence in the second- or higher-order derivative of the free energy, the transition can be referred as continuous. Additionally, phase transitions are frequently referred to by the order of the derivative that exhibits a discontinuity or divergence first; for example, a phase transition is referred to be second order if the free energy's second-order derivative exhibits a discontinuity or divergence first.

6.6 Classification of Phase Transition

Latent heat is required for most of natural transitions between phases, that occur at constant temperature. However, latent heat is not needed for certain phase transitions, such as the change of a material from a ferromagnetic to a paramagnetic phase at its Curie temperature, the change of a compound from a superconducting to a non-superconducting state, the change from liquid He I to liquid He II, etc. P. Ehrenfest proposed a classification of phase transitions and classified them into first and second order phase transitions based on the presence of latent heat.

6.7 First order Phase Transitions

It can be defined as, changes in Gibbs function with respect to pressure and temperature at the transition point. In other words the first derivatives of Gibb's function are discontinuous. However, the value of the Gibbs function is the same in both the phases at equilibrium. In these cases, as per the transfer of heat there is change in entropy and volume. These changes are represented graphically in Figure 6.5.

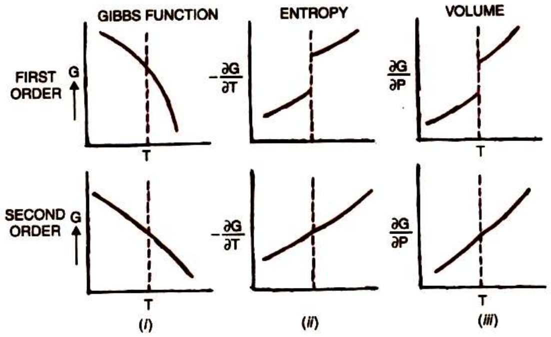


Fig: 6.2

6.8 Second order Phase Transition

Ehrenfest defined second order phase transitions as those in which the Gibbs function and its first derivatives are continuous during the phase transition but the Gibbs function's second derivatives are discontinuous. Second order phase transitions can be defined as the phenomenon that takes place with no change in entropy and volume at constant temperature and pressure. It has been found in case of transition from liquid helium I to liquid helium II, that neither a change in volume nor a transfer of heat occur. We refer to these transitions as second order phase transitions. Figure 6.2 shows a graphic representation of these modifications.

6.9 Clausius Clapeyron Equation and Ehrenfest equations

Clapeyron in 1834, and Clausius in 1850, deduced an important equation which describes conditions governing changes of state, such as melting of solids and boiling of liquids. It represented the 'Clausius-Clapeyron Latent Heat Equation'

The two isothermals at infinitely close temperatures T and (T+dT), each, should be represented by ABCD and EFGH. The portions AB and EF, with reference to Figure 6.2, depict the substance in its liquid state. Substance is restricted to its liquid condition at B and F. The change between the liquid and vapour states is ongoing along BC and FG, and they coexist in balance. The chemical is only in the vapor state at C and G. The chemical is in the vapor state from C to D and G to H. Let V1 and V2 be the substance's volumes at F and G, respectively, and let P and (P+dP) be the saturated vapour pressures of the liquid at temperatures T and (T+dT), respectively.

Let's sketch two adiabatics that meet the lower isothermal at M and N, respectively, from F and G. Consider the following scenario: 1 gm of the material is wrapped around a reversible Carnot cycle FGNMF, where it is compressed isothermally along NM and adiabatically along MF, and allowed to expand isothermally along FG and adiabatically along GN.

When a substance entirely transitions from a liquid state at F to a vapour state at G, the amount of heat Q1 absorbed along FG is equal to the latent heat of vaporization (L+dL) at temperature (T+dT). Furthermore, L, the latent heat at temperature T, is the amount of heat Q2 rejected all over the isothermal compression NM. Here, temperature is thought to affect latent heat.

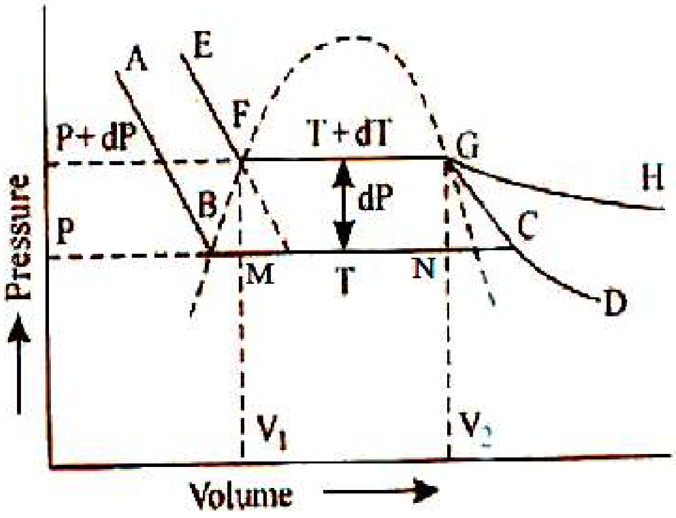


Fig : 6.3

Applying the principle of Carnot's reversible cycle

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \quad \text{or} \quad \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

or,

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

We have $Q_1 = L + dL, Q_2 = L, T_1 = T + dT$ and $T_2 = T$

$$Q_1 - Q_2 = L + dL - L = dL \text{ and } T_1 - T_2 = T + dT - T = dT$$

$$\frac{dL}{L} = \frac{dT}{T}$$

$$dL = \frac{L}{T} dT$$

The heat converted into work in cycle FGMNF is

$$Q_1 - Q_2 = L + dL - L = dL$$

But the work done during the Carnot cycle is given by the area FGMNF, which may betreated as a parallelogram.

Hence, dL (in work unit) = Area FGMNF = FG × perpendicular distance between FG and NM

$= (V_2 - V_1) \times dP$

Specific volume of vapour and liquid are represented by V2 and V1, and dP change in pressure between FG and NM.

Substituting this value of dL in equation (1)

$$dP(V_2 - V_1) = \frac{L}{T}dT$$

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \qquad (1)$$

Clapeyron's latent heat equation represented by eq. (1) .

Applications

1. By Rate of changing the pressure effect on melting point.

When a solid substance change into liquid:

(i) dP/dt is a positive if V_2 is greater than V_1. Melting point of the substance increase with increase in pressure and vice versa

(ii) dP/dt is negative if V_2 is less than V_1. Melting point of the substance decreases with increasing in pressure or vice-versa. For example, in case of melting of ice, volume of water after melting is less than volume of ice. Therefore, the melting point of ice decreases by increases in pressure.

Self-Assessment

1. Define thermodynamic potentials? Why they are known as potentials?
2. What is the physical significance of thermodynamic potentials.
3. Deduce Maxwell's relations using thermodynamic potentials.
4. Prove in an isobaric process change in enthalpy is equal to the heat transferred.
5. Prove that work done by the system is equal to decrement in Helmholtz free energy.
6. Four thermodynamic potentials are:

a) Pressure, Volume, Temperature and Internal energy function

b) Volume, Pressure, Internal Energy and Helmholtz function

c) Internal energy, Helmholtz function, Enthalpy and Gibbs function

d) None of these.

7. Saturated vapour pressure’s specific heat is:

a) Zero

b) Positive

c) Negative

d) Sometimes positive sometimes negative.

8. Paraffin wax contracts on solidification. The melting point of wax will

a) increase with pressure

b) decrease with pressure

c) no change with pressure

d) decrease linearly with pressure.

9. The change in each thermodynamic function:

a) depends on path between initial and final states

b) is independent of path between initial and final states

c) is always zero

d) none of above.

10. Which thermodynamic function represents the maximum amount of non-expansion work that can be extracted from a closed system at constant temperature and pressure?

a) Internal Energy (U)

b) Enthalpy (H)

c) Gibbs Free Energy (G)

d) Helmholtz Free Energy

Chapter 7

Classical Statistics

7.1 Introduction of classical statistics and theory of radiation

Classical statistics refers to the branch of statistics that deals with principles and techniques derived from the work of mathematicians and statisticians from the 18th and 19th centuries, such as Gauss, Laplace, and Fisher. It encompasses foundational concepts like probability theory, hypothesis testing, and estimation. Classical statistics typically assumes that data are generated from known distributions (e.g., normal distribution) and focuses on frequentist inference, where probabilities are interpreted as long-run frequencies of events.

On the other hand, the theory of radiation pertains to the study of the emission, transmission, and absorption of radiation, particularly electromagnetic radiation such as light, radio waves, and X-rays. This theory has applications across various scientific disciplines, including physics, chemistry, astronomy, and environmental science. It explores how radiation interacts with matter, how it propagates through different media, and its implications for phenomena ranging from atomic structure to the behavior of stars.

Together, the application of classical statistics in the theory of radiation involves using statistical methods to analyze experimental data related to radiation measurements, infer properties of radiation sources, assess uncertainties in measurements, and validate theoretical models. This integration allows scientists to make rigorous and quantitative assessments of radiation phenomena, contributing to advancements in both fundamental science and practical applications such

In thermodynamics, microstates and macrostates are key concepts that describe the state of a system at different levels of detail and abstraction.

7.2 Microstate

- A microstate refers to a specific, detailed configuration of all the microscopic constituents (atoms, molecules, particles) of a system at a particular instant in time. It is a snapshot that includes the exact positions and momenta (or velocities) of every particle in the system.
- Microstates are numerous and represent all possible configurations that the system's particles can occupy within the constraints of the system's energy, volume, and number of particles.

- In statistical mechanics, microstates are fundamental because they provide a complete description of the system's microscopic state.

7.3 Macrostate

A macrostate describes the state of a system in terms of macroscopic variables such as temperature, pressure, volume, and entropy. These variables are observable and measurable properties of the system that do not require knowledge of the exact microscopic details.

- A macrostate corresponds to a large number of microstates that share the same macroscopic properties. In other words, it represents a collection or ensemble of microstates that are indistinguishable in terms of macroscopic observables.
- Macrostates are useful because they simplify the description of a system by focusing on the average behavior of the system's constituents rather than on their individual behaviors.

7.4 Relationship Between Microstates and Macrostates

- The relationship between microstates and macrostates is central to statistical thermodynamics. The macroscopic properties of a system, such as temperature or pressure, arise from the statistical average over all possible microstates that are consistent with a given macrostate.
- Statistical mechanics uses this relationship to connect the microscopic behavior (described by microstates) with the macroscopic properties (described by macrostates) of a system. For example, The average kinetic energy of the gas particle is related to its temperature, which can be understood by considering the distribution of velocities across all possible microstates.
- The Boltzmann entropy formula, $S=k\ln(\Omega)$, where Ω is the number of microstates corresponding to a particular microstate, quantifies the relationship between microstates and macrostates by linking the statistical entropy (macroscopic property) to the multiplicity of microstates (microscopic configurations).

In summary, microstates and macrostates provide complementary perspectives on the state of a thermodynamic system: microstates describe detailed configurations of particles, while macrostates describe averaged properties that emerge from these configurations. Statistical mechanics uses these concepts to explain how macroscopic thermodynamic quantities arise from microscopic dynamics.

7.5 Elementary Concept of Ensemble

In the context of statistical mechanics, an ensemble is a theoretical construct used to describe the collective behavior of a large number of identical or similar systems that are in the same macroscopic state. The concept of an ensemble is fundamental to bridging the gap between the microscopic behavior of individual particles (microstates) and the macroscopic properties of a system (macrostates).

Key Concepts:

a. Ensemble Definition:

An ensemble represents a collection of many copies of a system that are identical in terms of their macroscopic properties (e.g., temperature, pressure, volume).

Each member of the ensemble is considered to be in a different microstate, reflecting the various possible configurations of the system's microscopic constituents (atoms, molecules, etc.).

b. Types of Ensembles

Microcanonical Ensemble: The ensemble describes a system with fixed volume, energy and number of particles and used for studying isolated systems.

Canonical Ensemble: its defines a system that can exchange energy with a heat bath at constant temperature. It is useful for describing systems in thermal equilibrium with a reservoir.

Grand Canonical Ensemble: Its defines a system that can exchange both energy and particles with a reservoir at constant temperature and chemical potential. It is used for systems with variable particle numbers, like gases.

c. Statistical Averages

The ensemble average of a physical quantity (e.g., energy, pressure) is obtained by averaging the corresponding quantity over all microstates weighted by their probabilities.

Ensemble averages provide a means to connect the statistical distribution of microstates with observable macroscopic properties of the system.

d. Equivalence of Ensembles

The principle of ensemble equivalence states that in the thermodynamic limit (large number of particles), different ensembles (microcanonical, canonical, grand canonical) yield the same macroscopic predictions for most physical quantities.

This equivalence allows different statistical approaches to yield consistent results and provides flexibility in choosing the most convenient ensemble for a particular problem.

e. Application in Statistical Mechanics

Ensembles are central to statistical mechanics as they provide a systematic framework for calculating thermodynamic properties from microscopic principles.

They enable predictions of how macroscopic properties (e.g., temperature, pressure) arise from the statistical behavior of individual particles, thus linking microscopic dynamics with observable phenomena.

In essence, the concept of an ensemble in statistical mechanics is crucial for understanding how statistical averages over many possible microscopic states lead to the emergence of macroscopic thermodynamic properties. It provides a powerful tool for describing and predicting the behavior of systems consisting of a large number of interacting particles.

7.6 Phase Space

Phase space in the context of classical mechanics refers to the abstract space in which all possible states of a system are represented, each state being determined by the positions and momenta (or velocities) of all particles in the system. Here are the key aspects and implications of phase space:

a. Definition and Dimensions

Phase space is a mathematical space where each point corresponds to a unique state of a system. For a system of N particles in three-dimensional space, the phase space is 6N-dimensional because each particle contributes 6 coordinates (3 for position and 3 for momentum).

The coordinates in phase space are often denoted collectively as {qi, pi}, where qi represents the position coordinate and pi represents the momentum coordinate of the i-th particle.

b. Hamiltonian Dynamics

In classical mechanics, the evolution of a system's state in phase space is governed by Hamilton's equations of motion. These equations describe how the positions and momenta of particles change over time in response to the forces acting on them.

Hamilton's equations are derived from the system's Hamiltonian, which is the total energy function of the system expressed in terms of positions and momenta.

c. Representation of State

A single point in phase space represents a microstate of the system, specifying the exact positions and momenta of all particles at a given instant.

The trajectory of a system in phase space traces out a path that represents its evolution over time, reflecting how the positions and momenta of particles change as the system moves under the influence of internal and external forces.

d. Statistical Mechanics

Phase space is also crucial in statistical mechanics, where it extends to include the distribution of possible states that a system can occupy. In this context, phase space represents all possible microstates that are consistent with the macroscopic properties (e.g., temperature, volume) of the system.

Statistical ensembles (such as microcanonical, canonical, and grand canonical ensembles) are defined in phase space, providing a framework for calculating thermodynamic quantities like entropy, temperature, and pressure from the statistical distribution of microstates.

e. Quantum Mechanics

In quantum mechanics, phase space is generalized to include operators that correspond to position and momentum observables, although the concept differs from classical phase space due to the principles of quantum uncertainty and wave-particle duality.

In summary, phase space is a fundamental concept in classical mechanics that provides a comprehensive description of a system's state in terms of both its positions and momenta. It serves as a crucial tool for analyzing the dynamics of physical systems and for connecting microscopic details with macroscopic observations and predictions in both classical and statistical mechanics.

