

Block

3

SECOND AND THIRD LAWS OF THERMODYNAMICS

UNIT 8

Carnot Cycle

7

UNIT 9

Entropy and the Laws of Thermodynamics

29

UNIT 10

The Thermodynamic Potentials

51

UNIT 11

Theory of Radiation

77

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BLOCK 3 : SECOND AND THIRD LAWS OF THERMODYNAMICS

In Block 2, you have learnt the basic terminology of thermodynamics and the basic concepts that will be used in this course. You have also learnt the zeroth law and the first law of thermodynamics as well as their applications. You now know that the first law of thermodynamics is essentially the principle of conservation of energy for thermodynamic systems. Moreover, each of these laws introduces a new thermodynamic variable, which has universal validity.

Block 3 deals with conversion of heat into work using a heat engine working in a cycle, an ideal Carnot engine and its efficiency. In this block, you will also learn the Kelvin-Planck and Clausius statements of the second law of thermodynamics and their equivalence, and Carnot theorem.

One of the most important concepts in thermodynamics is that of entropy introduced by Clausius. In fact, thermodynamics became an important science only after the introduction of entropy. A detailed study of entropy near absolute zero led Planck to the third law of thermodynamics. These developments were followed by the formulation of thermodynamic free energies.

Block 3 ends with a detailed discussion of the theory of black body radiation, which posed a huge challenge to physicists in the second decade of the twentieth century. To explain the observed results on spectral distribution of radiant energy, Planck presented his theory based on discrete nature of energy exchange.

In Unit 8, which is the first unit of Block 3, we have introduced the concept of heat engine. In this unit, we have obtained an expression for the efficiency of a completely reversible Carnot engine using T-S diagram. On inverting the sequence of processes occurring in a heat engine, we obtain a refrigerator. So, you will also learn about Carnot cycle as a refrigerator. Kelvin-Planck and Clausius summed up these observations in two different but equivalent statements. These are also discussed here. Carnot theorem – that no real engine can be more efficient than the Carnot engine – forms the subject of discussion in Sec. 8.5.

In Unit 9, you will learn about entropy, which is a property of state. We have obtained expressions for changes in entropy for an ideal gas under different physical conditions. Planck postulated that entropy of a system becomes zero as temperature approaches absolute zero. This led to the formulation of the third law of thermodynamics. You will realise why soon after Clausius introduced the concept of entropy, thermodynamics became a powerful science. (In Block 4, you will learn that entropy helps to connect thermodynamics with statistical mechanics. That is, entropy is a tool by which we can correlate the macroscopic and microscopic behaviours of a system.)

In Unit 10, we have discussed thermodynamic potentials, which are essential to determine the general condition of thermodynamic equilibrium. You will learn that these are a rich treasure of vast information. These are handy in obtaining Maxwell's relations, TdS equations, energy equations and involve a lot of good physics.

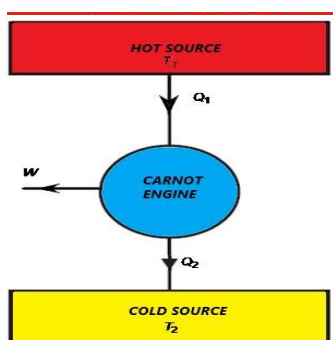
The mathematics used in this unit is quite simple and you are advised not to memorise relations. Instead, use mnemonic diagrams for deriving a relation of interest. Some illustrations to this effect are given in the text.

In the beginning of Unit 11, a few definitions and concepts about blackbody radiation are given. The Stefan-Boltzmann law, which relates the total energy density of black body radiation with temperature, is discussed in detail. But it does not give any information about the distribution of energy in different parts of the spectrum. We have discussed Planck's law and shown that Rayleigh-Jeans law, Wien's law and Stefan's law are contained in the Planck's law.

We hope that you enjoy studying the concepts discussed in this block. We wish you success.



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Carnot engine led to the industrialisation of Europe.

CARNOT CYCLE

Structure

- | | |
|---|--|
| <p>8.1 Introduction
Expected Learning Outcomes</p> <p>8.2 Heat Engines: Conversion of Heat into Work</p> <p>8.3 The Carnot Cycle
Efficiency of a Carnot Engine
Carnot Cycle as Refrigerator</p> | <p>8.4 The Second Law of Thermodynamics
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Equivalence of Kelvin-Planck and Clausius Statements</p> <p>8.5 Carnot Theorem</p> <p>8.6 Summary</p> <p>8.7 Terminal Questions</p> <p>8.8 Solutions and Answers</p> |
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STUDY GUIDE

In the previous units of this course, you have learnt about the zeroth law and the first law of thermodynamics. As you now know, these laws facilitated introduction of the concepts of temperature and internal energy, respectively. In this unit, you will learn about conversion of heat into work, Carnot cycle and the second law of thermodynamics.

In TQ 9 of Unit 7, you have obtained expression for the work done in Carnot cycle depicted on an indicator diagram. We will extend this result to calculate the efficiency of Carnot engine and show that no engine can be more efficient than a Carnot engine. As mentioned earlier, thermodynamics is a phenomenological science and its laws need no proof. In fact, the second law of thermodynamics has been stated in two different but equivalent forms by Kelvin-Planck and Clausius. You will learn these equivalent statements.

The mathematics used here is rather simple and basically, we will use the results derived in Unit 7. You are, therefore, advised to master that unit before reading this unit. Moreover, if you work out SAQs and TQs given in this unit on your own, you will appreciate the subject matter better.

***“Imagination is more important than knowledge.
Knowledge is limited. Imagination encircles the world.”***

Albert Einstein

8.1 INTRODUCTION

We now know that the first law of thermodynamics is a statement of conservation of energy for thermodynamic processes. But it does not give us information about the direction of flow of heat. For instance, it is a common experience that heat flows from a hotter body to a colder body spontaneously but it cannot flow by itself from a colder body to a hotter body. However, the first law of thermodynamics does not rule out this possibility. Similarly, it is a common experience that it is possible to completely convert work into heat via friction, say. But the first law of thermodynamics puts no definite limitation on conversion of heat into work, though engineering experience refrains us from achieving 100% conversion. If this were not true, we could convert virtually unlimited heat of the environment into work and energy crisis would not have been such an issue for present day civilisation. We can similarly consider many natural processes where energy is conserved but those never happen. This suggests that besides the first law, we must have some other fundamental principle which satisfactorily explains these facts of experience. This principle is known as the *second law of thermodynamics*. In fact, the second law goes far beyond conversion of heat into work.

In Sec. 8.2, we begin our discussion by considering convertibility of heat into work using a heat engine. For simplicity, we confine ourselves to the framework of reversible Carnot cycle. We derive an expression for the efficiency of a Carnot engine in Sec. 8.3. You will learn that the direction of operation of Carnot cycle determines whether a device acts as a heat engine or a refrigerator. It is for such reasons that Carnot cycle is the most important reversible cycle of great practical utility. You will also learn that Carnot engine has maximum efficiency but it is a theoretical idealisation.

It may be mentioned here that contributions of Carnot facilitated industrial revolution in Europe. As we now know, the work of Carnot led Clausius, Thomson (later Lord Kelvin) and Planck, among others, to study convertibility of heat into work. These studies led them to sum up generalisations of experiences in different statements of the second law. However, the two most well-known statements of the second law are due to Kelvin-Planck and Clausius. These statements are discussed in detail and their equivalence has also been established in Sec. 8.4. We show that if one statement is not obeyed, the other one is also violated. In Sec. 8.5, we have discussed Carnot theorem.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ derive the expression for the efficiency of a Carnot engine;
- ❖ explain the physics of the working of a heat engine and a refrigerator;
- ❖ state Kelvin-Planck and Clausius statements of the second law of thermodynamics, discuss their implications and prove their equivalence; and
- ❖ establish Carnot theorem.