Self-Assessment

1. Define a macrostate and a microstate in the context of statistical mechanics.
2. How are macrostates and microstates related in statistical mechanics?
3. What does entropy represent in terms of microstates and macrostates?
4. Explain why a macrostate can have multiple microstates associated with it.
5. How does Boltzmann's entropy formula relate to the concepts of macrostates and microstates?
6. In statistical mechanics, a macrostate is defined by:
   A) The specific arrangement of particles in a system
   B) The total energy of the system
   C) The overall properties of a system like temperature and pressure
   D) The number of particles in the system
7. A microstate refers to:

A) A large-scale observable property of a system

B) A specific configuration of the individual particles in a system

C) The average kinetic energy of particles in a system

D) The volume occupied by the system

8. The entropy of a system is related to:

A) The number of microstates corresponding to a given macrostate

B) The average energy per particle in the system

C) The rate of change of temperature with respect to energy

D) The density of the system

9. According to statistical mechanics, increasing the number of microstates corresponding to a macrostate generally leads to:

A) Decrease in entropy

B) Increase in entropy

C) No change in entropy

D) Increase in temperature

10. The Boltzmann distribution describes the:

A) Distribution of macrostates in a system

B) Distribution of microstates in a system

C) Distribution of energy levels in a system

D) Distribution of pressure and volume in a system

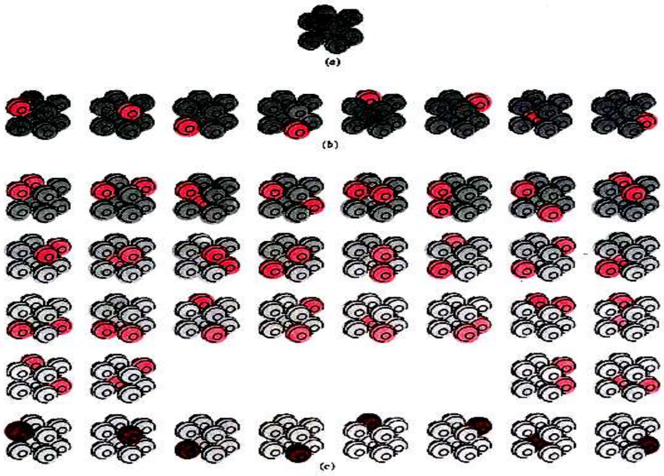
Chapter 8

Thermodynamic Probability

8.1. Thermodynamic Probability

As the section on atoms, molecules, and probability has demonstrated, we need to establish a generic method for assessing whether the final state is more likely than the initial state in order to forecast whether a chemical change is spontaneous or not. The thermodynamic likelihood, denoted by the number W, can be utilized for this purpose. The number of different microscopic configurations that lead to the same macroscopic state is known as W. After thinking about a few instances, the importance of this concept becomes clearer.

A crystal with just eight atoms at absolute zero temperature is shown in Figure 8.1a. Assume that a tiny amount of energy is added to cause one of the crystal's atoms to vibrate, thus raising the temperature a little. Since we could provide the energy to any one of the eight atoms, there are eight methods in which we could accomplish this. The eight options are displayed in Figure 8.2b.

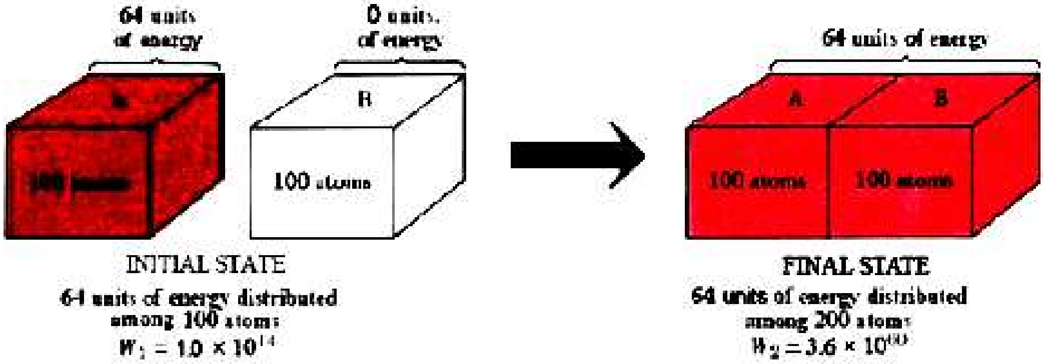


The thermodynamic probability W of an eight-atom crystal at three distinct temperatures is shown in Figure 8.1. (8.1 a) There is exactly one possible arrangement for the crystal at 0 K, ensuring that W = 1. (8.1 b) Eight equally likely configurations are available if sufficient energy is applied to cause any one of the atoms to vibrate (color), and W = 8. (8.1 c) Two distinct atoms can vibrate simultaneously (bright color) or one atom can have all the energy (dark color) if the energy is doubled. Compared to earlier, there are a lot more equally likely combinations (W = 36).

We state that W = 8 for the crystal at this temperature since all eight scenarios point to the crystal having the same temperature. It is important to acknowledge that the crystal will not remain in any of these eight configurations indefinitely. Every atom will continuously exchange energy with every other atom, making each of the eight configurations equally likely.

Now let's add another exact equal amount of energy to the first, so that there is just enough to cause the vibrations of two molecules. This energy can be allocated to the eight atoms in 36 distinct ways (Figure 8.3 c). For the crystal at this second temperature, we state that W = 36. Any one of the 36 potential configurations has an equal chance of containing the crystal since energy is constantly moving from one atom to another.

Our eight-atom crystal at absolute zero serves as a third illustration of W. There is only one feasible configuration, and W = 1, since there is no energy to be transferred between atoms. This holds true for both the hypothetical crystal and, most likely, a real crystal with a high number of precisely organized atoms at absolute zero.



In Figure 8.2 Heat transfer and likelihood of thermodynamics. Since there are many more ways to distribute 64 vibrational energy units among 200 atoms than there are to distribute 64 units among just 100 atoms, when two crystals—one containing 64 units of vibrational energy and the other (at 0 K) containing none—come into contact, the 64 units of energy will distribute themselves over the two crystals.

We can determine the degree of likelihood that certain situations have over others by using the thermodynamic probability W. Examine the heat transfer between crystals A and B, as depicted in Figure 16.5.216.5.2. We'll assume that there are 100 atoms in every crystal. Crystal B is initially at zero degrees Celsius. With 64 energy units—enough to cause 64 atoms to vibrate—Crystal A has a greater temperature. The molecules of A lose energy while those of B gain energy when the two crystals are brought together, resulting in an equal distribution of the 64 energy units between the two crystals.

The 64 energy units are split among 100 atoms in the initial state. Based on calculations, there are 1.0×10^{44} possible ways to create this distribution. Therefore, 1.0×10^{44} is the initial thermodynamic probability, or W1. The 100 crystal atoms A constantly trade energy with each other and quickly move from one of these 1.0×10^{44} configurations to another. There is an equal chance of discovering the crystal in any of the 1.0×10^{44} configurations at any given time.

The energy can disperse over twice as many atoms when the two crystals come into contact. There is an exponential increase in the number of conceivable configurations; W2, the thermodynamic probability for this new state, is 3.6 × 1060. There is an equal possibility for each of these 3.6 × 1060 combinations to occur in the ongoing shuffling of energy among the 200 atoms. But only 1.0 × 1044 of these match the scenario when crystal A contains all of the energy. As a result, the likelihood that the heat flow will reverse and all of the energy will return to crystal A is

$$\frac{W_1}{W_2} = \frac{1.0 \times 10^{44}}{3.6 \times 10^{60}} = 2.8 \times 10^{-17}$$

Stated differently, the ratio W1 to W2 indicates the proportional likelihood of discovering the system in its initial state as opposed to its end one.

This illustration demonstrates how W can be used as a broad standard to determine whether or not a reaction is spontaneous. Moving from a condition where W is less to a state where W is larger correlates to moving from a less probable to a more probable molecular scenario. Stated differently, W rises in the event of an unplanned shift.

Predicting whether a response will be spontaneous or not can be solved if a method for computing or measuring the start and final values of W can be found. The response will happen on its own if W2 is higher than W1. This approach to spontaneous processes is sound in theory, but it proves to be exceedingly difficult to implement in real life. W values for actual samples of matter are on the order of 101024, making them challenging to work with (compared to 200 atoms in the example of Figure 2). However, because $\log 10^{x} = x$, the logarithm of W is only on the order of 10^{24}.

This is more manageable, and chemists and physicists use a quantity called the entropy which is proportional to the logarithm of *W*.

This way of handling the extremely large thermodynamic probabilities encountered in real systems was first suggested in 1877 by the Austrian physicist Ludwig Boltzmann (1844 to 1906). The equation

$$S = k \ln W$$

…………….(1)

is currently inscribed on Boltzmann's tombstone. As one might expect, the proportionality constant k is also known as the Boltzmann constant. It can be expressed as the Avogadro constant NA divided by the gas constant R:

$$k = \frac{R}{N_A}$$

…………………..(2)

therefore rather than the gas constant per mole, we might think of it as the gas constant per molecule. The Boltzmann constant k has a value of 1.3805 × 10–23 J K–1 in SI units. In Equation 1, the sign ln represents a natural logarithm, or a logarithm to the base e. Considering that the formula relates base e and base 10 logarithms.

$$\ln x = 2.303 \log x$$

Converting from one to the other is simple. In base-10 logarithms, equation 1 thus becomes S=2.303k log W

8.2. Maxwell-Boltzmann Distribution Law

The Maxwell-Boltzmann distribution is a fundamental concept in statistical mechanics that describes the distribution of speeds (or velocities) of particles in a gas at a given temperature. It provides insights into the statistical behavior of particles based on their kinetic energies and the principles of classical mechanics. Here’s an explanation of the Maxwell-Boltzmann distribution:

a. Assumptions and Context

Ideal Gas Assumption: The Maxwell-Boltzmann distribution applies to an ideal gas, where particles (atoms or molecules) are point masses that do not interact except through elastic collisions.

Thermal Equilibrium: The gas is assumed to be in thermal equilibrium, meaning all particles have the same temperature T.

b. Distribution Function

The distribution function f(v) gives the probability density of finding a particle with speed v in the gas.

For a three-dimensional system, the Maxwell-Boltzmann distribution function is

$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}}$$

Where m, v, mass and speed of the particle, K_B is Boltzmann’s constant and T is the temperature of the gas.

c. Applications

Thermodynamics: The Maxwell-Boltzmann distribution is foundational in understanding the relationships between temperature, kinetic energy, and the statistical distribution of particles in thermal equilibrium.

Spectroscopy and Kinetics: It is used in various fields such as spectroscopy (to interpret Doppler broadening of spectral lines) and chemical kinetics (to model reaction rates based on collision frequencies).

Gas Dynamics: In studies of gas flow and dynamics, the distribution helps predict particle velocities and their impact on transport properties.

8.3. Partition Function

The partition function Z is a fundamental concept in statistical mechanics that plays a central role in calculating thermodynamic properties of a system, such as entropy, free energy, and average energy. It encapsulates the statistical distribution of the system's microstates in phase space and connects microscopic details with macroscopic observables. Here's an explanation of the partition function and its significance:

Definition: The partition function Z is defined differently depending on whether the system is in classical statistical mechanics or quantum statistical mechanics.

a. Classical Partition Function

For a classical system of N particles in thermal equilibrium with a heat bath at temperature T, the partition function Z is given by:

$$Z = \int e^{-\beta H(\{q_i, p_i\})} \, d\Gamma$$

Where,

$\beta = \frac{1}{KT}$ is the inverse temperature.

H ($\{q_i, p_i\}$) is the classical Hamiltonian function which is depends on the positions $\{q_i\}$ and momenta $\{p_i\}$ of all particles.

dT is the phase space volume element over all possible microstates of the system

b. Quantum Partition Function

For a quantum mechanical system, the partition function Z is typically expressed as a trace over the quantum states of the system.

$$Z = \mathrm{Tr}\left(e^{-\beta \hat{H}}\right)$$

Where, $\hat{H}$ is the Hamiltonian operator of the system, and Tr denotes the trace operation over the Hilbert space of quantum states.

8.4. Significance and Applications

1. Thermodynamic Properties: The partition function allows calculation of various thermodynamic properties using ensemble averages. For instance, the Helmholtz free energy F, entropy S, internal energy U, and other quantities can be derived from Z.
2. Connection to Observables: Physical observables such as pressure, temperature, and magnetization can be related to derivatives of the partition function with respect to external parameters (like volume, magnetic field).
3. Statistical Mechanics: Z provides a bridge between microscopic details (microstates) and macroscopic observations (thermodynamic quantities), enabling the applications of statistical mechanics to describe and predict system behaviour.

Self-Assessment

1. What is a blackbody radiator according to the Classical Theory of Radiation?
2. State Planck's law of blackbody radiation and its significance.
3. Explain the concept of the Stefan-Boltzmann law and its mathematical expression.
4. What is the Ultraviolet Catastrophe problem in the context of the Classical Theory of Radiation?How does Wien's displacement law relate to the temperature of a blackbody radiator?
5. Which of the following is a state function for an ideal gas?
   A) Heat capacity at constant pressure (Cp)
   B) Work done during an isothermal process ($W_{\text{isothermal}}$)
   C) Internal energy (U)
   D) Heat transferred during an adiabatic process ($Q_{\text{adiabatic}}$)
6. The equation of state for an ideal gas relates:
   A) Pressure, volume, and temperature
   B) Heat capacity, entropy, and temperature
   C) Work done, heat transferred, and pressure
   D) Kinetic energy, potential energy, and internal energy

7. Which thermodynamic function remains constant for an ideal gas during an adiabatic process?
   A) Temperature (T)
   B) Pressure (P)
   C) Volume (V)
   D) Entropy (S)
8. The heat capacity at constant pressure (Cp) of an ideal gas depends on:
   A) Temperature only
   B) Pressure only
   C) Volume only
   D) Both temperature and volume
9. The concept of negative temperature arises due to:
   A) Decreasing energy levels at higher temperatures
   B) Anomalies in the behavior of gases at extremely low temperatures
   C) Systems where energy distribution follows a Boltzmann distribution
   D) A population inversion in energy states

Chapter 9

Thermodynamic Functions

9.1. Thermodynamic Functions of an Ideal Gas

Thermodynamic functions of an ideal gas can be derived using statistical mechanics, specifically by leveraging the partition function and ensemble theory. Here's a breakdown of the key thermodynamic functions for an ideal gas:

a. Internal Energy U

The internal energy U of an ideal gas is the total energy of the gas due to the motion of its particles. For an ideal gas, which consists of non-interacting point particles, the internal energy depends solely on the temperature T and is given by:

$U = N k_BT$

Where, N is the number of the particles, k_B is the Boltzmann's constant and T is the temperature.

b. Helmholtz Free Energy F

The Helmholtz free energy F represents the thermodynamic potential that accounts for both the internal energy of the system and the entropy S. It is defined as:

$F= U-TS$

For an ideal gas, where entropy S can be derived from statistical mechanics as S

$$Nk_B\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mk_BT}{3h^2}\right)^{3/2}\right)+\frac{5}{2}\right],$$

The Helmholtz free energy simplifies to:

$$F=-Nk_BT\ln\left(\frac{V}{N}\left(\frac{4\pi mk_BT}{3h^2}\right)^{3/2}\right)$$

Where V is the volume of the gas, m is the mass of the particle, and h is Planck's constant.

c. Entropy S

The entropy S of an ideal gas can be derived using the Boltzmann entropy formula:

$$S=Nk_B\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mk_BT}{3h^2}\right)^{3/2}\right)+\frac{5}{2}\right]$$

This expression accounts for the logarithm of the number of microstates accessible to the system, reflecting the disorder or randomness of the gas.

d. Pressure P

The pressure P of an ideal gas can be obtained from the Helmholtz free energy F through the relation:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$ Substituting F $$P = \frac{Nk_BT}{V}$$

This result is consistent with the ideal gas law PV = Nk_BT.

e. Chemical potential μ

For an ideal gas in the grand canonical ensemble (where the number of particles N, volume V, and temperature T are all allowed to fluctuate) , the chemical potential μ is related to the number of particles N by :

$$\mu = k_BT \ln\left(\frac{V}{N}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right)$$

This equation describes the how the chemical potential depends on the temperature and volume of the gas.

Conclusion

Thermodynamic functions such as internal energy U, Helmholtz free energy F, entropy S, pressure P, and chemical potential μ for an ideal gas are derived from statistical mechanics using principles such as the partition function and ensemble theory. These functions provide a comprehensive framework for understanding and predicting the behavior of ideal gases under various conditions, from simple temperature changes to more complex scenarios involving volume and particle number fluctuations.

9.2. Classical Entropy Expression

For a classical system in thermal equilibrium with a heat bath at temperature T, The entropy S can be expressed as :

$$S = -k_B \sum_i P_i \ln P_i$$

Where, k_B is Boltzmann's constant, P_i is the probability of the system being in microstate i.

In terms of the partition function Z and the probility P_i of microstate I, the entropy can also be written as :

$$S = k_B \ln Z + k_BT\left(\frac{\partial \ln Z}{\partial T}\right)_{V,N}$$

Derivation Steps:

Partition Function Z :

The partition function sums over all possible microstates of the system:

$$Z = \sum_i e^{-\beta E_i}$$

Where E_i is the energy of microstate I, and $\beta = \frac{1}{kT}$.

Probability Pi : The probability of system being in microstate I is given by :

$$P_i = \frac{e^{-\beta E_i}}{Z}$$

Entropy expression: Using the definition of entropy

$$S = -k_B \sum_i P_i \ln P_i:$$

$$S = -k_B \sum_i \left(\frac{e^{-\beta E_i}}{Z}\right) \ln \left(\frac{e^{-\beta E_i}}{Z}\right)$$

Simplifying gives:

$$S = k_B \ln Z + k_B \beta \langle E \rangle$$

Where, $\langle E \rangle$ is the average energy of the system.

Interpretation and Application:

Microcanonical Ensemble: In the Microcanonical ensemble (fixed E, V, N), the entropy S relates directly to the multiplicity of microstates accessible to the system at a given energy.

Canonical Ensemble: In the canonical ensemble (fixed T, V, N), the entropy S characterizes the distribution of particle over energy states as influenced by temperature.

Statistical Mechanics: The classical entropy expression connects microscopic details (microstates) with macroscopic thermodynamic properties (entropy), providing a statistical basis for understanding the behavior of classical system in equilibrium.

Limitations:

The classical entropy expression assumes that particles are distinguishable and do not obey quantum statistics like Bose-Einstein or Fermi-Dirac statistics.

It applies to systems where quantum effects can be neglected, such as macroscopic systems at high temperatures.

In summary, the classical entropy expression in statistical mechanics quantifies the disorder or randomness of a classical system by averaging over all possible microstates weighted by their probabilities. It is a fundamental concept in understanding the thermodynamic properties of classical systems and forms the basis for deriving other important thermodynamic functions and relationships.

9.3. Gibbs Paradox

The Gibbs paradox refers to a conceptual issue in classical thermodynamics regarding the calculation of entropy for identical particles in an ideal gas. It revolves around the apparent contradiction between the classical definition of entropy and our intuitive understanding of indistinguishable particles. Here's a detailed explanation of the Gibbs paradox:

Classical Definition of Entropy:

In Classical thermodynamic, entropy S is defined using Boltzmann’s entropy formula:

S = k_B ln Ώ

Where k_B, and Ώ represent Boltzmann’s constant, number of microstates corresponding to a given macrostate.

Ideal gas assumption:

An ideal gas is composed of a large number of identical particles (atoms or molecules) that are assumed to be indistinguishable and non-interacting in classical thermodynamics.

The Paradox

Calculation of entropy: For an ideal gas composed of n identical particles, the classical entropy $S_{\text{classical}}$ would be :

$$S_{\text{classical}} = N k_B \ln\left(\frac{V}{N}\left(\frac{4\pi m k_B T}{3h^2}\right)^{3/2}\right) + \frac{5}{2} N k_B$$

Where V is the volume of the gas, t is the temperature, m is the mass of a particle, and h is Planck’s constant.

Gibbs’ calculation: If we consider the entropy of n distinguishable particles, each contributing

$k_B \ln\left(\frac{V}{N}\left(\frac{4\pi m k_B T}{3h^2}\right)^{3/2}\right)$, we would naively expect:

$$S_{\text{naive}} = N k_B \ln\left(\frac{V}{N}\left(\frac{4\pi m k_B T}{3h^2}\right)^{3/2}\right)$$

Contradiction: There is a $\frac{5}{2}Nk_B$ term difference between $S_{\text{classical}}$ and S_{naive}. This discrepancy arises because the classical calculation treats particles as distinguishable, which contradicts the fundamental quantum mechanical principle that identical particles are indistinguishable.

Resolution and understanding: Statistical Mechanics Perspective : In statistical mechanics, the correct calculation of entropy for identical particles (indistinguishable in nature) must account for this in distinguishability.

Quantum Mechanical Explanation: Quantum mechanics provides the correct framework to address the Gibbs paradox. According to quantum statistical (Bose-Einstein or Fermi-Dirac), identical particle are subject to statics that preserve their in distinguishability.

Symmetry factor : The correct entropy calculation involves dividing by a symmetry factor to account for in distinguishability. For example, for N identical particles, the correct entropy should account for N! Permutations of the particles.

Physical Interpretation : The resolution of the Gibbs paradox underscores the importance of quantum statistics in accurately describing the behavior of identical particles, particularly at low temperatures or hugh densities where quantum effects become significant.

Conclusion:The Gibbs paradox highlights a fundamental misunderstanding when applying classical thermodynamics to systems of indistinguishable particles. It emphasizes the necessity of quantum statistical mechanics for accurately describing entropy and other thermodynamic properties of systems involving identical particles, thereby reconciling classical definitions with quantum mechanical principles.

9.4. Sackur-Tetrode Equation

The Sackur-Tetrode equation is an important result in statistical mechanics that provides an expression for the entropy S of an ideal gas in terms of its thermodynamic variables. This equation is particularly notable because it extends the classical entropy expression for ideal gases to include quantum mechanical effects, such as the discrete energy levels of particles and the indistinguishability of particles obeying quantum statistics.

Expression of the Sackur-Tetrode Equation

For N particles in a volume V at temperature T, the Sackur-Tetrode equation is given by:

$$S = Nk_B \left[\ln\left(\frac{V}{N}\left(\frac{4\pi m k_B T}{3h^2}\right)^{3/2}\right) + \frac{5}{2}\right]$$

Here, S is the entropy of the system; m is the mass of the particle, k_B is the Boltzmann's constant, h is the Planck constant.

Key Points:

Quantum Effects: The Sackur-Tetrode equation incorporates quantum effects by considering the discrete energy levels of particle. It includes a correction to the classical entropy formula to account for these quantum states.

In distinguishability: It respects the in distinguishability of particles, which is crucial in quantum statistics. For identical particles, this correction ensures that the entropy calculation is consistent with quantum mechanics.

Temperature Dependence: The entropy S depends logarithmically on temperature T. This dependence reflects the statistical distribution of particles energies at different temperatures.

Volume Dependence: The entropy also dependence on the volume V of the syste. This reflects the phase space available to the particles, which influences their entropy.

Application and Context

Statistical Mechanics : The Sackur- Tetrode equation is derived from statistical mechanics, particularly from considerations of the partition function and the density of states in phase space.

Ideal Gas Limit : In the classical limit (high temperature or large volume), the sackur-Tetrode equation reduces to the classical entropy expression, demonstrating its consistency with classical thermodynamics.

Law of Equipartition of Energy (with proof)

The Law of Equipartition of Energy is a fundamental concept in classical statistical mechanics that states how energy is distributed among different degrees of freedom in a system at thermal equilibrium. Let's delve into the law itself, its proof, applications to specific heat, and its limitations.

9.5. Law of Equipartition of Energy

The law of Equipartition of energy states that for a system in thermal equilibrium at temperature T, each quadratic degree of freedom (e.g.,, each term in the Hamiltonian that depends quadratically on a coordinate or momentum) contributes $\frac{1}{2}k_B T$ to the average energy of the system.

Proof Outline

Consider a single degree of freedom

Let’s denote a generalized coordinate as q and its conjugate momentum as p.

The energy associated with this degree of freedom is $E = \frac{p^2}{2m} + \frac{1}{2}k\dot{q}^2$

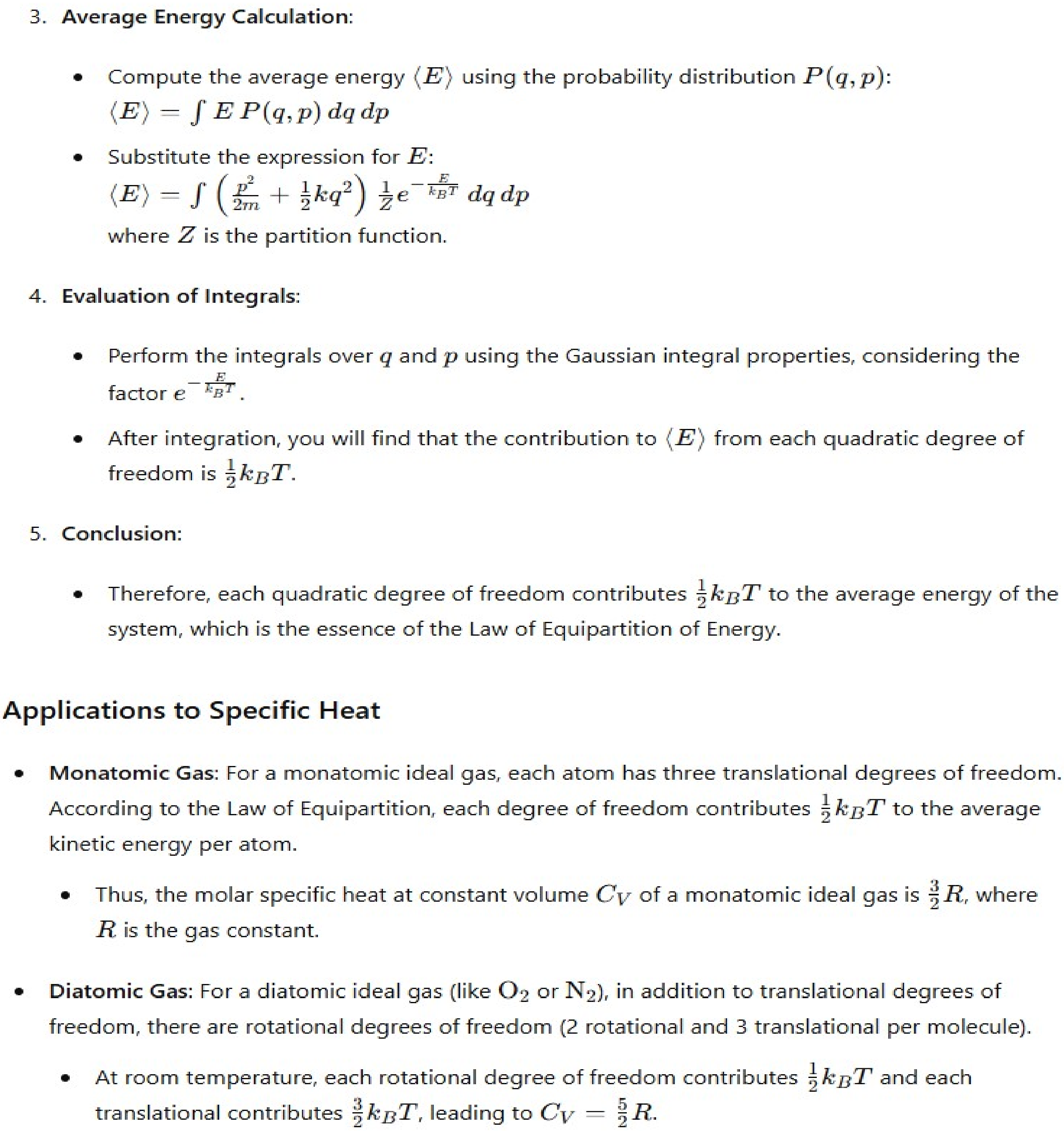
Where m is the mass of the particle, k is the force constant, $p = m\dot{q}$, and $\dot{q}$ i9s the velocity.

Canonical Ensemble:

The system is in contact with a heat reservoir at temperature T, Described by the canonical ensemble.

The probability distribution of the system’s states in phase space is governed by the Boltzmann distribution:

$$P(q, p) \propto e^{-\frac{E}{k_B T}}$$



3. **Average Energy Calculation**:
   - Compute the average energy $\langle E \rangle$ using the probability distribution $P(q, p)$:
     $\langle E \rangle = \int E\, P(q, p)\, dq\, dp$
   - Substitute the expression for E:
     $\langle E \rangle = \int \left(\frac{p^2}{2m} + \frac{1}{2} k q^2 \right) \frac{1}{Z} e^{-\frac{E}{k_B T}}\, dq\, dp$
     where Z is the partition function.
4. **Evaluation of Integrals**:
   - Perform the integrals over q and p using the Gaussian integral properties, considering the factor $e^{-\frac{E}{k_B T}}$.
   - After integration, you will find that the contribution to $\langle E \rangle$ from each quadratic degree of freedom is $\frac{1}{2} k_B T$.
5. **Conclusion**:
   - Therefore, each quadratic degree of freedom contributes $\frac{1}{2} k_B T$ to the average energy of the system, which is the essence of the Law of Equipartition of Energy.

Applications to Specific Heat

- **Monatomic Gas**: For a monatomic ideal gas, each atom has three translational degrees of freedom. According to the Law of Equipartition, each degree of freedom contributes $\frac{1}{2} k_B T$ to the average kinetic energy per atom.
  - Thus, the molar specific heat at constant volume C_V of a monatomic ideal gas is $\frac{3}{2} R$, where R is the gas constant.
- **Diatomic Gas**: For a diatomic ideal gas (like $\mathrm{O_2}$ or $\mathrm{N_2}$), in addition to translational degrees of freedom, there are rotational degrees of freedom (2 rotational and 3 translational per molecule).
  - At room temperature, each rotational degree of freedom contributes $\frac{1}{2} k_B T$ and each translational contributes $\frac{3}{2} k_B T$, leading to $C_V = \frac{5}{2} R$.

Limitations

Quantum Effects: The Law of Equipartition of Energy assumes classical particles with continuous energy levels. In reality, at low temperatures or in small systems, quantum effects such as discrete energy levels and quantum statistics (Fermi-Dirac or Bose-Einstein statistics) must be considered. This can lead to deviations from the equipartition theorem.

Non-Quadratic Terms: Degrees of freedom that do not follow quadratic dependencies (like an harmonic potentials) may not obey the Law of Equipartition of Energy. Higher-order corrections to the energy distribution need to be considered in such cases.

Phase Transitions: Near phase transitions or critical points, the behavior of specific heat can deviate significantly from the predictions of the equipartition theorem, requiring more sophisticated models to describe the system accurately.

In summary, while the Law of Equipartition of Energy provides a useful framework for understanding the distribution of energy in classical systems, its application is limited under certain conditions where quantum effects or non-ideal behavior dominate. Understanding these limitations is crucial for accurately modeling and predicting the thermodynamic properties of real-world systems.

9.6. Thermodynamic function of a Two Energy Level System

Let us explore the thermodynamic function of simple system of two energy levels E_1 and E_2, where $E_2 > E_1$.

Partition Function Z : The partition function Z for a system with two energy levels is the sum of Boltzmann factors over all possible states:

$$Z = e^{-\beta E_1} + e^{-\beta E_2}$$

Internal Energy U: The internal energy U is the average energy of the system

$$U = \langle E \rangle = \frac{E_1 e^{-\beta E_1} + E_2 e^{-\beta E_2}}{Z}$$

Helmholtz Free Energy F :The Helmholtz free energy F represents the thermodynamic potential that determins the equilibrium state of the system:

$$F = -k_B T \ln Z$$

Substituting the expression for Z:

$$F = -k_B T \ln \left(e^{-\beta E_1} + e^{-\beta E_2} \right)$$

Entropy S: The entropy S characterizes the disorder or randomness of the system:

$$S = \frac{U-F}{T}$$

Alternatively, using the partition function Z:

$S = k_B (\ln Z + \beta U)$

Specific Heat Capacity: Heat Capacity at constant Volume C_V

The heat capacity at constant volume C_V measures the amount of heat required to change the temperature of the system:

$$C_V = \frac{\partial U}{\partial T}$$

For a two-level system, the calculation involves differentiating U with respect to T:

$$C_V = k_B \beta^2 \frac{(E_2-E_1)^2 e^{-\beta E_1} e^{-\beta E_2}}{Z}$$

Physical Interpretation

Energy Levels: The system is characterized by two discrete energy levels E_1 and E_2, with $E_2>E_1$.

Temperature dependence: Thermodynamic functions vary with temperature T due to the Boltzmann factor $e^{-\beta Ei}$ in the partition function.

Entropy and free energy: Entropy S and free energy F provide information about the system's equilibrium and the availability of states at a given temperature.

Haet capacity: Cv reflects how the internal energy U changes with temperature, indicating the system's response to thermal fluctuations.

Limitations:

This model assumes two discrete energy levels, which is a simplification. Real systems often have continuous energy distributions or more complex energy landscapes.

Quantum effects are not explicitly considered in this classical treatment. For very low temperatures or small systems, quantum mechanical effects may become significant, requiring a quantum statistical mechanics approach.

In summary, the thermodynamic functions of a two-energy levels system provide a foundational understanding of how energy, entropy, and free energy behave in simple, discrete energy level systems. They serve as a starting point for understanding more complex systems and their thermodynamic properties.

9.7. Negative Temperature

Negative temperature is a concept in thermodynamics and statistical mechanics that describes a state of a system where the temperature, as defined by thermodynamic parameters, is negative on the Kelvin scale. This concept can be initially counterintuitive but is well-defined within the framework of statistical mechanics.

Definition and Concept

Temperature Scale: In thermodynamics, temperatures typically measured on the Kelvin scale, where $T \geq 0$ kelvin. Negative temperature does not imply temperatures below absolute zero in the traditional sense.

Thermodynamic Definition:

Negative temperature is defined based on how the entropy S of a system changes with energy E: $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$

If entropy increases with energy, T is positive: if entropy decreases with energy, T is negative.

Population inversion: System with negative temperature has a higher population of particles in higher energy states compared to lower energy state. This phenomenon is known as population inversion.

The probability distribution of particles in negative temperature behaviour. At certain conditions, the higher energy spin states can become more populated then lower energy states.