8.2 HEAT ENGINES: CONVERSION OF HEAT INTO WORK

Let us begin our discussion by stating the preliminaries of heat engines which convert heat into work.

Basic Terminology

We know that heat flows spontaneously from a hotter to a colder body. If we intercept this flow with a machine, some of it can be converted into work. A *machine that can convert heat into work is known as heat engine*. To be a useful device, a heat engine must operate continuously; absorb heat at a higher temperature and reject it at a lower temperature. That is to say, **a heat engine operates between two heat reservoirs** (Fig. 8.1). Moreover, the processes which take place inside an engine must not cause permanent changes. This means that **an engine has to operate in a cycle**.

The material used in the operation of an engine is called the *working substance*. The working substance can be solid, liquid or gas. In a steam engine, the working substance is steam (water). Other familiar working substances for automobile engines are petrol, diesel and CNG. In a refrigerator, the most widely used working substances used to be chlorofluorocarbon compounds. But these have now been phased out as these deplete the ozone layer present in stratosphere.

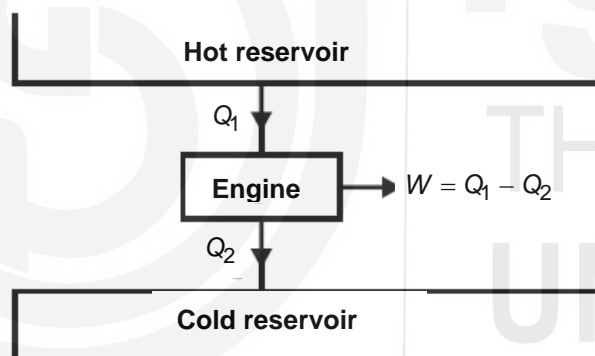


Fig. 8.1: Schematics of operation of a heat engine.

Efficiency

The efficiency of an engine is defined as the ratio of the net work done to the heat absorbed during one complete cycle. It is usually denoted by the symbol η (pronounced as eta):

$$\eta = \frac{\text{Useful work done}}{\text{Heat absorbed}} \quad (8.1)$$

After one complete cycle, the engine returns to its original state. Therefore, there will be no change in its internal energy, i.e. $\Delta U = 0$. Using the first law, we can write

$$\Delta U = Q_1 - Q_2 - W = 0$$

or

$$W = Q_1 - Q_2 \quad (8.2)$$



Nicolas Leonard Sadi Carnot (1796-1832) was a French physicist and engineer. With his pioneering work on heat engines, he successfully proposed an engine based on reversible thermodynamic processes, which offered maximum possible efficiency. Unfortunately, his work was not appreciated during his life time. Clausius and Kelvin used his ideas to propose the second law of thermodynamics.

Recap

where Q_1 is the heat absorbed from the source, Q_2 is the heat rejected to the sink and W is the work done during one cycle (Fig. 8.1). Note that in a real engine, heat is rejected to the surroundings in the form of hot exhaust gases or steam and, therefore, Q_2 contributes to *thermal pollution* of our environment.

From Eqs. (8.1) and (8.2), we can write

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \quad (8.3)$$

This result shows that efficiency of a heat engine will always be less than one. Nevertheless, it is desirable to design an engine with maximum efficiency. To know how high η can be, we have to consider the conditions in which an engine operates and the role of the working substance. You will learn about these in the following sections. However, it may suffice to say here that Carnot was the first researcher who recognised that for maximum efficiency, a heat engine should be (thermodynamically) reversible. That is, all stages of operation should be carried out infinitely slowly so that there are no dissipative losses due to friction or turbulence, leading to wastage of energy. (In practice, however, there are always some losses.) It may be mentioned here that any heat engine operating in a Carnot cycle is called a *Carnot engine* and the working substance exchanges heat with heat reservoirs. We will discuss it in some detail now. But before that let us now summarise what you have learnt in this section.

CONVERSION OF HEAT INTO WORK

- A machine responsible for conversion of heat into work is called a heat engine.
- In a steam engine (power-plant or an automobile) we burn fuel for generating heat which, in turn, makes the engine do work through the motion of a piston (turbine).
- The difference in the heat generated and the amount utilised to do work is released to surroundings and is one of the causes of thermal pollution of our environment.
- The ratio of work done and heat absorbed characterises the efficiency of a machine which converts heat into work.

8.3 THE CARNOT CYCLE

The Carnot cycle consists of four stages. These are schematically depicted in Fig. 8.2. Suppose that T_1 and T_2 are temperatures of the heat reservoirs such that $T_1 > T_2$. The working substance, say a gas, is contained within a cylinder fitted with a frictionless piston. To simulate the working of a real engine, we consider the following reversible sequence:

i) isothermal expansion, ii) adiabatic expansion, iii) isothermal compression, and iv) adiabatic compression.

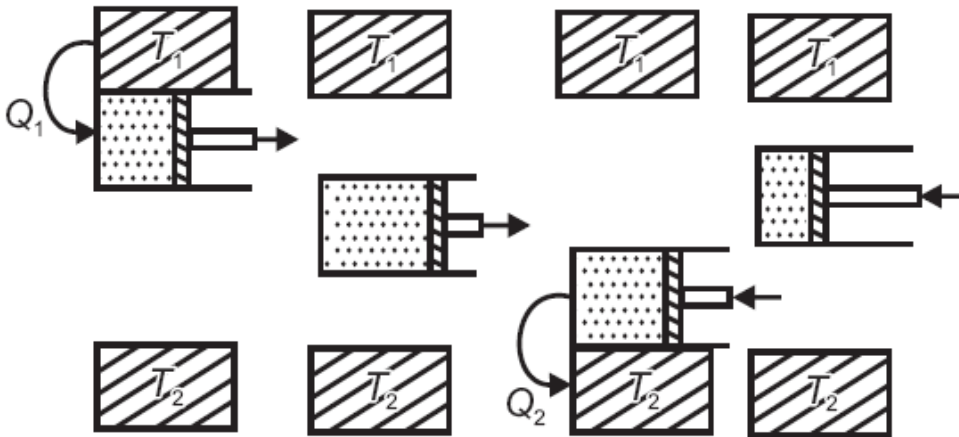


Fig. 8.2: Four stages in the Carnot cycle.

To realise the processes stated above in an engine, it is operated as follows:

1. We place the cylinder in thermal contact with the hot reservoir and let the gas undergo *reversible isothermal expansion*. Suppose heat Q_1 flows from the reservoir into the gas in this process. We have indicated this change as A to B on the p - V diagram in Fig. 8.3. (It was similarly depicted in Fig. 7.8 in TQ 9 in Unit 7). Note that the process is reversible so that the temperature of the working substance continues to be equal to the temperature of the reservoir during heat transfer.

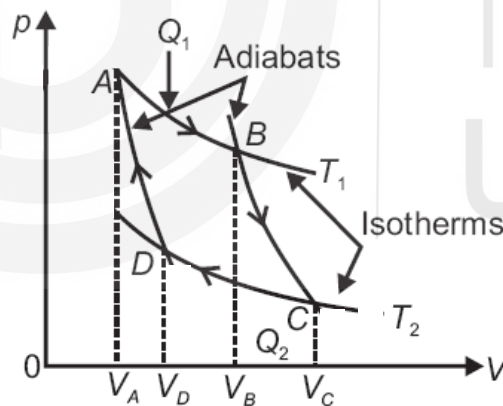


Fig. 8.3: Carnot cycle on indicator diagram.