Examples and Physical Interpretation

Spin systems: Nuclear spins in a magnetic field can exhibit negative temperature behaviour. At certain conditions, the higher energy spin states can become more populated than lower energy states.

Particle Systems: Some systems, like certain laser-cooled atomic system, can exhibit effective negative temperature due to the way energy states are populated under certain experimental conditions.

Mathematical Description: Mathematically, negative temperature is described by a negative value of $\beta = \frac{1}{KT}$. This implies that the system's entropy increases with increasing energy.

Limitations and Context:

Statistical Mechanics Framework: Negative temperature is a concept derived from statistical mechanics and does not contradict the laws of thermodynamics. It is a valid state with in this theoretical framework.

Physical Meaning: Negative temperature does not imply that particles have negative kinetic energy. Instead, it describes the distribution of particles among energy states.

Rare in Nature: Natural occurrences of negative temperature states are rare and typically observed under carefully controlled laboratory conditions where energy distributions are manipulated.

Conclusion

Negative temperature is a fascinating concept in thermodynamics and statistical mechanics that challenges our intuitive understanding of temperature. It describes a state where entropy increases with energy, leading to a higher population of particles in higher energy states. Understanding negative temperature involves grasping its statistical mechanics basis and the implications for energy distributions in physical systems.

Self-Assessment

1. What does the Maxwell-Boltzmann distribution law describe, and what are its key features?
2. Define the partition function in statistical mechanics and explain its significance in calculating thermodynamic properties.
3. Discuss the thermodynamic functions of an ideal gas and how they relate to the microscopic properties of gas molecules.
4. What is the classical entropy expression, and how does it relate to the number of microstates in a system?
5. Explain the Gibbs paradox and its implications for the statistical interpretation of entropy.
6. According to the Classical Theory of Radiation, the energy radiated by a blackbody per unit area per unit time is proportional to:
   A) Temperature of the blackbody
   B) Surface area of the blackbody
   C) Square of the temperature of the blackbody
   D) Cube of the temperature of the blackbody
7. The distribution of electromagnetic radiation emitted by a blackbody at a given temperature follows:
   A) Planck's distribution law
   B) Wien's displacement law
   C) Stefan-Boltzmann law
   D) Rayleigh-Jeans law

8. According to the Stefan-Boltzmann law, the total power radiated per unit area by a blackbody is proportional to:
   A) Fourth power of its temperature
   B) Square of its temperature
   C) Cube of its temperature
   D) Inversely proportional to its temperature
9. The Ultraviolet Catastrophe problem in the Classical Theory of Radiation refers to:
   A) The excessive radiation emitted by stars in the ultraviolet spectrum
   B) The divergence of the predicted radiation intensity at short wavelengths
   C) The inability to explain the observed radiation spectrum of blackbodies
   D) The lack of understanding of radiation emission from hot objects
10. According to Wien's displacement law, the wavelength of maximum intensity emitted by a blackbody is inversely proportional to:
   A) Its temperature
   B) The speed of light
   C) Planck's constant
   D) Boltzmann's constant

Chapter 10

Theory of Radiation

10.1. Classical Theory of Radiation:

The classical theory of radiation refers to the understanding of electromagnetic radiation based on classical electrodynamics, primarily developed before the advent of quantum mechanics. This theory was pivotal in explaining various phenomena related to light and radiation, including blackbody radiation and the behavior of electromagnetic waves.

Properties of Thermal Radiation

- **Emissivity**: Emissivity (ϵ) of a surface quantifies its ability to emit thermal radiation compared to a blackbody at the same temperature. It ranges from 0 to 1, where 0 indicates perfect reflectivity (no emission) and 1 indicates perfect blackbody behavior.
- **Absorptivity**: Absorptivity (α) is the complement of reflectivity and measures the fraction of incident radiation that a surface absorbs.
- **Reflectivity**: Reflectivity (ρ) is the fraction of incident radiation that is reflected by a surface.
- **Transmissivity**: Transmissivity (τ) is the fraction of incident radiation that passes through a material without being absorbed or reflected.
- **Directionality**: Thermal radiation is omnidirectional, meaning it is emitted in all directions. The intensity of radiation varies with the angle of emission, following Lambert's cosine law.
- **Temperature Dependence**: The intensity and spectral distribution of thermal radiation depend strongly on the temperature of the emitting body. Higher temperatures emit radiation with shorter wavelengths and higher intensities according to Planck's law.

10.2. Blackbody Radiation

It refers to the radiation emitted by a perfect black body, this is an ideal physical body that absorbs all incident radiation without any reflection. This phenomenon is crucial in understanding many aspects of thermal radiation and has significant implications in physics, including the development of quantum mechanics and modern thermodynamics. Here are the key aspects of blackbody radiation:

All normal matter at temperatures above absolute zero emits electromagnetic radiation, which represents a conversion of a body's internal thermal energy into electromagnetic energy, and is therefore called *thermal radiation*. Conversely, all normal matter *absorbs* electromagnetic radiation to some degree. An object that absorbs ALL radiation falling on it, at all wavelengths, is called a blackbody. When a blackbody is at a uniform temperature, its emission has a characteristic frequency distribution that depends on the temperature. This emission is called *blackbody radiation*.

A room temperature blackbody appears black, as most of the energy it radiates is infra-red and cannot be perceived by the human eye. Because the human eye cannot perceive light waves at lower frequencies, a black body, viewed in the dark at the lowest just faintly visible temperature, subjectively appears grey, even though its objective physical spectrum peaks in the infrared range. When it becomes a little hotter, it appears dull red. As its temperature increases further it becomes yellow, white, and ultimately blue-white.

Figure 10.1: Blackbody Radiation. When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as a horseshoe forged by a blacksmith, appears red, whereas a higher-temperature object, such as the surface of the sun, appears yellow or white

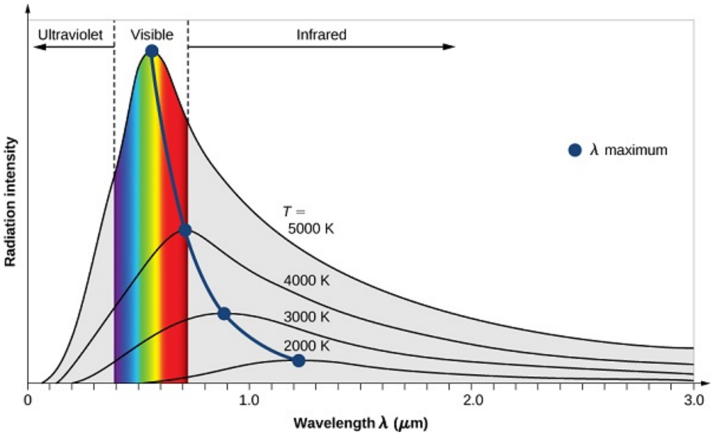


Figure 10.2: Graphic representation of spectral distribution of blackbody radiation at different temperatures. The Stefan-Boltzmann's Law is observed as the increase in the emission

amplitude with increasing temperature and the Wien's Displacement Law is observed as the shift to smaller wavelength with increasing temperature.

10.3. Characteristics of Blackbody Radiation

Spectral Distribution: The intensity of radiation emitted by a blackbody depends on its temperature T and wavelength λ. At a given temperature, the spectral distribution of blackbody radiation follows Planck's law:

$$I(\lambda, T) = \frac{2\pi hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

Where,

- h Planck's constant (6.626x 10^{-34} J.s),
- c is the speed of light (3.00x10^{8} m/s),
- k_B is the Boltzmann's constant (1.38x10^{-23} J/K),
- T is the temperature in kelvin

Wien's Displacement Law: This law relates the peak wavelength λ_{max} of emitted radiation to the temperature T of the blackbody :

$\lambda_{max} = b$

Where b is Wien's displacement constant (b≈2.897x10^{-3} m. K).

Stefan-Boltzmann Law :This law describes the total power radiated per unit surface are A of a blackbody:

$P= \sigma A T^4$

Where σ is the Stefan-Boltzmann constant (σ≈5.67x10^{-8} W/m^2.K^4)

Key Properties and Concepts

Perfect Absorber: A blackbody absorbs all incident radiation and reflects none. This property makes it an idealized object for studying thermal radiation.

Universal Nature: Blackbody radiation is independent of the material of the blackbody and only depends on its temperature. This universality was a significant puzzle in classical physics, leading to the development of quantum theory.

Ultraviolet Catastrophe: Before quantum mechanics, classical theory predicted an infinite energy density at short wavelengths (the ultraviolet catastrophe), which was resolved by Planck's quantization hypothesis.

Applications

- **Infrared Astronomy**: Studying the thermal emission of celestial bodies using telescopes sensitive to infrared radiation.
- **Thermography**: Using infrared cameras to measure temperature distribution in various applications, including medicine, building inspections, and industrial processes.
- **Climate Science**: Understanding the Earth's energy balance and the role of greenhouse gases in radiative forcing.

Material Characterization: Analyzing the thermal properties of materials based on their emissivity and spectral characteristics.

Conclusion

Blackbody radiation is a fundamental concept in physics that describes the emission of electromagnetic radiation from an idealized object that absorbs all incident radiation. Its theoretical foundation in quantum mechanics revolutionized our understanding of radiation and laid the groundwork for many modern applications and scientific advances. Understanding blackbody radiation is crucial for various fields, from astronomy to materials science, and continues to be a cornerstone in the study of thermal physics and electromagnetic waves.

10.4. Kirchhoff’s law

Kirchhoff's law refers to two fundamental principles in physics related to the behavior of electromagnetic radiation and thermal equilibrium. These principles were formulated by the German physicist Gustav Kirchhoff in the mid-19th century and have wide-ranging applications in fields such as optics, thermodynamics, and astrophysics.

10.5. Kirchhoff's First Law (Radiation Law)

Kirchhoff's first law, also known as the radiation law, states:

"At thermal equilibrium, the ratio of the emissive power to the absorptive power of a surface is the same for all bodies at a given temperature and wavelength."

This law implies that for a body in thermal equilibrium, the emissivity ε (λ, T) of its surface equals its absorptivity α (λ, T) at a particular wavelength λ and temperature T. mathematically, it can be expressed as:

$$\varepsilon(\lambda, T) = \alpha(\lambda, T)$$

Emissivity (ε): Emissivity of a surface is the ratio of the energy radiated by the surface to that radiated by a perfect blackbody at the same temperature and wavelength, It varies with temperature and wavelength and ranges from 0 to 1.

Absorptivity (α): Absorptivity of a surface is the fraction of incident radiation absorbed by the surface. Like emissivity, it also varies with temperature and wavelength and ranges from 0 to 1.

10.6. Kirchhoff's Second Law (Displacement Law)

Kirchhoff's second law, often referred to as the displacement law, relates to the spectral distribution of black body radiation. It states:

"The ratio of the emissive power of a black body to its absorptivity is the same for all bodies at the same temperature and for all wavelengths".

Mathematically, it can be expressed as:

$$\frac{E_{emit}\ (\lambda,T)}{\alpha(\lambda,T)} = f(\lambda, T)$$

Where $E_{emit}\ (\lambda,T)$ is the emissive power of the blackbody at wavelength λ and temperature T.

$\alpha(\lambda,T)$ is absorptivity of the blackbody at wavelength λ and temperature T, and f(λ, T) is a universal function of wavelength and temperature.

- ➢ Kirchhoff's second law is fundamental in understanding the spectral distribution of radiation emitted by blackbodies at different temperatures, as described by Planck's law.

Applications and Implications

- **Thermodynamics**: Kirchhoff's laws are essential in the study of thermal radiation, helping to explain and predict the behavior of heat transfer and radiation emission in systems at thermal equilibrium.
- **Optics**: These laws are crucial in optics for understanding the interaction of light with materials, such as in the design of coatings and thermal radiation shields.
- **Astrophysics**: Used extensively in astrophysics to analyze the radiation emitted by stars and other celestial bodies, aiding in determining their temperatures and compositions.

In summary, Kirchhoff's laws provide fundamental principles governing the interaction of electromagnetic radiation with materials and are pivotal in fields ranging from thermodynamics to astrophysics. They play a critical role in understanding and predicting the behavior of radiation in equilibrium conditions and have broad applications across scientific and engineering disciplines.

10.7. Stefan-Boltzmann law: Thermodynamic proof

The Stefan- Boltzmann law describes the total power radiated per unit surface area A of a blackbody at temperature T. it states,

$P = \sigma A T^4$

Where;

- P is the total power radiated,
- Σ is the Stefan-Boltzmann constant ($\sigma = 5.67 \times 10^{-8}$ W/m^2.K^{-4})
- A is the surface area of the blackbody, and
- T is the absolute temperature in kelvin.

The Stefan-Boltzmann Law is easily observed by comparing the integrated value (i.e., under the curves) of the experimental black-body radiation distribution in Figure 10.3 at different temperatures. In 1884, Boltzmann derived this T^4 behavior from theory by applying classical thermodynamic reasoning to a box filled with electromagnetic radiation, using Maxwell's equations to relate pressure to energy density. That is, the tiny amount of energy coming out of the hole would of course have the same temperature dependence as the radiation intensity inside.

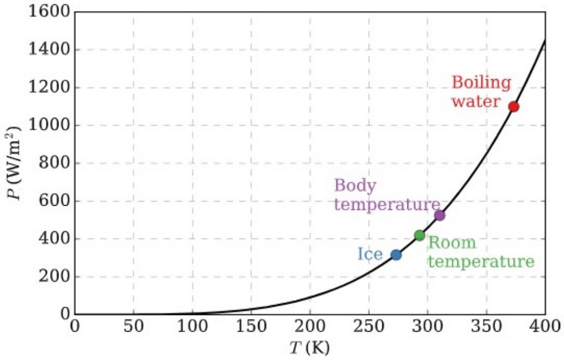


Figure 11.3: Graph of a function of total emitted energy of a blackbody proportional to the fourth power of its thermodynamic temperature T according to the Stefan-Boltzmann law.

Thermodynamic Proof:

The Stefan-Boltzmann law can be derived using fundamental principles from thermodynamics, particularly considering the relationship between the entropy change and the energy transfer associated with radiation. Here’s a step-by-step outline of the thermodynamic proof:

Consider a Blackbody in Thermal Equilibrium:

Imagine a blackbody at temperature T in thermal equilibrium. According to thermodynamics, the total energy radiated per unit time by the blackbody is related to its temperature and surface area.

Energy Density of Blackbody Radiation:

The energy density u(ν, T) of blackbody radiation at temperature T and frequency ν is given by Planck’s law:

$$u(\nu,T) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\frac{h\nu}{k_BT}}-1}$$

Integrating over all frequencies gives the total energy density u(T):

$$u(T) = \int_0^\infty u(\nu,T)\,d\nu$$

Substituting Planck’s law into this integral and performing the integration yields:

$$u(T) = \frac{4\sigma}{c}T^4$$

Here, $\sigma = \frac{4\pi^2 k_B^4}{60\hbar^3 c^2}$ is the Stefan-Boltzmann constant in terms of fundamental constants k_B (Boltzmann constant), $\hbar$ (reduced Planck’s constant), and c (speed of light).

3**. Power Radiated by the Blackbody:**

The power P radiated per unit area A by the blackbody is obtained by multiplying the energy density u(T) by the speed of light c and surface area A:

P = u(T) . A. c

Conclusion:

This law quantitatively describes the total power radiated by a blackbody as a function of its temperature and surface area, providing a fundamental connection between thermodynamics, radiation, and the properties of matter.

10.8. Radiation Pressure

Radiation pressure refers to the pressure exerted by electromagnetic radiation on a surface. It is a fundamental concept in physics and has applications in various fields, including astrophysics, optics, and materials science. Here's an explanation of radiation pressure and its key aspects:

Definition and Concept

Photon Momentum: Electromagnetic radiation, such as light, consists of photons, which are packets of energy and momentum. Despite being massless, photons carry momentum given by: p=E/c=hν/c. Here p is the momentum of the photon, E is its energy, c is the speed of light, h is Planck's constant, and ν is the frequency of the radiation.

Pressure from Photon Momentum: When photons strike a surface, they transfer momentum to it. The rate of transfer of momentum per unit area is the radiation pressure Prad =I/c, where I is the intensity of radiation (power per unit area) and c is the speed of light.

Characteristics and Calculation

Intensity of Radiation: The radiation pressure depends directly on the intensity of the incident radiation. Higher intensities lead to higher radiation pressure.

Directionality: Radiation pressure acts perpendicular to the surface upon which the radiation impinges. The pressure is exerted in the direction of photon propagation.

Applications in Astrophysics: Radiation pressure plays a crucial role in stellar dynamics, where it contributes to phenomena such as stellar winds, radiation-driven outflows, and the pressure balance within stars.

Optical Tweezers: In optics, highly focused laser beams can exert significant radiation pressure on small particles, allowing for precise manipulation and trapping of microscopic objects.

Mathematical Formulation

Pressure from Radiation: For a surface absorbing or reflecting radiation, the pressure exerted due to the absorbed or reflected photons can be derived from the change in momentum per unit time.

Blackbody Radiation: For a perfectly absorbing blackbody, the radiation pressure can be derived from the rate of change of momentum imparted by the absorbed photons.

Astrophysical Implications

Stellar Evolution: Radiation pressure from nuclear fusion reactions in stars contributes to their internal dynamics and stability.

Radiation Pressure Dominated Environments: In astrophysical scenarios such as around black holes or in active galactic nuclei, radiation pressure can be a dominant force influencing the surrounding gas and dust.

Conclusion

Radiation pressure is a fundamental concept in physics that arises from the momentum carried by electromagnetic radiation. It is crucial for understanding the dynamics of radiation interaction with matter, from everyday optical phenomena to the behavior of stars and galaxies in the cosmos. The concept is essential in both theoretical and applied contexts across various scientific disciplines.

10.9. Wien’s Displacement law

Wien's Displacement Law is a fundamental principle in physics that relates the peak wavelength (λmax) of the emitted radiation from a blackbody to its temperature (T). It provides insights into the spectral distribution of thermal radiation emitted by objects based on their temperature. Here’s a detailed explanation of Wien’s Displacement Law:

Statement of Wien’s Displacement Law

"The wavelength λmax at which the intensity of radiation emitted by a blackbody is maximum is inversely proportional to the absolute temperature T of the blackbody."

Mathematical Formulation

Wien's Displacement Law can be expressed as:

λmaxT=b

Where:

λmax is the peak wavelength of radiation emitted by the blackbody,

T is the absolute temperature of the blackbody in Kelvin,

b is Wien's displacement constant, which has a value of approximately 2.897×10−3 Meter. Kelvin (m .K).

Derivation and Understanding

Wien's Displacement Law can be derived using Planck's law for blackbody radiation and considerations of maximizing the intensity I(λ, T) with respect to wavelength λ at a given temperature T.

1. Planck’s Law: The spectral radiance B(λ, T) of blackbody radiation is given by :

$$B(\lambda, T) = \frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

2. Maximizing intensity: The wavelength λ_{max} at which B(λ, T) is maximum (peak intensity) can be found by differentiating B(λ, T) with respect to λ, setting the derivative equal to zero, and solving for λ.

3. Wien’s displacement Constant : Upon derivation and solving, it is found that $\lambda_{max}T = b$, where b is a constant that relates the peak wavelength to the temperature of the blackbody.

Implications and Applications

- **Temperature Determination**: Wien's Displacement Law allows astronomers and physicists to determine the temperature of stars and other celestial objects based on the peak wavelength of their emitted radiation.
- **Color Temperature**: In lighting and photography, the color temperature of light sources is directly related to Wien's displacement constant, influencing the perceived color of light emitted.
- **Thermal Imaging**: Infrared thermography utilizes Wien's Displacement Law to measure and interpret the temperature of objects based on the infrared radiation they emit.
- **Technology and Materials Science**: Understanding thermal radiation and its spectral distribution is crucial for designing materials with specific thermal properties and for developing advanced technologies based on infrared radiation.

In summary, Wien's Displacement Law is a foundational principle in the study of blackbody radiation, providing a direct relationship between the temperature of a blackbody and the wavelength at which its emission intensity peaks. It has broad implications across multiple disciplines, influencing both theoretical understanding and practical applications involving the

10.10. Saha's Ionization Formula

Saha's ionization equation, formulated by the Indian astrophysicist Meghnad Saha in 1920, describes the ionization state of a gas in thermal equilibrium. It provides a way to calculate the relative populations of atoms and ions of a particular element at different temperatures and pressures. This equation is particularly important in astrophysics for understanding the ionization conditions in stellar atmospheres and other high-temperature environments. Here's a detailed explanation of Saha's ionization formula:

Saha Equation

Saha's ionization equation relates the number densities of atoms, ions, and electrons in a gas in thermal equilibrium. It is given by:

$$\frac{N_{r+1}}{N_r} = \frac{U_{r+1}}{U_r}\frac{2}{N_e}\left(\frac{2\pi m_e k_B T}{h^2}\right)^{3/2} e^{-\chi_r/k_B T}$$

Where

N_{r+1} and N_r are the number densities of ions with ionization state r+1 and r, respectively.

U_{r+1} and U_r are the partition functions of the ions r+1 and r, which account for the statistical weights of the energy levels of each ionization stage.

- N_e is the number density of electrons.
- M_e is the mass of an electron.
- K_B is Boltzmann's constant.
- T is the temperature in Kelvin.
- H is Planck constant
- χ_r is the ionization energy (or ionization potential) of the r-th ionization stage.

Key Points

1. **Ionization Balance**: Saha's equation helps determine the balance between different ionization stages of an element in a plasma or gas at a given temperature and electron density.
2. **Temperature Dependence**: The exponential term $e^{-\chi_r}/k_B T$ shows that higher temperatures favour higher ionization stages (since χ_r typically with ionization stage r.)
3. **Electron Density Influence**: The term $\frac{1}{N_e}$ indicates that higher electron densities lead to greater ionization.
4. **Partition Functions:** U_{r+1} and U_r are functions that account for the statistical mechanics of the ion's internal energy levels. They encapsulate the degeneracy and energy spacing of these levels.
5. **Applications:**
    - **Stellar Atmospheres:** Saha's equation is used to model and understand the ionization states of elements in stellar atmospheres, providing insights into the spectral lines observed in stellar spectra.
    - **Astrophysical Plasmas**: It is applied in astrophysical contexts, such as in the study of nebulae, where higher temperatures and densities can significantly affect the ionization equilibrium.
    - **Laboratory Plasma Physics**: Used in laboratory plasma experiments to understand and control the ionization processes within controlled environments.

    Limitations

    - **Assumptions**: Saha's equation assumes thermal equilibrium, neglects radiation pressure, and assumes a one-dimensional model of the plasma.

- **Non-Ideal Conditions**: In highly non-equilibrium plasmas or where radiation transport effects are significant, modifications or more complex models may be required.

Saha's ionization formula remains a cornerstone in astrophysics and plasma physics, providing a fundamental tool for analysing and interpreting the ionization states of elements under various conditions of temperature and electron density.

10.11. Rayleigh-Jean’s Law

Lord Rayleigh and J. H. Jeans developed an equation which explained blackbody radiation at low frequencies. The equation which seemed to express blackbody radiation was built upon all the known assumptions of physics at the time. *The big assumption which Rayleigh and Jean implied was that infinitesimal amounts of energy were continuously added to the system when the frequency was increased*. Classical physics assumed that energy emitted by atomic oscillations could have any continuous value. This was true for anything that had been studied up until that point, including things like acceleration, position, or energy. Their resulting **Rayleigh-Jeans Law** was:

$$\begin{aligned} d\rho(\nu, T) &= \rho_\nu(T)\, d\nu \\ &= \frac{8\pi k_B T}{c^3}\nu^2 d\nu \end{aligned}$$

Experimental data performed on the black box showed slightly different results than what was expected by the Rayleigh-Jeans law (Figure 11.1). The law had been studied and widely accepted by many physicists of the day, but the experimental results did not lie, something was different between what was theorized and what actually happens. The experimental results showed a bell type of curve, but according to the Rayleigh-Jeans law the frequency diverged as it neared the ultraviolet region.

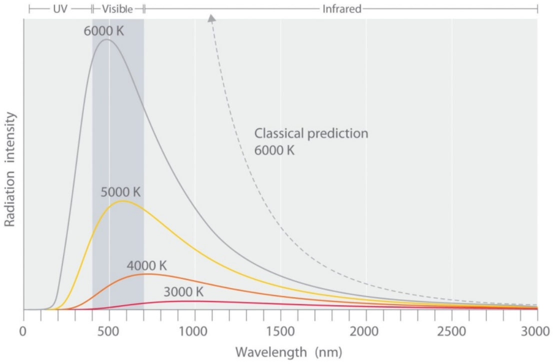


Figure 11. 4 : Relationship between the temperature of an object and the spectrum of

blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the hot metalwork in Figure 11.4 is due to the small amount of radiation emitted at wavelengths less than 700 nm, which the eye can detect. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities.

10.12. Ultraviolet Catastrophe.

The Ultraviolet Catastrophe refers to a theoretical prediction in classical physics, particularly in the context of blackbody radiation, where the intensity of radiation diverges to infinity as the wavelength decreases towards zero. This catastrophic prediction arose from the application of classical electromagnetic theory to describe the thermal radiation emitted by a blackbody.

10.13. Historical Context

In the late 19th century, physicists attempted to understand the spectrum of electromagnetic radiation emitted by a blackbody at thermal equilibrium. A blackbody is an idealized physical object that absorbs all incident radiation and emits radiation at all wavelengths. Classical electromagnetic theory, specifically the Rayleigh-Jeans Law, was initially used to describe this radiation spectrum.

10.14. Rayleigh- Jeans Law

Rayleigh-Jeans law describes the spectral radiance $B_{RJ}(\lambda, T)$ of blackbody radiation as:

$$B_{RJ}(\lambda, T) = \frac{2ck_BT}{\lambda^4}$$

Where, C is the speed of light, k_B is Boltzmann' constant, T is the temperature of the blackbody, and λ is the wavelength of radiation.

The Problem: Divergence at Short wavelengths:

According to Rayleigh-Jeans Law, the intensity of radiation $I(\lambda, T)$increases without bound as λ approaches zero:

$$\mathbf{I_{RJ}(\lambda, T)} \propto \frac{1}{\lambda^4}$$

This implies that the total radiated power becomes infinite as shorter and shorter wavelengths are considered. In practical term, this means that the blackbody would emit an infinite amount of energy in the ultraviolet region and beyond, which contradicts experimental observations.

Resolution by Planck

Max Planck resolved the Ultraviolet Catastrophe in 1900 by introducing a revolutionary concept: quantization of energy. He proposed that the energy emitted or absorbed by a blackbody is not continuous but occurs in discrete packets or quanta, each associated with a specific frequency ν and energy $E=h\nu$ where h is Planck's constant.

Planck's Law

Planck's law for blackbody radiation incorporates this quantization principle:

$$B(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

Planck's law accurately describes the spectral distribution of blackbody radiation across all wavelengths and temperatures, resolving the divergence predicted by Rayleigh-Jeans Law at short wavelengths. It reconciles with experimental data and laid the foundation for modern quantum mechanics.

Significance

The Ultraviolet Catastrophe and its resolution by Planck were pivotal in the development of quantum mechanics and the understanding of the interaction between matter and radiation. It highlighted the inadequacy of classical physics in describing certain phenomena and led to a paradigm shift towards quantum theory, revolutionizing physics in the early 20th century.

Self –Assessment

1. What is a blackbody radiator according to the Classical Theory of Radiation?
2. State Planck's law of blackbody radiation and its significance.
3. Explain the concept of the Stefan-Boltzmann law and its mathematical expression.
4. What is the Ultraviolet Catastrophe problem in the context of the Classical Theory of Radiation?
5. How does Wien's displacement law relate to the temperature of a blackbody radiator?
6. Which of the following is a state function for an ideal gas?
   A) Heat capacity at constant pressure (Cp)
   B) Work done during an isothermal process ($W_{isothermal}$)
   C) Internal energy (U)

D) Heat transferred during an adiabatic process ($Q_{adiabatic}$)

7. The equation of state for an ideal gas relates:

A) Pressure, volume, and temperature

B) Heat capacity, entropy, and temperature

C) Work done, heat transferred, and pressure

D) Kinetic energy, potential energy, and internal energy

8. Which thermodynamic function remains constant for an ideal gas during an adiabatic process?

A) Temperature (T)

B) Pressure (P)

C) Volume (V)

D) Entropy (S)

9. The heat capacity at constant pressure (Cp) of an ideal gas depends on:

A) Temperature only

B) Pressure only

C) Volume only

D) Both temperature and volume

10. The concept of negative temperature arises due to:

A) Decreasing energy levels at higher temperatures

B) Anomalies in the behavior of gases at extremely low temperatures

C) Systems where energy distribution follows a Boltzmann distribution

D) A population inversion in energy states

Chapter 11

Bose-Einstein Statistics

11.1. Introduction

Phase Space:

At any instant state of motion of particle (with 3-degrees of freedom) can be determined completely in terms of its three position coordinates (x, y, z) in Euclidean space and corresponding components (P_x. P_y, P_z) of its momentum. These components are considered as coordinates of the particle in momentum space. Thus the state of motion of the particle is completely determined by the six coordinates (x, y. x. P_x. P_y, P_z). Mathematically these coordinates are the coordinates of the point in the space of six dimensions. Such six dimensional space is called phase space (u-space). The point representing the particle in phase space is called phase point. Each particle has its own phase space and phase point.

Unit cell:

Suppose at an instant the position and momentum coordinates in the phase space of a particle are within the range x to x+dx, y to y+dy, to zdz and P_x. to P+ dP_x, P_y to $P_y + dP_y$, P_z to P_z +d P_z.. Therefore at that instant the point will lie in the element of the phase space of a particle of volume, given by

$d\Gamma = dxdydzdP_xdP_ydP_z$

$d\Gamma = (dxdydz)\,(dP_xdP_ydP_z)$

$d\Gamma = (dV_x)\,(dV_p)$

Where dV: the volume element of the physical space and dV_p, the volume element of the momentum space.

Consider the minimum volume of this element, i.e.

$d\Gamma = (dxdydz)_{min}\,(dP_xdP_ydP_z)_{min}$

$d\Gamma = (dxdP_x)\ (dydP_y)\ (dzdP_z)$

According to Heisenberg's uncertainty principle ,the minimum value of each of the products is approximately equal to Planck's constant h

Therefore, $d\Gamma = (h)\,(h)\,(h) = h^3$ Such element (cell) of minimum volume is called unit cell.

The phase point of particle in phase space must be considered as being located somewhere in the unit cell. The volume of the unit cell (4) in phase space is considered as the volume of each available quantum state of energy in phase space.

Number of Unit Cells or Quantum States in Energy Range between E and E+dE:

Consider a system of particles having energies in the range between E and E + dE. Let the physical volume of the system of particles is V.

A finite volume of phase space available to a particle $= \iiint dxdydz \iiint dP_x\, dP_y\, dP_z$

The volume of unit cell in the phase space is h^2.

Therefore number of unit cells in the volume of the phase space is given by

$$g = \frac{1}{h^3} \iiint dxdydz$$

The first integral is physical volume occupied by the particles, ie,

$$V = \iiint dxdydz$$

The second integral is to be evaluated within energy range E and E+ dE. This integral is the element dV_p ' of momentum space, containing particles having energies in the range between E and E+dE.

To evaluate this integral imagine two concentric spheres of radius P and P + dP in momentum space as shown in fig.

All points on the surface of the sphere of radius $P = \sqrt{2mE}$ in momentum space, represents the particles of energy E.

All points on the surface of the sphere of radius $P + dP = \sqrt{2m(E+dE)}$ in momentum space, represents the particles of energy E+dE.

$$\therefore dV_p = \iiint dP_x dP_y dP_z = 4\pi P^2 dP$$

$$= 4\pi(2mE)\, d(2mE)^{1/2} \qquad \{\text{As}, P = \sqrt{2mE}\ \}$$

$$= 4\pi(2mE)\, (2m)^{1/2} d(E)^{1/2}$$

$$= 4\pi(2m)^{3/2} E \frac{1}{2}\, E^{-1/2} dE$$

$$= 2\pi(2m)^{3/2}\, E^{1/2} dE$$

Therefore volume dV_p ' is the volume of spherical shell between to spheres,

$$\therefore g(E)dE = \frac{2\pi V}{h^3}(2m)^{3/2}\ E^{1/2} dE$$

Substituting this value of integral in equation (1), writing g (E) dE in place of g for the energy range.

This equation gives the number of unit cells or quantum state of energy available to having energies in the range between E and E+ dE.

Density of Quantum States of Energy g(E)

Any interval dE of energy contains a large number of possible quantum states. For example, if dE= 10^{-3}eV then minimum number of quantum states in this interval are 1000. Density of quantum states g(E) is defined as the number of quantum states per unit energy range at given energy E.

According to the definition the quantity g(E) dE represents the number of quantum states with energies in the range between E and E+ dE.

Microstate and Macrostate of a system:

Suppose we divide the phase space of a system of particles into small cells. Each cell corresponds

to a small region of position and momentum and hence to a small range of energy. For defining microstate of the system we should specify to which cell each molecule of the system belongs at particular instant. A macrostate, on the other hand, is specified by just giving number of molecules in each cell of phase space.