2. Next, the gas is thermally isolated and allowed to undergo *reversible adiabatic expansion*. The temperature falls from T_1 to T_2 , the temperature of the cold reservoir. Do you know, why the temperature drops? It is because work is done by the gas at the cost of its internal energy. This change is indicated as B to C on the p - V diagram.
3. On attaining the state defined by C , the working substance is at relatively low pressure and to use it in a cycle, it has to be restored to its initial state. Therefore, the gas is compressed in two stages: First isothermally and then adiabatically. This is done by placing the cylinder in thermal contact with the cold reservoir at lower temperature T_2 and compressing the gas

isothermally and reversibly. Suppose heat Q_2 is given up by the gas to the cold reservoir. This change is indicated as C to D .

- Next, the gas is thermally isolated and compressed under reversible adiabatic conditions till its original state is restored.

8.3.1 Efficiency of a Carnot Engine

While answering TQ 9 of Unit 7, you have obtained expression for the work done by the gas in a Carnot engine. We just quote the result here:

$$W = nRT_1 \ln(V_B / V_A) - nRT_2 \ln \frac{V_C}{V_D} \tag{8.4}$$

To simplify this expression, we note that B and C (in Fig. 8.3) lie on the same adiabatic curve. Then, using Eq. (7.21), we can write

$$T_1 V_B^{\gamma-1} = T_2 V_C^{\gamma-1}$$

or
$$\frac{T_1}{T_2} = \left(\frac{V_C}{V_B} \right)^{\gamma-1} \tag{8.5}$$

Similarly, for states D and A we can write

$$\frac{T_1}{T_2} = \left(\frac{V_D}{V_A} \right)^{\gamma-1} \tag{8.6}$$

To simplify Eq. (8.7) we use the algebraic theorem that if powers are positive and equal, the bases are also equal.

On comparing Eqs. (8.5) and (8.6), we get

$$\left(\frac{V_C}{V_B} \right)^{\gamma-1} = \left(\frac{V_D}{V_A} \right)^{\gamma-1} \tag{8.7}$$

We can rewrite it as

$$\left(\frac{V_C}{V_B} \right) = \left(\frac{V_D}{V_A} \right)$$

or
$$\frac{V_B}{V_A} = \frac{V_C}{V_D}$$

Using this result in Eq. (8.4), we get

$$W = nR(T_1 - T_2) \ln(V_B / V_A) \tag{8.8}$$

On substituting this expression for W in Eq. (8.4), we can express the efficiency of a Carnot engine in terms of the temperatures within which it operates:

$$\begin{aligned} \eta &= \frac{W}{Q_1} = \frac{nR}{nRT_1} \frac{(T_1 - T_2) \ln(V_B / V_A)}{\ln(V_B / V_A)} \\ &= \frac{(T_1 - T_2)}{T_1} = 1 - \frac{T_2}{T_1} \end{aligned} \tag{8.9}$$

We can draw the following conclusions from this result:

You have learnt in TQ 9 in Unit 7 that using the first law of thermodynamics for an isothermal process, we can write

$$W_1 = Q_1$$

since $\Delta U = 0$

Work done by the gas on the piston is given by

$$W_1 = \int_A^B p dV$$

$$W_1 = Q_1 = nRT_1 \int_{V_A}^{V_B} \frac{dV}{V}$$

$$\therefore Q_1 = nRT_1 \ln(V_B / V_A)$$

1. Efficiency of a Carnot engine depends on the temperature difference between the source and the sink; greater the difference, higher will be efficiency. In practice, the temperature of the sink is limited by the surroundings and the only way to increase η is to raise temperature of the source, T_1 . It means that heat is more useful when it is supplied at a higher temperature. This explains why saturated steam at high pressure is a more efficient working substance.
2. Efficiency of a Carnot engine is less than one. This is a fundamental limitation imposed on the convertibility of heat into work by the second law of thermodynamics. (We know that most of the electricity is generated in large fossil fuel (coal, oil, gas) or nuclear power plants. These are basically heat engines (where energy is released in chemical or nuclear reactions).

The working substance, water, gets heated in a boiler and converted into steam at high pressure. It is made to expand adiabatically in a turbine, which is coupled to a generator and converts mechanical energy into electrical energy. The maximum efficiency of a power plant is about 50%. (This is also true of diesel and petrol engines.) It means that only half of the heat generated (fuel used) in a plant is converted into useful work. In fact, a substantial amount of our expensive fuel ends up as waste heat; it is released in the environment and causes thermal pollution, which is responsible for various ecological problems. It is, therefore, desirable to design maximum efficiency engines.

3. If the source and the sink are at the same temperature, the efficiency will be zero. It means that we cannot operate an engine (and convert heat into work) if there is no temperature difference. To understand this, consider the following situation:

You take a motor boat to sea and run out of fuel. (If you are lucky, you may be rescued by another boat.) The first law of thermodynamics permits you safe return as the ocean has a vast amount of energy. But the second law tells us that this energy cannot be converted into useful work because ocean surface is at an almost uniform temperature.

4. The efficiency of a Carnot engine is independent of the nature of the working substance. You may expect that real engines will also be independent of the working substance and ask: Why are we then so concerned about a particular fuel? The answer to this question lies in their availability, economics, technological feasibility and environmental factors. That is to say, thermodynamic considerations alone do not decide between various fuels and methods of harnessing energy sources.
5. On comparing the expressions of efficiency given in Eqs. (8.3) and (8.9), we can correlate the ratios of heat absorbed and heat rejected to temperature of the source and temperature of the sink:

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

Before proceeding further, answer the following SAQ.

SAQ 1 – Carnot engine

Can efficiency of a Carnot engine be increased more effectively by increasing T_1 or lowering T_2 ? Explain your answer.

You should now go through the following solved example.

EXAMPLE 8.1: EFFICIENCY CALCULATION

The cluster of nuclear power plants at Tarapur produces 540 MW electric power. In the reactor core, energy is released (as heat) at the rate of 1600 MW. Steam produced in the reactor enters the turbine at a temperature of 560K and leaves it at 350K. Calculate the efficiency of the power plant.

SOLUTION ■ The thermodynamic efficiency is given by Eq. (8.9):

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{350\text{K}}{560\text{K}} = 0.375$$

That is, the system is only 37.5% efficient.

The actual efficiency of a power plant is defined as the ratio of the electric power output to the thermal power produced:

$$\eta = \frac{540\text{MW}}{1600\text{MW}} = 0.337$$

The waste heat of 1060 MW is normally discharged in a river (like Ganges, Mahanadi) or sea. This is a huge amount of energy and harmful for aquatic life.

To reduce problems arising out of this, the designers of the power plant at Narora (UP) made use of cooling towers where expanding steam is made to cool by releasing heat to the atmosphere (air) rather than to water. This nevertheless causes thermal pollution in the troposphere.

Diesel engines used in vehicles constitute another example of heat engines. A typical automobile engine operates at about 800K and releases exhaust gases to the environment at about 300K.

The maximum possible efficiency is then

$$\eta = 1 - \frac{300\text{K}}{800\text{K}} = 0.63$$

In practice, the actual efficiency is much lower (~ 40%) and emanating hot gases are responsible for thermal pollution of our environment.

You may now like to answer an SAQ.

SAQ 2 – Efficiency of a Carnot engine

- a) In the tropics, the temperatures at the surface of the ocean and at a depth of 300m are 25°C and 5°C, respectively. Will you recommend to tap this energy? Discuss.
- b) A Carnot engine is made to work between ice point (273K) and nitrogen temperature (77K). Calculate its efficiency. Is it possible to attain this figure in actual practice?

Now go through the following example.

EXAMPLE 8.2: EFFICIENCY OF A CARNOT ENGINE

A Carnot engine has an efficiency of 60% when its sink temperature is at 27°C. Calculate the change in the source temperature for increasing its efficiency to 70%.

SOLUTION ■ Let the initial temperature of the source be T_1 . The temperature of the sink, $T_2 = 27^\circ\text{C} = 300\text{K}$.