For example:

Consider distribution of four particles (a, b, c, d) in two cells. There are five possible arrangements as (0, 4), (1, 3), (2, 2), (3, 1), (4, 0), each arrangement is called macrostates of the system. Each macrostate of the system may contains different microstates as given below.

Macrostates	Microstates
(0, 4)	(-, abed)
(1. 3)	(a, bed), (b, acd), (c, abd), (d, abc)
(2,2)	(ab, cd), (ac, bd), (ad, bc), (be, ad), (bd, ac), (cd, ab)
(3, 1)	(abe, d), (abd, c), (acd, b), (bed,a)
(4,0)	(abed, --)

11.2. Thermodynamic Probability

According to theory of probability, the probability of occurrence of an event is defined as the ratio of the number of favorable cases for the occurrence of the event to the total number of possible cases. Maximum value of this probability is 1.

In thermodynamics it is convenient to consider simply the total number of favorable cases.

This number is called Thermodynamic Probability.

The thermodynamic probability for occurrence of given a macrostate of a system in equilibrium is the total number of possible microstates of the system corresponding to the given microstate.

Principle of Equal Priori Probability:

Principle of Equal Priori Probability states that "all different quantum states of an isolated system in equilibrium are equally probable".

In other words, in an isolated system in equilibrium the probability for any one particle to be in a given quantum state is the same.

11.3. Distinguishable & Indistinguishable Particles

In classical mechanics identical particles do not lose their identity despite the similarity of their physical properties, since individual particles follow sharp trajectories during the course of experiment. As result classical mechanical particles can be distinguished from one another, hence they are distinguishable.

As an example consider the molecules of a gas at N.T.P.

Molecular density = 10^{25} molecules/m^3

Therefore volume available for each molecule = 10^{25} molecules/m^3

Molecular radius 10^{-10} m

Therefore volume of molecule = $4/3\pi r^3 = 10^{-30}$ m^3

As the molecule is much smaller than the volume available for it, hence we can identify every molecule of the gas. Hence they are distinguishable.

In quantum mechanics a particle in motion is represented by a wave packet of finite size and spread. Hence there is no way of keeping track of individual particles separately, since wave packets of individual particles considerably overlap to each other. As result quantum mechanical particles cannot be distinguished from one another, hence they are indistinguishable.

As an example consider the free electrons in metal

Density of free electrons in metal = 10^{28} m^{-3}

Therefore volume available for each electron =10^{-28} m^3

For electrons of energy leV, the momentum, p= √ (2mE)

[2 x 9.1 x 10 x 1.6 x 102 0.5 x 10 kg m/sec

$$\Delta q = \frac{h}{\Delta p}$$

$$\Delta q \approx \frac{6.63\times10^{-34}}{0.5\times10^{-24}} \approx 1.3\times10^{-9}\, m$$

Minimum uncertainty in position of electron

Therefore volume of the wave packet = $\approx \frac{4}{3}\times3.14\times\left(1.3\times10^{-9}\right)^{3} m \approx 10^{-27} m^{3}$

Thus, for the free electrons in metal volume available is less than volume of its wave packet, ie, their wave packets overlap considerably. Hence free electrons in metal cannot be identified separately. Hence they are indistinguishable.

In classical statistics, the probability of a cell containing two or more particles is considered insignificant, allowing the particles to be treated as distinguishable. However, in all natural systems, the uncertainty principle is followed, and the minimum size of a cell in phase space is h^3. As a result, the number of cells g_i is constrained by the value of h^3. When the occupation index is taken into account, the particles cannot be treated as distinguishable, rendering classical statistics inapplicable.

These difficulties were resolved by the use of Quantum statistics and can be divided as:

1. Bose Einstein (BE) statistics
2. Fermi Dirac (FD) statistics

11.4. Bose-Einstein Statistics

It is quantum statistics. The particles obeying this statistics are called Bosons. The Bosons are identical, indistinguishable with spin angular momentum equal to nh where, n= 0,1,2 and there is no restriction on the number of particles in the quantum state ie, they do not obey Pauli's exclusion principle. The Bosons have symmetric wave function. Examples of Bosons are photons, a-particles, - mesons, etc.

Consider system of particles in equilibrium at absolute temperature T, total energy U, volume and total number of particles N.

Let n_1, n_2, n_3……..n_i…..n_s be the number of particles in the energy level E_1, E_2, E_3………E_i-------E_s respectively and g_1, g_2, g_3-------g_i----g_s be the number of energy states associated with the energy levels .

$$n_1 + n_2 + \ldots. + n_i + \ldots + n_s = N$$

$$\sum_{i=1}^{s} n_i = N \qquad \text{------(1)}$$

$$E_1 n_1 + E_2 n_2 + \ldots. + E_i n_i + \ldots + E_s n_s = U$$

$$\sum_{i=1}^{s} E_i n_i = U \qquad \text{------(2)}$$

Taking differential of equation (1) and (2) , we get

$$\sum_{i=1}^{s} dn_i = dN = 0 \qquad \text{-----------(3)}$$

$$\sum_{i=1}^{s} E_i dn_i = dU = 0 \qquad \text{----------(4)}$$

Suppose we have to distribute n_i, indistinguishable particles in g_i distinguishable states and there is no restriction on the number of particles in the quantum state. It is similar to distribute n_i particles about (g_i-1) partitions. The number of possible distributions is $n_i + g_i - 1_{C_{n_i}}$

Therefore total number of possible distributions of all N particles in all quantum states is given by

$$W = {}^{n_1+g_1-1}C_{n_1}\; {}^{n_2+g_2-1}C_{n_2} \ldots\ldots {}^{n_i+g_i-1}C_{n_i} \ldots\ldots {}^{n_s+g_s-1}C_{n_s}$$

$$W = \prod_{i=1}^{s} {}^{n_i+g_i-1}C_{n_i}$$

$$W = \prod_{i=1}^{s} \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \; C$$

As, $g_i >> 1$

$$W = \prod_{i=1}^{s} \frac{(n_i + g_i)!}{n_i! g_i!}$$

This is called thermodynamic probability.

Taking log on both sides, we get

$$\log W = \sum_{i=1}^{s} \log \frac{(n_i + g_i)!}{n_i! g_i!}$$

$$\log W = \sum_{i=1}^{s} \log(n_i + g_i)! - \sum_{i=1}^{s} \log n_i! - \sum_{i=1}^{s} \log g_i!$$

Using Stirling's formula, we get

$$\log W = \sum_{i=1}^{s}[(n_i+g_i)\log(n_i+g_i)-(n_i+g_i)] - \sum_{i=1}^{s}(n_i \log n_i - n_i) - \sum_{i=1}^{s}(g_i \log g_i - g_i)$$

$$\log W = \sum_{i=1}^{s}(n_i+g_i)\log(n_i+g_i) - \sum_{i=1}^{s}(n_i+g_i) - \sum_{i=1}^{s} n_i \log n_i + \sum_{i=1}^{s} n_i - \sum_{i=1}^{s}(g_i \log g_i - g_i)$$

Taking differential of above equation, we get

$$d(\log W) = \sum_{i=1}^{s}(n_i+g_i)\frac{1}{(n_i+g_i)}dn_i + \sum_{i=1}^{s}\log(n_i+g_i)dn_i - \sum_{i=1}^{s}dn_i - \sum_{i=1}^{s}n_i\frac{1}{n_i}dn_i - \sum_{i=1}^{s}\log n_i dn_i + \sum_{i=1}^{s}dn_i$$

$$d(\log W) = \sum_{i=1}^{s}\log(n_i+g_i)dn_i - \sum_{i=1}^{s}\log n_i dn_i \qquad \{\text{As}, \sum_{i=1}^{s}dn_i = 0\}$$

$$d(\log W) = \sum_{i=1}^{s}\log\frac{(n_i+g_i)}{n_i}dn_i$$

For most probable distribution d(log(W)) = 0 therefore

$$\therefore \sum_{i=1}^{s}\log\frac{(n_i+g_i)}{n_i}dn_i = 0 \qquad \text{---------------(5)}$$

l ined multiplier, i.e, multiplying equation (3) by (-a) & equation (4) by (- β) then adding in equation (5).

$$\sum_{i=1}^{s}\log\frac{(n_i+g_i)}{n_i}dn_i - \alpha\sum_{i=1}^{s}dn_i - \beta\sum_{i=1}^{s}E_i dn_i = 0$$

$$\sum_{i=1}^{s}\left(\log\frac{(n_i+g_i)}{n_i} - \alpha - \beta E_i\right)dn_i = 0$$

As, dn_i represents change in number of particles, therefore $dn_i \neq 0$

$$\therefore \left(\log\frac{(n_i+g_i)}{n_i} - \alpha - \beta E_i\right) = 0$$

$$\therefore \frac{(n_i+g_i)}{n_i} = e^{(\alpha+\beta E_i)}$$

$$\therefore 1 + \frac{g_i}{n_i} = e^{(\alpha+\beta E_i)}$$

$$\therefore \frac{g_i}{n_i} = e^{(\alpha+\beta E_i)} - 1$$

$$\therefore \frac{n_i}{g_i} = \frac{1}{e^{(\alpha+\beta E_i)} - 1}$$

This equation is known as Bose Einstein law of distribution of particles among the energy levels.

Self-Assessment

1 What types of particles obey Bose-Einstein statistics?

2 Describe the key feature of the Bose-Einstein distribution function.

3 What is Bose-Einstein condensation (BEC)?

4 How does Bose-Einstein statistics differ from Fermi-Dirac statistics?

5 What are the implications of Bose-Einstein condensation in physics?

6 What type of particles obey Bose-Einstein statistics?

A. Fermions B. Bosons C. Quarks D. Leptons

7 State the fundamental principle of Bose-Einstein statistics:

A. Pauli exclusion principle

B. No two fermions can occupy the same quantum state

C. Bosons can occupy the same quantum state simultaneously

D. Bosons obey the conservation of parity

8 Which parameter plays a crucial role in the Bose-Einstein distribution function?

A. Mass of the particle

B. Spin of the particle

C. Temperature

D. Charge of the particle

9 At what temperature does Bose-Einstein condensation typically occur in an ideal Bose gas?

A. Absolute zero

B. Below the critical temperature

C. Above the critical temperature

D. At any temperature

10 Bose-Einstein condensation occurs when:

A. The temperature exceeds the critical temperature

B. The number of particles becomes very large

C. Particles occupy the same quantum state

D. The system reaches equilibrium

Chapter 12

Fermi – Dirac Statistics

12.1. Introduction

Fermi-Dirac Statistics:

It is quantum statistics. The particles obeying this statistics are called Fermions. The Fermions are identical, indistinguishable with spin angular momentum equal to (2n+1)/2 where, n=0,1,2 and there can be only one particle in each quantum state i.e., they obey Pauli's exclusion principle. The Fermions have anti-symmetric wave function. Examples of Fermions are electrons, protons, neutrons, etc.

Consider system of particles in equilibrium at absolute temperature T, total energy U, volume V and total number of particles N.

Let $n_1, n_2, n_3 \ldots\ldots n_i \ldots\ldots n_s$ be the number of particles in the energy level $E_1, E_2, E_3 \ldots\ldots E_i$-------$E_s$ respectively and g_1, g_2, g_3-------g_i----g_s be the number of energy states associated with the energy levels .

$$n_1 + n_2 + \ldots + n_i + \ldots + n_s = N$$

$$\sum_{i=1}^{s} n_i = N \qquad \text{------(1)}$$

$$E_1 n_1 + E_2 n_2 + \ldots + E_i n_i + \ldots + E_s n_s = U$$

$$\sum_{i=1}^{s} E_i n_i = U \qquad \text{------(2)}$$

Taking differential of equation (1) and (2) , we get

$$\sum_{i=1}^{s} dn_i = dN = 0 \qquad \text{----------(3)}$$

$$\sum_{i=1}^{s} E_i dn_i = dU = 0 \qquad \text{----------(4)}$$

Suppose we have to distribute n_i, indistinguishable particles in g_i distinguishable states and there is no restriction on the number of particles in the quantum state. It is similar to distribute n_i particles about (g_i-1) partitions.

The number of possible distributions is $n_{i_{C_{n_i}}}$

$$W = {}^{g_1}C_{n_1}\,{}^{g}C_{n_2}\ldots\ldots{}^{g_i}C_{n_i}\ldots\ldots{}^{g_s}C_{n_s}$$

$$W = \prod_{i=1}^{s} {}^{g_i}C_{n_i}$$

$$W = \prod_{i=1}^{s} \frac{g_i\,!}{n_i\,!(g_i - n_i)!}$$

Therefore total number of possible distributions of all N particles in all quantum states is given by

$$\log W = \sum_{i=1}^{s} \log \frac{g_i\,!}{n_i\,!(g_i - n_i)!}$$

$$\log W = \sum_{i=1}^{s} \log g_i\,! - \sum_{i=1}^{s} \log n_i\,! - \sum_{i=1}^{s} \log(g_i - n_i)!$$

This is called thermodynamic probability.

Taking log on both sides, we get

$$\log W = \sum_{i=1}^{s} \log \frac{g_i\,!}{n_i\,!(g_i - n_i)!}$$

$$\log W = \sum_{i=1}^{s} \log g_i\,! - \sum_{i=1}^{s} \log n_i\,! - \sum_{i=1}^{s} \log(g_i - n_i)!$$

Using Stirling's formula, we get

$$\log W = \sum_{i=1}^{s}(g_i \log g_i - g_i) - \sum_{i=1}^{s}(n_i \log n_i - n_i) - \sum_{i=1}^{s}\left[(g_i - n_i)\log(g_i - n_i) - (g_i - n_i)\right]$$

$$\log W = \sum_{i=1}^{s}(g_i \log g_i - g_i) - \sum_{i=1}^{s} n_i \log n_i + \sum_{i=1}^{s} n_i - \sum_{i=1}^{s}(g_i - n_i)\log(g_i - n_i) + \sum_{i=1}^{s}(g_i - n_i)$$

Taking differential of above equation, we get

$$d(\log W) = 0 - \sum_{i=1}^{s} n_i \frac{1}{n_i} dn_i - \sum_{i=1}^{s} \log n_i\ dn_i + \sum_{i=1}^{s} dn_i + \sum_{i=1}^{s}(g_i - n_i)\frac{1}{(g_i - n_i)} dn_i + \sum_{i=1}^{s} \log(g_i - n_i)\ dn_i - \sum_{i=1}^{s} dn_i$$

$$d(\log W) = \sum_{i=1}^{s} \log(g_i - n_i)\, dn_i - \sum_{i=1}^{s} \log n_i \; dn_i \qquad \{\text{As, } \sum_{i=1}^{s} dn_i = 0\,\}$$

$$d(\log W) = \sum_{i=1}^{s} \log \frac{(g_i - n_i)}{n_i} \; dn_i$$

For most probable distribution (log W)= 0, therefore

$$0 = \sum_{i=1}^{s} \log \frac{(g_i - n_i)}{n_i} \; dn_i$$

…………..(5)

Using Lagrange's method undetermined multiplier, i.e, multiplying equation (3) by (- α) & equation (4) by (-β) then adding in equation (5).

$$\sum_{i=1}^{s} \log \frac{(g_i - n_i)}{n_i} \; dn_i - \alpha \sum_{i=1}^{s} dn_i - \beta \sum_{i=1}^{s} E_i dn_i = 0$$

$$\sum_{i=1}^{s} \left(\log \frac{(g_i - n_i)}{n_i} - \alpha - \beta E_i \right) dn_i = 0$$

As, dn_i represents change in number of particles, therefore $dn_i \neq 0$

$$\therefore \left(\log \frac{(g_i - n_i)}{n_i} - \alpha - \beta E_i \right) = 0$$

$$\therefore \log \frac{(g_i - n_i)}{n_i} = \alpha + \beta E_i$$

$$\therefore \frac{g_i}{n_i} - 1 = e^{(\alpha + \beta E_i)}$$

$$\therefore \frac{g_i}{n_i} = e^{(\alpha + \beta E_i)} + 1$$

$$\therefore \frac{n_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)} + 1}$$

This equation is known as Fermi Dirac law of distribution of particles among the energy levels.

12.2. Fermi function and Fermi Energy

It is quantum statistics. The particles obeying this statistics are called Fermions. The

Fermions are identical, indistinguishable with spin angular momentum equal to (2n+1)/2 where, n=0,1,2 and there can be only one particle in each quantum state i.e., they obey Pauli's exclusion principle. The Fermions have anti-symmetric wave function. Examples of Fermions are electrons, protons, neutrons, etc.

Consider system of particles in equilibrium at absolute temperature T, total energy U, volume V and total number of particles N.