Using Eq. (8.9) for a Carnot engine, we can write

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{T_1} = 0.6$$

On rearranging terms and solving for T_1 , we get

$$T_1 = 750 \text{ K}$$

Let the temperature of the source be raised to $(750 + T)\text{K}$ for efficiency to become 70%. Thus, we can write

$$\eta = 1 - \frac{300}{(750 + T)} = 0.7$$

On solving this, we get, $T = 250\text{K}$

Hence, the temperature of the source should be raised by 250 K.

SAQ 3 – Efficiency of a Carnot engine

An engine has an efficiency of 40%. Its efficiency is to be raised to 45%. By how much must the temperature of the source be increased if heat is released to atmosphere at 27°C?

You will now agree that the beauty of Carnot cycle lies in the fact that all its stages are completely reversible. So if you invert the sequence of processes occurring in a heat engine, you will obtain a refrigerator. Do you know that an air conditioner is also a refrigerator designed to cool a room? (The first

modern electrical air conditioner was designed by Willis Carrier in 1902 in Buffalo, New York.) Let us now understand the physics of this device.

8.3.2 Carnot Cycle as Refrigerator

Most of us now use refrigerators in our homes to keep various food items fresh so that they do not get stale and lose taste. This is done by keeping these cool. Have you ever thought: How is cooling achieved in a refrigerator? The most beautiful aspect of a Carnot engine is that we can run the whole system backward so that the sequence of events and their functions are reversed. Thus, Carnot cycle working in the reverse direction will act as an ideal *refrigerator*, in which heat is extracted from the reservoir at lower temperature and transferred to the reservoir at higher temperature. Therefore, in a sense, a refrigerator is also a heat engine.

Let us re-examine Fig. 8.3 again. If the directions of the arrows are reversed, the cycle $ABCD A$ becomes $ADCBA$. Since each process is reversible, the cycle is also reversible. Therefore, magnitudes of heat taken, heat rejected and the work done remain the same, except that their signs are reversed. It means that heat Q_2 is absorbed by the working substance from the lower temperature reservoir and heat Q_1 is rejected to the reservoir at higher temperature. And the work W represents the work done on the system (Fig. 8.4). In a domestic refrigerator, heat is pumped out of its interior, which is at a temperature lower than the surroundings and work is done by the motor driving the refrigerator. Thermodynamically, a refrigerator makes heat to flow from a lower temperature to a higher temperature, i.e., in a direction it does not spontaneously go. You can feel it by putting your hand near the coils, body, of the refrigerator. (You should not however touch the coils.)

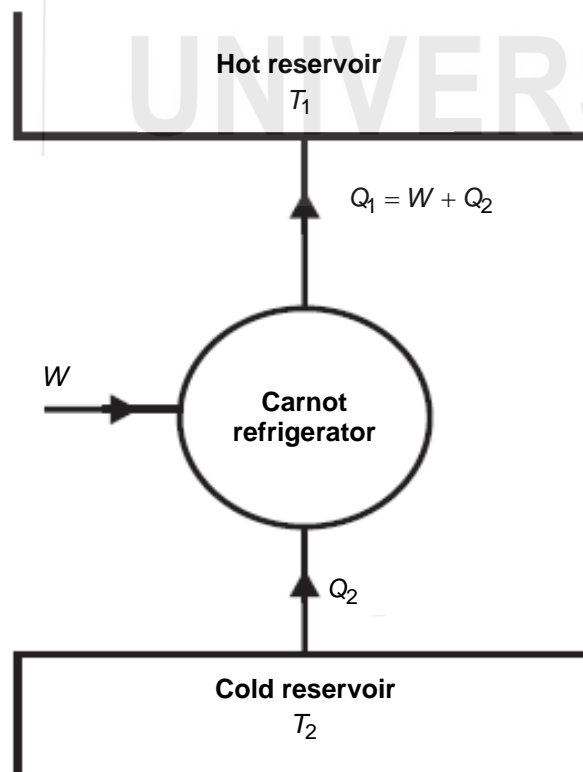


Fig. 8.4: A Carnot refrigerator.

The ability of a refrigerator is rated in terms of the *coefficient of performance* or *figure of merit*. We denote it by the symbol ω and define it as

$$\omega = \frac{\text{heat extracted at low temperature from the object to be refrigerated}}{\text{work input}}$$

Mathematically, we write

$$\omega = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} \quad (8.10)$$

where Q_2 is heat absorbed at the low temperature (cooler body) and Q_1 is heat rejected at higher temperature (kitchen environment).

In terms of temperatures of the eatables kept inside the refrigerator and the kitchen environment, we can express the coefficient of performance as

$$\omega = \frac{T_2}{T_1 - T_2} \quad (8.11)$$

where T_1 and T_2 , respectively denote the temperatures of the kitchen environment and the eatables kept inside the refrigerator.

On comparing the expressions for ω given by Eqs. (8.10) and (8.11), we can write

$$W = Q_2 / \omega = Q_2 \left(\frac{T_1 - T_2}{T_2} \right) \quad (8.12)$$

We can derive following conclusions from Eqs. (8.11) and (8.12):

- i) ω is directly proportional to T_2 . That is, the coefficient of performance will be small when T_2 is low. In fact, ω approaches zero as $T_2 \rightarrow 0$. This means that more work will have to be done or more energy will be used up by the refrigerator for transferring the same amount of heat as T_2 decreases. If $T_2 = 0$, infinite amount of work will be required to produce cooling. This essentially implies that it is not possible to attain absolute zero mechanically.
- ii) ω is inversely proportional to $T_1 - T_2$, i.e., lesser the difference between the hot and cold bodies, greater will be the coefficient of performance. As $(T_1 - T_2)$ approaches zero, ω approaches infinity. This means that a refrigerator will be most effective when eatables/chemicals placed inside it are close to the temperature of surroundings. So to conserve energy, it is advisable to put eatables in a kitchen refrigerator while they have cooled to room temperature. (You may have seen your maid/mother/sister allowing boiled milk to cool down to room temperature before putting it in the refrigerator. If they are not doing so, advise them accordingly.)
- iii) Unlike the efficiency of a heat engine, the coefficient of performance of a refrigerator can be *greater than unity*. That is, the amount of heat removed from the refrigerated space can be greater than the work input. (In fact, one of the reasons for expressing the efficiency of a refrigerator by another nomenclature – the coefficient of performance – is the intention to avoid confusion of having thermal efficiencies greater than unity.) To give you an

idea about the figure, let us consider that freezer in a refrigerator or cold storage is maintained at -10°C and the room temperature is 30°C . You can readily convince yourself that the value of coefficient of performance in this case will be $\omega = \frac{263}{40} = 6.58$.

You should now go through the following examples to grasp the ideas discussed in this section.

EXAMPLE 8.3: COEFFICIENT OF PERFORMANCE

A typical home freezer operates between -18°C and 30°C . Calculate the maximum value of ω of this refrigerator. With this ω , how much electrical energy would be required to freeze 0.5 kg of water, initially at 0°C . Given latent heat of fusion = 334 kJ kg^{-1} .

SOLUTION ■ The coefficient of performance is given by Eq. (8.11) as

$$\omega = \frac{T_2}{T_1 - T_2} = \frac{255\text{K}}{303\text{K} - 255\text{K}} = \frac{255\text{K}}{48\text{K}} = 5.3$$

To produce 0.5 kg of ice, you have to extract heat from water. It is given by

$$Q = mL$$

where L is latent heat of fusion. Hence,

$$Q_2 = (0.5 \text{ kg}) \times (334 \text{ kJ kg}^{-1}) = 167 \text{ kJ}$$

Using Eq. (8.10), you can write: $W = \frac{Q_2}{\omega} = \frac{167\text{kJ}}{5.3} = 31.5\text{kJ}$

In actual practice, ω would be lower and the corresponding work input would be higher because a real engine is not completely reversible.

EXAMPLE 8.4: COEFFICIENT OF PERFORMANCE

A domestic refrigerator is driven by a 1000 W electric motor, which operates at an efficiency of 60%. If the refrigerator can be treated as a reversible heat engine operating between -10°C and 20°C , calculate the time required by it to freeze 10 kg of water which is at 0°C . Neglect heat losses. Take latent heat of fusion of ice as 334 kJ kg^{-1} .

SOLUTION ■ We know that work done by a refrigerator is given by

$$W = Q_2 \left(\frac{T_1}{T_2} - 1 \right)$$

Here $T_1 = 20^{\circ}\text{C} = 293 \text{ K}$, and $T_2 = -10^{\circ}\text{C} = 263 \text{ K}$. Since the refrigerator is being driven by a motor of 1000 W with 60% efficiency, we get

$$W = 1000 \times \frac{60}{100} = 600 \text{ W} = 600\text{Js}^{-1}$$

$$\text{Hence, } Q_2 = W \times \frac{T_2}{T_1 - T_2} = 600 \times \frac{263K}{293K - 263K} = 5260 \text{ Js}^{-1}.$$

But the heat required to freeze 10 kg of water = $mL = 10 \times 334$ KJ. Hence the time required to extract 334×10^4 J of heat

$$t = \frac{334 \times 10^4 \text{ J}}{5260 \text{ Js}^{-1}} = 635 \text{ s} = 10 \text{ min } 35 \text{ s}$$

In a household refrigerator, Freon-12 is used as the working substance. It has a boiling point of -29°C . (Freon-12 is a gas at room temperature.) Freon gas in a tube is made to expand suddenly from high pressure to low pressure. In this process it cools and a vapour-liquid mixture is obtained. This cold fluid, circulated through expansion coil around the region to be cooled, absorbs heat from the eatables kept inside the refrigerator and the entire liquid in the mixture changes into vapour. The vapour is compressed and work is done by the compressor on the vapour. The temperature as well as pressure of the vapour rise. The compressed vapour rejects heat to the surrounding medium such as the kitchen air and condenses through a set of tubes (called condenser and located at the back of the refrigerator).

It has been observed that CFCs adversely affect the life protecting layer of ozone in our atmosphere. So, there is now growing emphasis on phasing out CFCs. In India, non-CFC refrigerators are available.

An air-conditioner is also a refrigerator and the refrigerated space is a room rather than the food compartment. A window air-conditioning unit produces cooling by discharging heat of the air in the room outside. (When you travel by an aeroplane, sit in an air-conditioned room/office for long hours, it is advisable to drink water every half-hourly to avoid dehydration due to loss of body heat in the form of perspiration.) The same unit can also be used as heat pump by installing it backward. Now-a-days, systems fitted with controls so as to operate them as air-conditioners in summer and as heat pump in winter are available in the market.

We hope that now you appreciate the importance of Carnot's work on convertibility of heat into work. In fact, Carnot's genius lay in his imagination that a heat engine is the most efficient machine when it is operated in a reversible cycle. Historically, the work of Carnot led to the formulation of the second law of thermodynamics, which is a generalization of certain experiences and observations about the direction of transfer of thermal energy. This law has been stated in two different ways: (i) by Kelvin and Planck and (ii) by Clausius. We now discuss these in turn.

8.4 THE SECOND LAW OF THERMODYNAMICS

Kelvin and Planck confined themselves to the working of a heat engine and summarised the fact that it converts only a part of heat into work; the rest is rejected to a sink at a lower temperature. Let us now learn about it.

8.4.1 The Kelvin-Planck and Clausius Statements

Kelvin-Planck statement of the second law of thermodynamics is as follows:

No process is possible whose sole result is complete conversion of heat into work.

This statement implies that one cannot devise a machine which just absorbs heat from a reservoir and produces 100% work. That is, we need two reservoirs for exchange of heat and running an engine in a cycle.

There are other processes in which energy is conserved but they do not occur. For example, it is a fact of experience that heat does not flow on its own from a body at a lower temperature to a body at higher temperature. That is, spontaneous heat flow is unidirectional and is a fact of experience. It is contained in the Clausius statement of the second law of thermodynamics, which is as follows:

No process is possible whose sole result is the transfer of heat from a body at a lower temperature to a body at a higher temperature.

Note that Clausius statement is relevant for the working of a refrigerator. An important implication of this statement is that it is not possible to transfer heat from a cold body to a hot body without some change somewhere, including the working substance/surroundings of the system.

Note that the two statements of the second law apparently seem different or unconnected but they are equivalent. In fact, each statement implies the other. If one statement is untrue, will the other statement necessarily be untrue? Indeed, it is so and the truth of either form is both a necessary and sufficient condition for the truth of the other. We now discuss the equivalence of Kelvin-Planck and Clausius' statements.

8.4.2 Equivalence of Kelvin-Planck and Clausius Statements

The equivalence of these statements implies that if one statement is untrue, the other statement is necessarily untrue.

1. Let us suppose that the Clausius statement of the second law is violated by a hypothetical refrigerator A . Suppose that it transfers Q_2 units of heat in each cycle from a cold reservoir at temperature T_2 to a hot reservoir at temperature T_1 without expenditure of any work (Fig. 8.5a). Let us now assume that a heat engine working between the same heat reservoirs draws an amount of heat Q_1 from the hot reservoir and rejects heat Q_2 to the low temperature reservoir and performs work $W_{net} = Q_1 - Q_2$ in one cycle. Further, suppose that the heat engine operates at such a rate that it completes one cycle in the same period as does the refrigerator.

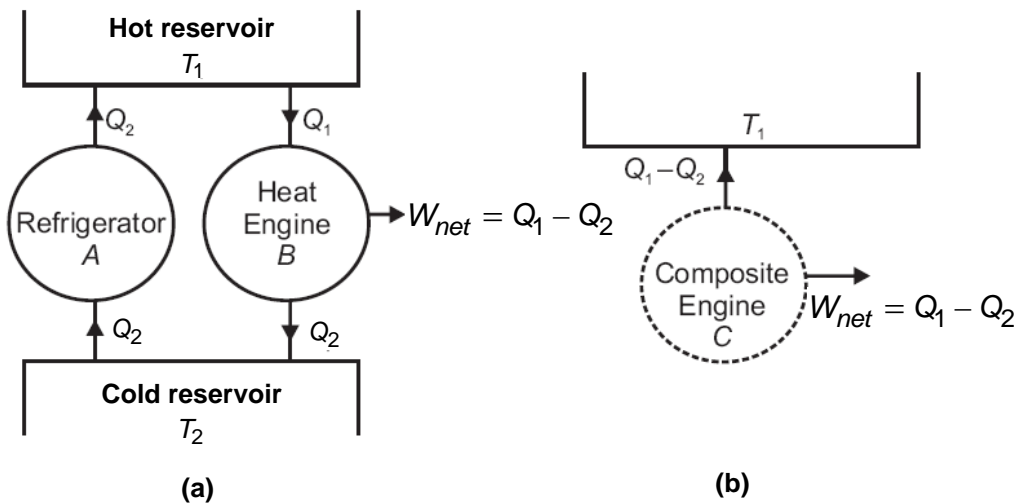


Fig. 8.5: a) Refrigerator *A* supposedly violates the Clausius statement of the second law, whereas *B* does not violate the law; b) the composite engine violates the Kelvin-Planck statement.

Now suppose that a composite engine is formed by considering the refrigerator and the heat engine to act together (Fig. 8.5b).

Since the heat drawn by the heat engine Q_2 is equal to the heat rejected by the refrigerator, the need for the hot reservoir will be eliminated completely, if heat Q_1 were fed to the heat engine by the hotter reservoir. That is, even though the composite engine exchanges heat with only one reservoir at a fixed temperature, there is net work output in each cycle.