Let n_1, n_2, n_3……..n_i…..n_s be the number of particles in the energy level E_1, E_2, E_3………E_i-------E_s respectively and g_1, g_2, g_3-------g_i----g_s be the number of energy states associated with the energy levels .

According to Fermi Dirac statistics, most probable distribution is given by.

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + i\beta}+1} \text{-------(1)}$$

As α is dimension less constant, hence we can put $\alpha = -\frac{E_F}{kT}$

This means that in this system ,E_F is constant with units of energy corresponding to a particular temperature T , also $\beta = \frac{1}{kT}$

$$\frac{n_i}{g_i} = \frac{1}{e^{(E_i - E_F)/kT}+1}$$

We denote $\frac{n_i}{g_i}$ by F(E_i) and it is called as Fermi function for i^th^ energy level . thus

$$F(E_i) = \frac{1}{e^{(E_i - E_F)/kT}+1} \text{-------(2)}$$

This expression gives the probability that particular quantum states of energy E_i is occupied at temperature T.

Now discuss the effect temperature on Fermi function .

1) At absolute zero temperature (T = 0K)
   (a) Suppose that E_i is smaller than E_F i.e. $E_i << E_F$, at absolute zero , equation (2) leads to

$$F(E_i) = \frac{1}{e^{(-\infty)}+1} = 1$$

That is quantum state of energy E_i is occupied .

   (b) Suppose that E_i is smaller than E_F i.e. $E_i >> E_F$, at absolute zero , equation (2) leads to

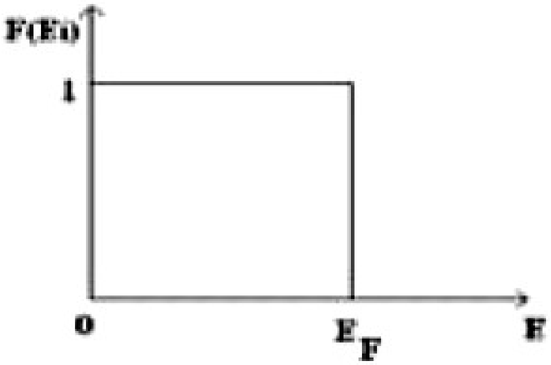
$$F(E_i) = \frac{1}{e^{(\infty)}+1} = 0$$

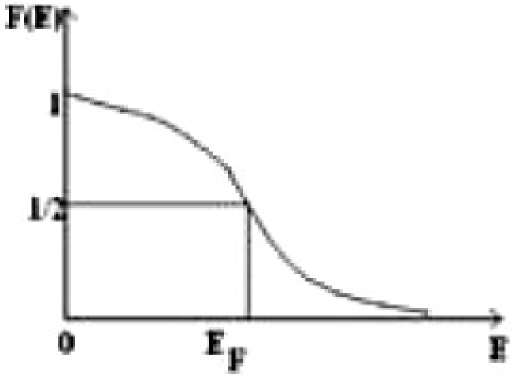
This is quantum state of energy E_i is empty .

Thus at absolute temperature ($T = 0^0$ K) all states with energies less than E_F are filled and all states with energies more than E_F are vacant .

(c) At absolute temperature , Suppose that E_i is equal to E_F i.e. $E_i = E_F$, at absolute zero , equation (2) leads to

$$F(E_i) = \frac{1}{e^{(0)} + 1} = \frac{1}{2}$$





Therefore Fermi energy at any temperature is defined as " the energy of the level with quantum states 50 % occupied and 50% empty .

12.3. Free Electron in Metal

Suppose energy levels of the system are very closed together, then the number of particles n(E)dE. with energies between E and E+ dE is given by

$$n(E)dE = F(E)\, g(E)\, dE \qquad \text{----------------(1)}$$

Where g (E) dE, the number of states between E and E+ dE is given by

$$g(E)dE = \frac{2\pi V}{h^3}(2m)^{\frac{3}{2}}E^{\frac{1}{2}}\, dE$$

For particles like spin angular momentum of electron is equal to ±1/2h i.e. it means that there two possible spin orientations .for a system of such particles g(E)dE is given by

$$g(E)dE = 2\frac{2\pi V}{h^3}(2m)^{\frac{3}{2}}E^{\frac{1}{2}}\, dE \text{------------(2)}$$

$$F(E_i) = \frac{1}{e^{(E_i - E_F)/kT+1}} \text{------------(3)}$$

Using equation (2) and (3) in equation (1)

$$n(E)dE = \frac{4\pi V}{h^3}(2m)^{\frac{3}{2}}\frac{E^{\frac{1}{2}}}{e^{(E_i - E_F)/kT} + 1}dE$$

This equation is known as Fermi energy distribution law for the free electrons in metal . This gives the number of electrons with energies between E and E+ dE.

12.4. Expression for Fermi Energy for Free Electrons in a Metal at Absolute Zero Temperature (E_{F0})

The total number N of the free electrons in a metal of volume is given by

$$N = \int_0^\infty n(E)dE$$

$$n(E)dE = F(E)\, g(E)$$

$$\therefore N = \int_0^\infty F(E)\, g(E)\ \ dE$$

$$\therefore N = \int_0^{E_{F_0}} F(E)\, g(E)\ \ dE + \int_{E_{F_0}}^\infty F(E)\, g(E)\ \ dE$$

We know that at T=0 , if E<E_{F0}Fm then F(E) = 1 and at T = 0 if E>E_{F0} , then F(E) = 0 Hence above equation becomes

$$N = \int_0^{E_{F_0}} g(E)\ \ dE$$

As g(E)dE is given by

$$g(E)dE = \frac{4\pi V}{h^3}(2m)^{3/2}\ \ E^{1/2}dE$$

$$\therefore N = \frac{4\pi V}{h^3}(2m)^{3/2}\int_0^{E_{F_0}}\ \ E^{1/2}dE$$

$$\therefore N = \frac{4\pi V}{h^3}(2m)^{3/2}\,\frac{2}{3}E_{F_0}^{3/2}$$

$$\therefore N = \frac{8}{3}\frac{\pi V}{h^3}(2m)^{3/2}E_{F_0}^{3/2}$$

This expression gives total number of electrons in the metal at absolute zero.

$$E_{F_0}^{3/2} = \frac{3N}{8\pi V}\left(\frac{h^2}{2m}\right)^{3/2}$$

Taking 2/3 rd power of both sides , we get

$$E_{F_0} = \frac{h^2}{2m}\left[\frac{3N}{8\pi V}\right]^{2/3}$$

$$E_{F_0} = \frac{h^2}{2m}\left[\frac{3n}{8\pi}\right]^{2/3}$$

Where n = N/V = number of free electrons in the metal at absolute zero. This expression gives Fermi energy of electrons in the metal at absolute zero. The total energy of electrons at absolute zero temperature is given by

$$E_0 = \int_0^{E_{F_0}} E\, n(E)\ dE$$

$$\therefore E_0 = \int_0^{E_{F_0}} E\, g(E)\ dE$$

$$\text{As } g(E)dE = \frac{4\pi V}{h^3}(2m)^{3/2}\ E^{1/2}dE$$

$$\therefore E_0 = \frac{4\pi V}{h^3}(2m)^{3/2}\int_0^{E_{F_0}} E^{3/2}dE$$

$$\therefore E_0 = \frac{8\pi V}{5h^3}(2m)^{3/2}E_{F_0}{}^{5/2}$$

$$\text{Since } N = \frac{8}{3}\frac{\pi V}{h^3}(2m)^{3/2}E_{F_0}^{3/2}$$

$$\therefore E_0 = \frac{3}{5}NE_{F_0}{}^{5/2}$$

$$\therefore \frac{E_0}{N} = \frac{3}{5}E_{F_0}{}^{5/2}$$

Thus the average energy per electron at absolute zero T = 0K is equal to 3/5 times the fermi energy.

Self Assessment

1 Define Fermi energy in the context of solid-state physics.
2 What physical property does Fermi energy determine in a material?

3 Explain how Fermi energy relates to the concept of the Fermi level.

4 How does Fermi energy influence the electrical conductivity of a material?

5 Describe how Fermi energy changes with temperature in a solid.

6 Which particles obey Fermi-Dirac statistics?

A. Bosons

B. Quarks

C. Fermions

D. Leptons

7 At what temperature does a Fermi gas become completely degenerate?

A. High temperatures

B. Room temperature

C. Very low temperatures

D. Absolute zero

8 What happens to the Fermi energy of a Fermi gas as the number of particles increases?

A. Increases

B. Decreases

C. Remains constant

D. Fluctuates

9 Fermi energy is defined as:

A. The energy of the highest occupied state at absolute zero

B. The energy of the lowest unoccupied state at absolute zero

C. The average energy of particles in a thermal system

D. The energy of particles at the point of phase transition

10 Which of the following factors affect the Fermi energy of a fermion gas?

A. Temperature

B. Volume

C. Particle mass

D. All of the above

Chapter 13

Application of Bose- Einstein and Fermi –Einstein Statistics

13.1. Introduction

Let's take a boson gas as an instance of the Bose-Einstein distribution. This gas made of number of identical bosons enclosed within a box that has rigid-walls and a constant volume. While the bosons have the freedom to move within the box, they are constrained from moving beyond its walls. Energy exchange occurs between the bosons during occasional collisions. To simplify matters, we assume that the bosons possess a spin of zero, thereby eliminating any degeneracy associated with different spin states.

First, let us examine the characteristics of the coefficient B found in the equation for the Bose-Einstein distribution. This value represents the partition function in the Boltzmann distribution or the chemical potential in the Fermi-Dirac distribution. The determination of B is governed by the following constraint:

$$\sum_i n_i = N \text{----(1)}$$

Here N is the number of particles. Now determine variable B depends on temperature.

$$g(\varepsilon) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{\varepsilon}.$$

Let's consider the possibility of substituting a sum over distinct energy levels with an integral over a range of energy levels. As a result, equation (1) transforms into .

$$\sum_i n_i \approx \int_0^\infty n(\varepsilon)d\varepsilon = N.$$

Using the Bose-Einstein distribution and the density of states, this becomes:

$$\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\int_0^\infty \frac{\sqrt{\varepsilon}}{Be^{\frac{\varepsilon}{kT}}-1}d\varepsilon = N.$$

Lets define a new variable, y, such that:

$$y = \frac{\varepsilon}{kT}.$$

In terms of y, the equation for B becomes:

$$\frac{V}{4\pi^2}\left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}}\int_0^\infty \frac{\sqrt{y}\,dy}{Be^{y}-1} = N.$$

We define the function F(B):

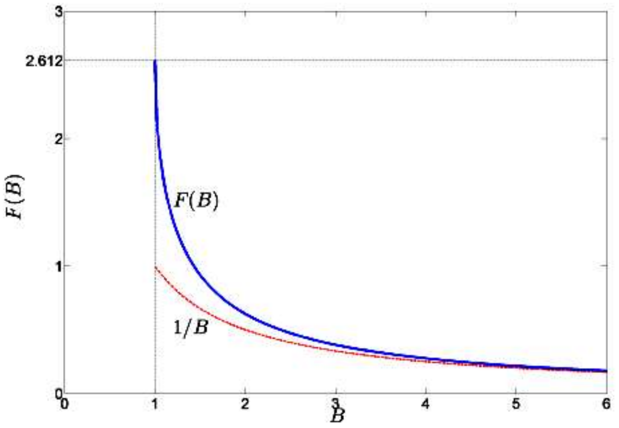
$$F(B) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{y}\, dy}{Be^y - 1}.$$

In terms of F(B), the equation for B becomes:

$$V \left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{3}{2}} F(B) = N.$$

---------------(2)

To understand the function F(B), let us draw a graph of it:



When B is large, we can approximate F(B) to be approximately equal to 1/B. This approximation is valid when B is much greater than 1, and can be expressed

$$\frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{y}\, dy}{Be^y - 1} \approx \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{y}\, dy}{Be^y} = \frac{1}{B}.$$

as:

Thus, from equation (2) becomes ,

$$V \left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{3}{2}} F(B) = N,$$

we find that, for large B (or, equivalently, for high temperature):

$$B \approx \frac{V}{N} \left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{3}{2}}$$

However, it is crucial to acknowledge that the integral cannot be assessed below B = 1 due to the existence of a singularity at this precise point. From a physical perspective, this carries substantial significance. The Bose-Einstein distribution is:

$$n_i = \frac{g_i}{Be^{\frac{\varepsilon_i}{kT}} - 1}.$$

If B is less than 1, it is possible for there to exist an energy level εi where the number of particles ni is less than 0. It is evident that having a negative number of particles in any energy level is not feasible, thus we anticipate B to be greater than or equal to 1.

We see that F(B) takes a maximum value, at B = 1. The maximum value of F(B) is given by:

$$F(1) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{y}\, dy}{e^y - 1} = \zeta\left(\frac{3}{2}\right) \approx 2.612.$$

Here, ζ(x) is the Riemann zeta function, defined by:

$$\zeta(x) = \sum_{n=1}^{\infty} \frac{1}{n^x}.$$

Since F(B) has a maximum value of for B =1 i.e. F(1) ≈ 2.612, we expect from equation

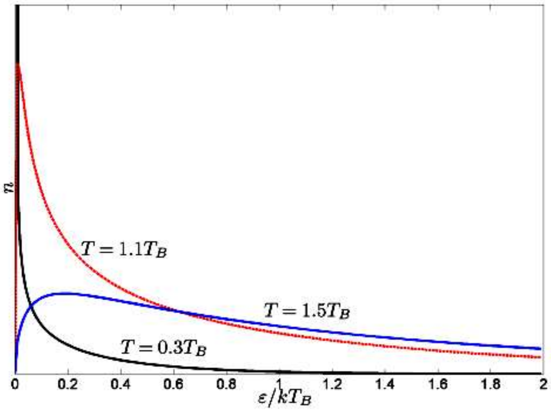
$$V\left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{3}{2}} F(B) = N,$$

As the temperature decreases, F(B) must increase. However, if F(B) has a finite maximum value, then below a certain temperature TB, the integrated Bose-Einstein distribution yields a particle count lower than N, the total number of particles in the system.

$$\text{if } T < T_B, \text{ then } \quad \frac{V}{4\pi^2}\left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{\sqrt{y}\, dy}{Be^y - 1} < N$$

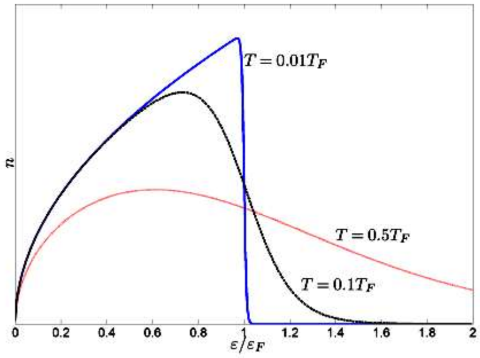
The population density n(ε) as a function of energy ε provides clarity to the situation when plotted for various temperatures. When the temperature T is greater than T_B, a smooth distribution curve emerges, which closely resembles the expected distribution for a Maxwell-Boltzmann gas, particularly at high temperatures. It is worth noting that the area under the curves for $T > T_B$ remains unaffected by the temperature T.

However, when the temperature T is lower than T_B, it becomes challenging to evaluate the population density as we lack a solution for the parameter B. In such cases, we make the best possible approximation by setting B = 1 for $T < T_B$. This approximation results in a distribution that exhibits a sharp peak at low energy levels. However, the height of this peak is insufficient to accurately determine the number of particles in the system based on the area under the curve.



13.2. The Fermi gas population distribution

The population distribution of the Bose-Einstein gas can be contrasted with that of a Fermi gas. Notably, the population distribution of a Fermi gas remains well-behaved even as the temperature approaches absolute zero, T → 0..



The temperature T_B at which particles start to "disappear" is given by:

$$V\left(\frac{mkT_B}{2\pi\hbar^2}\right)^{\frac{3}{2}}\zeta\left(\frac{3}{2}\right) = N,$$

$$T_B = \frac{2\pi\hbar^2}{mk}\left(\frac{N}{\zeta\left(\frac{3}{2}\right)V}\right)^{\frac{2}{3}}.$$

The Bose-Einstein condensation, when we replaced the summation over discrete energy levels by an integral over a continuum of energies in equation

$$\sum_i n_i \approx \int_0^\infty n(\varepsilon)d\varepsilon = N.$$

Given that the lower limit of the integral is zero, it is necessary to assume (for the sake of consistency) that the ground state possesses zero energy. However, considering the distribution function g(ε) ∝√ε, it can be observed that at zero energy, the density of states becomes zero as well. Consequently, the population within the narrow energy range of 0 to dε is also zero.

13.3. Planck's Law of Black Body Radiation

To derive Planck's law, we will examine a black body chamber with a volume V that is maintained at a constant temperature T. This chamber is filled with radiant energy, which can be viewed as a collection of photons. When the number of photons in the chamber is significantly large, the spacing between two consecutive energy levels becomes minuscule, resulting in nearly continuous energy levels. Consequently, if the energy of photons falls within the range of E to E + dE, the degenerate states g should be substituted with g(E)dE, and the total number of photons n in these states should be replaced with n(E)dE in the B-E distribution function. Therefore, we can express the number of photons with energy ranging from E to E+dE as follows.

$$n(E)dE = \frac{g(E)dE}{e^{(\alpha+\beta E)}-1} \text{-----------------(1)}$$

In black body radiation, the total number of particles is not conserved as photons are absorbed and re-emitted frequently by the walls of the chamber.

i.e.$\sum_i N_i \neq 0 \rightarrow \alpha = 0$

Hence equation (1) becomes

$$n(E)dE = \frac{g(E)dE}{e^{(E/kT)}-1} \text{-------------(2)}$$

Now the number of quantum states in momentum range p to p+ dp is

$$g(p)dp = g_s\frac{4\pi V p^2}{h^3}\,dp$$

In quantum physics, the spin degeneracy of a quantum state, represented by gs, is indicative of the number of available spin orientations. For photons, with two spin orientations in the transverse direction, the spin degeneracy is equal to 2.

$$g(p)dp - \frac{8\pi V p^2}{h^3}\,dp \text{--------------(3)}$$

The momentum of a photon with frequency ν can be calculated using the equation p = hν/c, where h is Planck's constant and c is the speed of light in free space. Additionally, the energy of the photon can be determined using the equation E = hν.

$$dp = \frac{h}{c}dv$$

Substituting the values of p and dp in equation (3), we get the number of quantum states having frequency range between v to v+dv as

$$g(v)dv = \frac{8\pi V v^2}{c^3}\,dv$$

Hence equation (2) becomes in terms of v as ,

$$N(v)dv = \frac{g(v)dv}{e^{(hv/kT)} - 1}$$

The chamber of volume at temperature T provides information about the quantity of photons within the frequency range of v to v+ v.

Therefore, the energy density of photons within frequency range between ν to ν+d ν is given by

$$u(v)dv = hv\,\frac{N(v)dv}{V} = \frac{8\pi h v^3}{c^3}\,\frac{1}{e^{(hv/kT)} - 1}\,dv$$

This is Plank’s law of black body radiation.

13.4. Thermodynamics of an ideal Fermi gas

The focus of our study is an ideal Fermi gas within the grand canonical ensemble, specifically looking at the temperature and chemical potential. Our aim is to establish the general formula for the thermodynamic potential and the average number of fermions. To simplify the derivation, we temporarily ignore the nonzero spin of fermions and concentrate on the fully spin-polarized Fermi gas. Let's begin by analyzing the basic scenario of a single energy level ε1 that can be filled by fermions. As per the Pauli exclusion principle, this level can either be vacant or occupied, resulting in a unique form of the grand canonical partition function.

$$Z^{(1)} = 1 + e^{-\beta\varepsilon_1 + \beta\mu}$$

Now, we will introduce an additional level ε2. Once again, in accordance with the Pauli exclusion principle, there are four distinct scenarios that can occur:

1) Both levels are unoccupied.

2) Level ε_1 is occupied while level ε_2 remains unoccupied.

3) Level ε_1 is unoccupied while level ε_2 is occupied.

4) Both levels are occupied.

As a result, the grand canonical partition function is modified accordingly.

$$
\begin{aligned}
\mathcal{Z}^{(2)} &= 1 + e^{-\beta\varepsilon_1+\beta\mu} + e^{-\beta\varepsilon_2+\beta\mu} + e^{-\beta(\varepsilon_1+\varepsilon_2)+2\beta\mu} \\
&= \left(1 + e^{-\beta\varepsilon_1+\beta\mu}\right)\left(1 + e^{-\beta\varepsilon_2+\beta\mu}\right).
\end{aligned}
$$

The factorization of the grand partition function Z into independent factors for each energy level is clearly illustrated. This factorization can be generalized to encompass any arbitrary number of energy levels.

$$\mathcal{Z} = e^{-\beta\Omega} = \prod_{a,\sigma}\left(1 + e^{-\beta\varepsilon_{a,\sigma}+\beta\mu}\right)$$

The orbital degrees of freedom are listed here, with σ representing the projection of the fermion spin. The total number of particles can be determined from the equation..

$$N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = \sum_{a,\sigma} f_F(\varepsilon_{a,\sigma}), \qquad f_F(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)}+1}.$$

The function f_F (ε) is called the Fermi-Dirac distribution function.

13.5. Thermodynamics of an ideal Bose gas

We are examining an ideal Bose gas in the grand canonical ensemble, specifically at a given temperature and chemical potential. Our aim is to derive the general expression for the thermodynamic potential and the average number of bosons. To simplify the derivation, we will focus on zero-spin bosons.

Let's start with the simplest situation, which involves a single energy level ε1 that can be occupied by bosons. Since bosons do not follow the Pauli exclusion principle, this level can be empty, occupied by one boson, occupied by two bosons,

$$\mathcal{Z}^{(1)} = \sum_{n=0}^{\infty}(1 + e^{-\beta\varepsilon_1 n+\beta\mu n})$$

Let's introduce an additional level ε_2. Because of the lack of the Pauli exclusion principle, we observe the following scenario: level ε_1 is filled with n_1 bosons, while level ε_2 is filled with n_2 bosons. $n_{1,2}$ = 0, 1, 2, ... The grand canonical partition function becomes

$$\mathcal{Z}^{(2)} = \sum_{n_{1,2}=0}^{\infty} e^{\beta\mu(n_1+n_2)-\beta(\varepsilon_1 n_1+\varepsilon_2 n_2)} = \left(1 - e^{\beta\mu-\beta\varepsilon_1}\right)^{-1}\left(1 - e^{\beta\mu-\beta\varepsilon_2}\right)^{-1}$$

The factorization of function Z into components for each energy level is apparent. This principle can be easily applied to a varying number of levels.

$$\mathcal{Z} = e^{-\beta\Omega} = \prod_{a,\sigma} \left(1 - e^{-\beta\varepsilon_{a,\sigma} + \beta\mu}\right)^{-1}$$

The orbital degrees of freedom are listed here, while the symbol 'a' represents the z-projection of the spin of a boson. The equation can be used to determine the number of particles.

$$N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = \sum_{a,\sigma} f_B(\varepsilon_{a,\sigma}), \qquad f_B(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} - 1}.$$

The function $f_B(\varepsilon)$ is termed as the Bose-Einstein distribution function.

13.6. Liquid Helium

Investigating the superfluid transition of liquid helium at 2.2K provides an application for Bose-Einstein Statistics to understand its qualitative nature. It is noteworthy that ordinary helium is predominantly comprised of neutral atoms of the isotope. ${}^4_2He$.

The Bose-Einstein Statistics provide an explanation for the peculiar properties of helium at low temperature, as the total angular momentum of its atoms is zero. It has been discovered that helium displays distinct behaviors under these specific conditions.

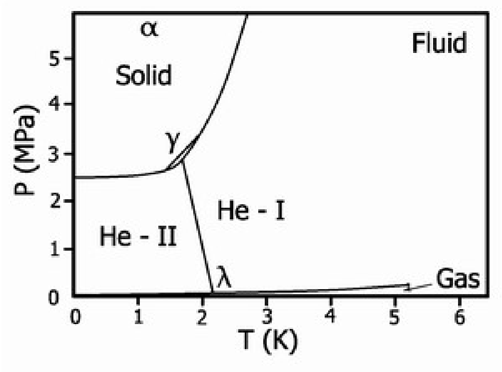
1. Helium gas at atmospheric pressure condenses at 4.3 K into a liquid of very low density about 0.124 gm/cm^3 (Its critical temperature is 5.2 K
2. Further cooling to about 0.82 K does not freez it and it is believed that it remains liquid all the way down to absolute zero. The solid state of helium does not form unless it is subjected to an external pressure of at least 23 atmospheres.
3. For ${}^4_2He$ in liquid phase there is another phase transition called $\lambda - transistion$, which divides the liquid state into two phases $He - IandHe - II$, while liquefying helium noted that at about 2.2K density appeared to pass through an abrupt maximum and decreasing slightly thereafter. It is also revealed that critical temperature is at 2.186 K and that it represents a transition to a new state of matter known as liquid $He - II$.

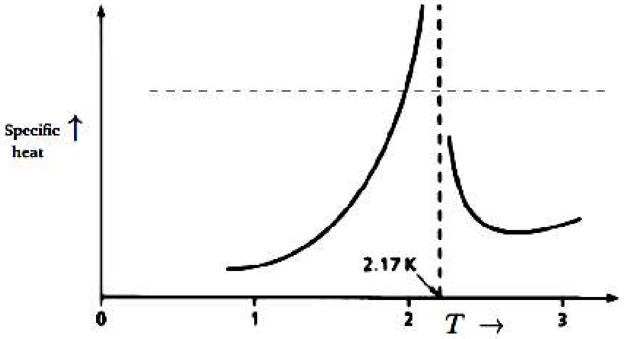
In liquid $He - II$ it is found that

a) Heat conductivity is very large of the order of 3.106 times greater

b) Co-efficient of viscosity gradually diminishes as the temperature is lowered and appears to be approaching zero at absolute zero tempature.

c) Specific Heat measurement shows that specific heat curve discontinuous at 2.186K. The shape of the specific heat curve resembles the shape of λ and therefore this peculiar transition is $\lambda - transistion$ and the discontinuity temperature 2.186K is called $\lambda - point$. Liquid helium state has no latent heat concluded that $HeI \rightrightarrows HeIIat\lambda T$is a second order transition.

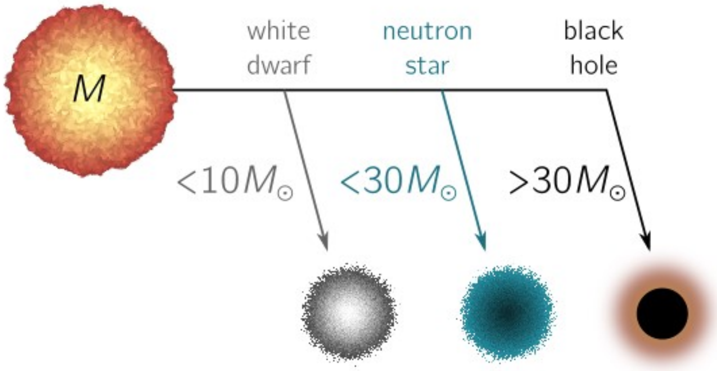




13.7. White Dwarf Stars and Chandrasekhar Mass Limit

When stars exhaust their fuel, the temperature drops to zero, leading them to depend on the Pauli exclusion principle for survival via degeneracy pressure. These stars, supported by electron degeneracy pressure, are classified as white dwarfs. Moreover, besides the fermions' kinetic energy $E_{kinetic}$ in the system, there is also gravitational energy. Assuming uniform density within a star of radius R,

$$E_{\text{grav}} = -\frac{3}{5}\frac{G_N M^2}{R}$$



A flow-chart for the fate of old stars.

The objective is to minimize $E_{\text{grav}}+E_{\text{kinetic}}$ in the assignment to establish the connection between the star's mass and radius, with GN denoting Newton's constant.

$$R \sim M^{-1/3}$$

When the star decreases in size, the Fermi energy decreases as well. At some point, it reaches a level similar to the electron mass me, causing our non-relativistic approximation to no longer be valid. To address this, we can recalculate using the relativistic formula for the density of states (adjusted by a factor of 2 to consider spin degeneracy). In the case of ultra-relativistic electrons, where $E \gg$ me, the density of states can be expanded.

$$g(E) = \frac{V}{\pi^2 \hbar^3 c^3}\left(E^2 - \frac{m^2 c^4}{2} + \ldots\right)$$

from which we can determine the kinetic energy due to fermions, replacing the non- relativistic result by

$$E_{\text{kinetic}} = \frac{V}{\pi^2 \hbar^3 c^3} \left(\frac{1}{4} E_F^4 - \frac{m^2 c^4}{4} E_F^2 + \dots \right)$$

The Fermi energy can be expressed in terms of the particle number by

$$N = \frac{V}{\pi^2 \hbar^3 c^3} \left(\frac{1}{3} E_F^3 - \frac{m^2 c^4}{2} E_F + \dots \right)$$

The total energy of the system is then given by,

$$E_{\text{grav}} + E_F = \left[\frac{3\hbar c}{4} \left(\frac{9\pi M^4}{4 m_p^4} \right)^{1/3} - \frac{3}{5} G_N M^2 \right] \frac{1}{R} + \mathcal{O}(R)$$

Where m_p is the proton mass (and we're taking $M = Nm_p$ as a good approximation to the full mass of the star). If the term above is positive then the star once again settles into a minimum energy state, where the 1/R term balances the term that grows linearly in R. But if the 1/R term is negative, the star is unstable to gravitational collapse and will shrink to smaller and smaller values of R. This occurs when the mass exceeds the Chandrasekhar limit, $M > Mc$. Neglecting factors of 2 and π, this limit is

$$M_C \sim \left(\frac{\hbar c}{G_N} \right)^{3/2} \frac{1}{m_p^2}$$

The mass of this object is approximately 1.5 times that of the Sun. Stars surpassing this threshold will not undergo white dwarf formation. Instead, their collapse could be halted by neutron degeneracy pressure, leading to the creation of a neutron star. Alternatively, if the collapse is not impeded, a black hole may form.

Self-Assessment

1 Explain the concept of Bose-Einstein condensation (BEC) and its occurrence in a Bose gas.

2 Provide a qualitative description of the properties of liquid helium.

3 Outline the derivation of Planck’s law of blackbody radiation using Bose-Einstein statistics.

4 What happens if a white dwarf exceeds the Chandrasekhar mass limit?

5 Why is the Chandrasekhar mass limit important in astrophysics?

6 **Planck's law of blackbody radiation can be derived from:**

A. Bose-Einstein statistics B. Fermi-Dirac statistics

C. Maxwell-Boltzmann statistics D. Boltzmann statistics

7 **Which system is best described as a photon gas according to statistical mechanics?**

A. X-ray emission from a star B. Blackbody radiation

C. Visible light from a light bulb D. Infrared radiation from a heater

8 **Which thermodynamic function is most relevant for describing a strongly degenerate Bose gas?**

A. Helmholtz free energy B. Gibbs free energy

C. Internal energy D. Entropy

9 **Which property of liquid helium distinguishes it qualitatively from other substances?**

A. It remains liquid at very low temperatures.

B. It exhibits superfluidity at low temperatures.

C. It has a high boiling point.

D. It shows ferromagnetic properties at low temperatures.

10 **The thermodynamic function most directly related to the energy distribution in a photon gas is:**

A. Entropy B. Internal energy

C. Helmholtz free energy D. Gibbs free energy

11 Liquid helium-4 exhibits which unique property at temperatures close to absolute zero?

A. Ferromagnetism B. Superfluidity

C. Insulating behavior D. High thermal conductivity

Key Words

Thermodynamics:

1. **System**: The portion of the universe under study.
2. **State Variables**: Quantities that describe the state of a system (e.g., temperature, pressure, volume).
3. **Process**: A change in the state of a system.
4. **First Law of Thermodynamics**: Conservation of energy principle.
5. **Second Law of Thermodynamics**: Describes the direction of natural processes (e.g., entropy increase).
6. **Entropy**: Measure of disorder or randomness in a system.
7. **Equilibrium**: State where no spontaneous change occurs.
8. **Heat**: Energy transferred due to temperature difference.
9. **Work**: Energy transferred due to a force acting through a distance.
10. **Enthalpy**: Heat content of a system at constant pressure.

Statistical Physics:

1. **Microstate**: Complete description of a system at the microscopic level.
2. **Macrostate**: Description of a system in terms of macroscopic variables (like temperature, pressure).
3. **Boltzmann Distribution**: Distribution of particles in energy states at thermal equilibrium.
4. **Statistical Ensemble**: Collection of all possible states of a system.
5. **Partition Function**: Sum over all microstates weighted by their Boltzmann factors.
6. **Thermal Equilibrium**: Condition where no net exchange of energy occurs between systems.
7. **Maxwell-Boltzmann Distribution**: Distribution of velocities of particles in an ideal gas.
8. **Canonical Ensemble**: Statistical ensemble where temperature, volume, and number of particles are fixed.
9. **Entropy in Statistical Physics**: Measure of the number of microstates corresponding to a given macrostate.
10. **Equipartition Theorem**: Energy is equally distributed among all degrees of freedom in thermal equilibrium.

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