Such a composite engine obviously violates Kelvin-Planck statement, which implies that no engine can run with just one reservoir.

- To prove that if Kelvin-Planck statement is violated, the Clausius statement is also violated, let us consider a hypothetical heat engine which extracts heat Q_1 from the hot reservoir, converts it completely into work and rejects no heat to the low temperature reservoir (Fig. 8.6a).

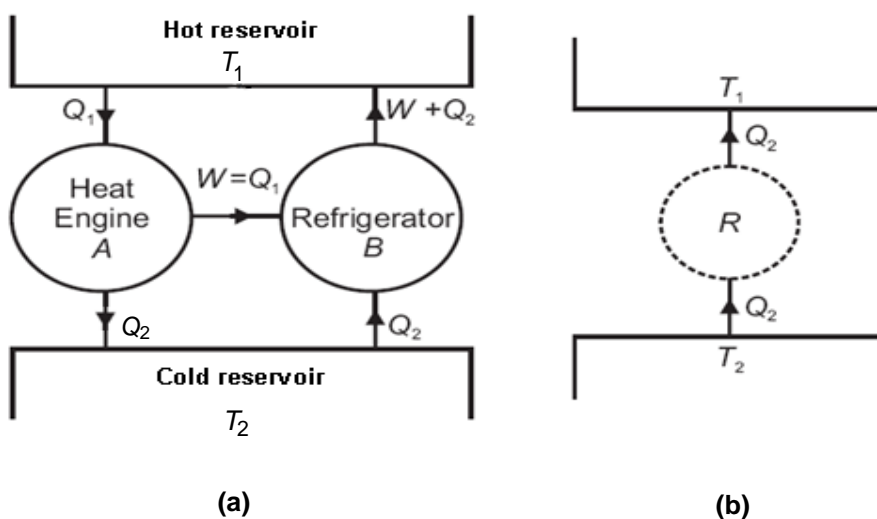


Fig. 8.6: a) Heat engine *A* violates Kelvin-Planck statement of the second law, whereas refrigerator *B* does not violate the law; b) the composite engine violates Clausius' statement.

Suppose that the work performed by the heat engine is used to drive a refrigerator operating between reservoirs at temperatures T_1 and T_2 . Further, suppose that the refrigerator absorbs heat Q_2 from the low temperature reservoir and rejects heat $W + Q_2$ to the hot reservoir per cycle. As before, we also assume that the refrigerator completes one cycle in the same period as does the heat engine.

You will agree that the refrigerator by itself does not violate any law but when it is made to form a composite engine with a heat engine (Fig. 8.6b), the net result of operation of the composite system will be to transfer heat Q_2 from the low temperature reservoir to the higher temperature reservoir **without any external work**. This obviously violates Clausius statement of the second law. You can now conclude that both the statements of the second law are equivalent.

Having analysed the operation of Carnot cycle, we can do two things: a) show that no real engine can be more efficient than the Carnot engine, i.e., prove *Carnot theorem*, and b) introduce the concept of *thermodynamic temperature*.

Let us now discuss Carnot theorem.

8.5 CARNOT THEOREM

Carnot theorem states that *of all heat engines working between the same (constant) temperatures, the reversible Carnot engine has the maximum efficiency*. Let us consider an irreversible engine (I) and a reversible engine (R) operating between the same reservoirs which are at temperatures T_1 and T_2 . Suppose that the irreversible engine is more efficient than a reversible engine. That is, we assume that

$$\eta_I > \eta_R$$

And Carnot theorem demands that this assumption is to be proved wrong. So, if the assumption is valid, then we must have

$$\frac{W}{Q_1} > \frac{W}{Q'_1} \quad (8.13)$$

where Q_1 is heat absorbed by the irreversible engine and $W = Q_1 - Q_2 = Q'_1 - Q'_2$. This implies that $Q'_1 > Q_1$. That is, heat absorbed by the reversible engine is more than that absorbed by an irreversible engine.

We now couple these engines and regard the system of combined engines to be a single device. Now suppose that the work produced by the irreversible engine is used to drive the reversible engine backwards so that it acts as a (Carnot) refrigerator, as shown in (Fig. 8.7). Thus, the overall effect of the combined engine is to transfer a net amount of heat

$(Q_1 - W) - (Q'_1 - W) = Q_1 - Q'_1$ from the cold reservoir to the hot reservoir on its own. That is, the combined engine acts as a self-acting device, which requires no external input. But this is forbidden by the Clausius statement of the second law. Therefore, the assumption that $\eta_I > \eta_R$ is not valid, i.e., an irreversible engine cannot have efficiency greater than that of the reversible engine i.e., $\eta_I < \eta_R$. In fact, the efficiency of a Carnot engine is maximum.

We should expect it physically because friction and heat losses in an irreversible engine will make it less efficient.

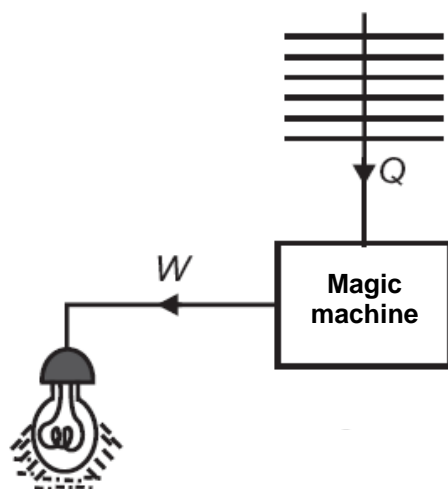


Fig. 8.7: Illustrating the proof of Carnot's theorem.

A corollary of Carnot theorem is: *All reversible engines operating between the same temperature limits have the same efficiency.*

It may be remarked here that Carnot engine is an ideal device because all losses due to conduction, radiation or friction are assumed to be absent. However, in real appliances, some useful energy is always dissipated. Yet, a study of this idealized engine helps us to understand the working of a real engine. You should now go through the following example.

EXAMPLE 8.5: Carnot theorem

For a reversible engine, show that $\sum \frac{Q}{T} = 0$.

SOLUTION ■ According to Carnot theorem: $\eta_I \leq \eta_R$

where η_R denotes the efficiency of a Carnot engine and η_I is the efficiency of any other engine operating between the same temperature limits. In terms of heats exchanged, we can write

$$1 - \frac{Q'_2}{Q'_1} \leq 1 - \frac{Q_2}{Q_1} \quad \text{or} \quad \frac{Q'_2}{Q'_1} \geq \frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

Hence,
$$\frac{Q'_1}{T_1} - \frac{Q'_2}{T_2} \leq 0$$

Therefore, for any cycle in which heat exchange takes place with two reservoirs only, the algebraic sum

$$\sum \frac{Q}{T} \leq 0.$$

Note that the equality sign holds for a reversible cycle, whereas the inequality sign holds for an irreversible cycle.

We now sum up what you have learnt in this unit.

8.6 SUMMARY

Concept	Description
Efficiency of a Carnot engine	<ul style="list-style-type: none"> The efficiency of Carnot's engine is maximum. The efficiency of a heat engine is given by: $\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$
Second law of thermodynamics	<ul style="list-style-type: none"> Two equivalent statements of second law of thermodynamics are due to Kelvin-Planck, and Clausius. The Kelvin-Planck statement governs the working of a heat engine. It states that <i>it is impossible to construct an engine, no matter how ideal, which, working in a cycle, will transform the entire heat into</i> The Clausius statement of second law governs the working of a refrigerator. It states that <i>it is impossible to make a refrigerator operate in a cycle so that its sole effect is transfer of heat from a cooler body to a hotter body.</i>
Coefficient of performance	<ul style="list-style-type: none"> The coefficient of performance of a refrigerator is given by: $\omega = \frac{Q_2}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2}$

8.7 TERMINAL QUESTIONS

- A reversible engine works between two temperatures and the difference of two temperatures is 110°C. If it absorbs 756 J of heat from the source and gives 536 J to the sink, calculate the temperature of source and sink.
- A Carnot engine whose sink is at 300 K has an efficiency of 40 percent. (i) Determine the source temperature. (ii) Obtain the increment in the temperature of source to increase the efficiency by 25 percent of original efficiency?
- A Carnot engine has efficiency 25%. It operates between reservoirs of constant temperature with temperature difference of 80 K. Calculate the temperature of the low-temperature reservoir in Celsius.
- The efficiency of a Carnot's engine at particular source and sink temperatures is $\frac{1}{2}$. When the sink temperature is reduced by 100°C, the engine efficiency becomes $\frac{2}{3}$. Calculate the new source temperature.

5. An ideal Carnot engine, whose efficiency is 40%, receives heat at 500 K. If its efficiency is 50%, calculate the intake temperature for the same exhaust temperature.

8.8 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. The efficiency of a Carnot engine can be increased more effectively by increasing the temperature of source. Increasing the temperature of sink will have opposite effect.

$$2. \text{ a) } \quad \eta = 1 - \frac{T_2}{T_1} = 1 - \frac{278}{298} = \frac{20}{298} = 0.07 = 7\%$$

This is a highly inefficient system and it is not advisable to tap this source of energy.

$$\text{b) } \quad \eta = 1 - \frac{77}{273} = \frac{196}{273} = 0.72 = 72\%$$

It is too high to be attainable in practice.

3. From Eq. (8.9) we recall that

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

Here $T_2 = 273 + 27 = 300$ K and $\eta = 0.40$.

Using this data, we can easily calculate the temperature of the source:

$$0.40 = 1 - \frac{300}{T_1}$$

$$\text{so that } T_1 = \frac{300}{0.60} = 500\text{K}$$

For the increased efficiency, we can write

$$T_1' = \frac{300}{0.55} = 545.5 \text{ K} \quad (\text{ii})$$

Hence the temperature of the source should be raised by

$$\Delta T = T_1' - T_1 = (545.5 - 500) \text{ K} = 45.5 \text{ K}$$

Terminal Questions

1. Let the temperature of the source and sink be T_1 and T_2 , respectively. It is given that

$$T_1 - T_2 = 110^\circ\text{C} = 110\text{K}$$

(As temperature differences in Celsius and Kelvin scales are the same.)

Using Eq. (8.9), the efficiency of the heat engine is given by

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \quad \left(\text{as } \frac{Q_1}{Q_2} = \frac{T_1}{T_2} \right)$$

$$\text{or } \eta = \frac{T_1 - T_2}{T_1}$$

$$\frac{T_1}{T_2} = \frac{Q_1}{Q_2} = \frac{756}{536} \Rightarrow \frac{T_2}{T_1} = \frac{536}{756}$$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{536}{756} = \frac{220}{756}$$

$$\text{or } \frac{110}{T_1} = \frac{220}{756} \quad (\text{since } T_1 - T_2 = 110\text{K})$$

On solving the above equation, we get

$$T_{1_{\text{source}}} = 378\text{K} \quad \text{and}$$

$$T_{2_{\text{sink}}} = 268\text{K} \quad (\because T_1 - T_2 = 110\text{K})$$

2. i) Using Eq. (8.9), we can write

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

where T_1 is the temperature of the source and T_2 that of the sink. On inserting the values in the above expression, we get

$$\frac{40}{100} = 1 - \frac{300}{T_1}$$

$$\text{Hence, } \frac{2}{5} = 1 - \frac{300}{T_1}$$

$$\text{or } 2T_1 = 5T_1 - 1500$$

$$\therefore T_1 = 500\text{K}$$

Hence, the source temperature is 500 K.

ii) 25% of original efficiency = 10%. Therefore, we can write

$$\frac{40 + 10}{100} = 1 - \frac{300}{T_1 + x}$$

where x is the increment in temperature. On solving, we get

$$\frac{1}{2} = \frac{T_1 + x - 300}{T_1 + x}$$

$$\text{or } T_1 + x = 2T_1 + 2x - 600$$

$$\text{or } 500 + x = 1000 + 2x - 600$$

$$\text{or } 500 + x = 400 + 2x$$

$$\therefore x = 100 \text{ K}$$

Hence, the temperature of source should be raised by 100 K.

3. We use the expression of efficiency,

$$\eta = 1 - \frac{T_L}{T_H},$$

where T_L and T_H are the temperatures of reservoirs in Kelvin.

$$\therefore \frac{1}{4} = 1 - \frac{T_L}{T_H} \quad (\text{i})$$

$$\text{or } T_H = \frac{4}{3} T_L \quad (\text{ii})$$

Also, it is given that $T_H - T_L = 80$

On substituting the value of T_H from Eq. (i), we can write

$$\frac{4}{3} T_L - T_L = 80 \text{ K}$$

$$T_L \left(\frac{4}{3} - 1 \right) = 80 \text{ K}$$

$$\text{or } T_L \left(\frac{4-3}{3} \right) = 80 \text{ K}$$

$$\text{or } T_L = 240 \text{ K}$$

In Celsius, $T_L = (240 - 273)^\circ\text{C} = -33^\circ\text{C}$

4. The expression for efficiency is given by Eq. (8.9) as

$$\eta = 1 - \frac{T_2}{T_1} \quad (\text{i})$$

Substituting the value of $\eta = \frac{1}{2}$ in Eq. (i), we can write

$$\eta = \frac{1}{2}$$

$$\therefore 1 - \frac{(T_2 - 100)}{T_1} = \frac{2}{3} \quad (\text{ii})$$

On solving Eq. (i), we get

$$\frac{T_2}{T_1} = \frac{1}{2} \quad (\text{iii})$$

Similarly, solving Eq. (ii), we get

$$\frac{(T_2 - 100)}{T_1} = \frac{1}{3} \quad (\text{iv})$$

Dividing Eq. (iii) by Eq. (iv), we get

$$\frac{T_2}{(T_2 - 100)} = \frac{3}{2}$$

or $2T_2 = 3T_2 - 300$

or $T_2 = 300 \text{ K}$

$$T_1 = 600 \text{ K.}$$

Hence, the new source temperature will be 600 K.

5. We can write the expression of efficiency using Eq. (8.9) as

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

On substituting the values, we can write

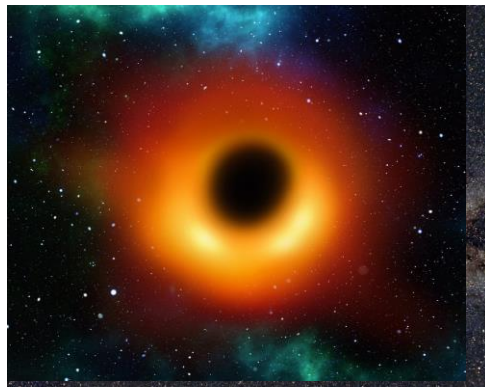
$$0.4 = 1 - \frac{T_2}{500}$$

On solving, we get

$$T_2 = 300 \text{ K}$$

Now, $0.5 = 1 - \frac{300}{T_1}$

$$\therefore T_1 = 600 \text{ K}$$



The entropy of the universe is continuously increasing.

(Picture source: <https://pixabay.com/illustrations/black-hole-abstract-photoshop-4118711/>)

ENTROPY AND THE LAWS OF THERMODYNAMICS

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STUDY GUIDE

In the previous unit, you have learnt how to obtain the expression for efficiency of Carnot engine and coefficient of performance of a refrigerator using an indicator diagram. In this unit, you will learn about entropy, which is a variable of state and used to state the second law of thermodynamics. You will learn that entropy is a mathematical tool. That is, unlike temperature and pressure, entropy cannot be measured. You will also learn how to obtain expressions for entropy changes for a few typical thermodynamic systems.

The expression for efficiency of a Carnot engine can be obtained rather easily using the temperature-entropy (T - S) diagram. You will learn that the calculation of the absolute value of entropy is not possible even for a reversible process. However, the behaviour of entropy at low temperatures approaching absolute zero led Nernst to postulate the third law of thermodynamics. This statement was subsequently modified by Planck. You will learn about these developments here. The mathematics used in this unit is very simple but physical concepts are of fundamental importance. Therefore, you should focus on understanding the underlying physics. Answering SAQs and solving TQs on your own would help you enjoy this unit.

“Our greatest weakness lies in giving up. The most certain way to succeed is always to try just one more time.”

***Thomas Alva
Edison***

9.1 INTRODUCTION



Rudolf Julius Emanuel Clausius (1822-1888) was a German physicist, who is famous for his significant contributions to kinetic theory of gases and thermodynamics. His pioneering work on convertibility of heat into work led to the formulation of the second law of thermodynamics in 1850. Later on, he also introduced the concept of entropy.

From experience we know that heat flows from a body at higher temperature to a body at lower temperature spontaneously. But the reverse is not true, i.e., heat does not flow **on its own** from a body at lower temperature to a body at higher temperature. This is because cooling is a **unidirectional** natural process. You may be familiar with many other unidirectional processes occurring in physically diverse systems. We may mention spontaneous expansion of a gas into fixed volume (free expansion), battery discharge when in operation (chemical process), and intermixing of two fluids (diffusion), among others.

Do you know why natural processes take place in a particular direction? To discover an answer to this question, we need to know: What determines the direction of a natural process? Can we give a quantitative thermodynamic criterion which governs this change?

The answer to these and many other such questions was given by Clausius in 1850 when he introduced a new thermodynamic function called **entropy** (from the Greek word *tropos*, which means 'change'). Clausius showed that for natural processes, entropy of the universe always increases. That is, natural processes evolve in the direction of increase of entropy.

But you may now ask: What is entropy? Entropy characterises disorder in a system. It is a mathematical tool, an abstract property and it cannot be measured like temperature, pressure or volume. For simplicity, we first define entropy with reference to a reversible process in Sec. 9.2, though all natural processes are irreversible and this definition holds for these as well.

In Sec. 9.3, we have postulated the second law of thermodynamics in terms of entropy and established the combined form of the first and second laws of thermodynamics. You will learn how to derive expressions for changes in entropy of an ideal gas in Sec. 9.4. This is followed by the derivation of the expression for the efficiency of a Carnot engine using T - S diagram. In Sec. 9.6, you will learn about the behaviour of entropy at absolute zero and the third law of thermodynamics.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ define entropy and state second law of thermodynamics in terms of entropy;
- ❖ calculate entropy change for a system when it undergoes a reversible/irreversible change;
- ❖ represent Carnot cycle on T - S diagram and derive expression for efficiency of a heat engine; and
- ❖ state third law of thermodynamics and discuss its important consequences.

9.2 DEFINING ENTROPY

To define entropy, let us consider n moles of an ideal gas at temperature T and pressure p enclosed in an insulated cylinder fitted with a frictionless piston. On a p - V diagram, this state of the system is represented as shown in Fig. 9.1. Suppose that now an infinitesimal amount of heat δQ is added reversibly along the path 1A2 to the system. Using the first law of thermodynamics, we can write:

$$\delta Q_{rev} = nc_V dT + pdV \quad (9.1a)$$

The subscript *rev* signifies that we are considering a *reversible* process.

On dividing Eq. (9.1a) throughout by T , we can write:

$$\frac{\delta Q_{rev}}{T} = nc_V \frac{dT}{T} + \frac{p}{T} dV \quad (9.1b)$$

Using the equation of state for an ideal gas ($pV = nRT$), we can write:

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

Using this result in Eq. (9.1b), we obtain:

$$\frac{\delta Q_{rev}}{T} = nc_V \frac{dT}{T} + nR \frac{dV}{V}$$

Now suppose that as a result of addition of heat, the system changes from initial state 1 to final state 2. Then, the net change in the value of $\frac{\delta Q_{rev}}{T}$ is given by:

$$\int_1^2 \frac{\delta Q_{rev}}{T} = \int_1^2 nc_V \frac{dT}{T} + nR \int_1^2 \frac{dV}{V}$$

Let us now suppose that the initial and final states are characterized by the thermodynamic variables (V_1, T_1) and (V_2, T_2) , respectively. If we assume that c_V does not change when heat is added reversibly, we can readily carry out integration to obtain:

$$\int_1^2 \frac{\delta Q_{rev}}{T} = nc_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right) \quad (9.2)$$

Before proceeding further, let us interpret this result. It tells us that the value of $\frac{\delta Q_{rev}}{T}$ depends on V_1, V_2, T_1 and T_2 .

In other words, the value of $\frac{\delta Q_{rev}}{T}$ can be determined by considering the temperatures and volumes corresponding to the initial and final states of the system. We express this by saying that $\frac{\delta Q_{rev}}{T}$ defines a new property of the gas and is characteristic of the state.

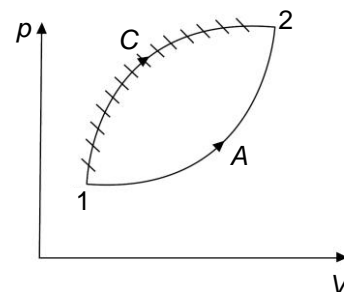


Fig. 9.1: Representation of a reversible process on p - V diagram.

You would recognise that it is immaterial how the system got in that state. How can you justify this?

To this end, we recall from Unit 7 of Block 2 that δQ_{rev} is an inexact differential, i.e., a function of path. But the value of $\frac{\delta Q_{rev}}{T}$, which is the ratio of a path function and a state variable, is determined only by the initial and final states. This is possible only when $\frac{\delta Q_{rev}}{T}$ defines a change in some new function. This function is called **entropy** and is denoted by the symbol S . So, we write:

$$dS = \frac{\delta Q_{rev}}{T} \quad (9.3)$$

You will recognise that we have postulated existence of entropy in Eq. (9.3).

Mathematically, an inexact differential can be made exact by introducing an *integrating factor*. Therefore, we can say that here T^{-1} acts as an integrating factor for δQ_{rev} .

In words, when we add an infinitesimal amount of heat δQ_{rev} reversibly to a system at constant temperature T , its entropy changes by $\frac{\delta Q_{rev}}{T}$.

In SI units, entropy is expressed in joule per kelvin (JK^{-1}). Like pressure, volume and temperature, entropy is also a thermodynamic state variable. Can we classify entropy as an extensive variable? Certainly yes, and we define *specific entropy* as entropy per mole or per unit mass.

$$s = \frac{S}{n} \quad \text{or} \quad s = \frac{S}{m}$$

Let us now pause for a while and ask: How good is the relation contained in Eq. (9.3)? It may be mentioned here that although we arrived at Eq. (9.3) by considering a gaseous system, it holds for every thermodynamic system. Moreover, this equation enables us to write an expression for the change in entropy for any system:

$$S_2 - S_1 \equiv \Delta S = \int_1^2 \frac{\delta Q_{rev}}{T} \quad (9.4)$$

The limits on the integral refer to two thermodynamic states of entropies S_1 and S_2 . You can draw the following inferences from Eq. (9.4):

- i) For a reversible cycle, net change in entropy will be zero, i.e., entropy does not change or is conserved in a reversible process.
- ii) We can calculate change in entropy rather than its absolute value.
- iii) The entropy of a system in a given state relative to some arbitrary intermediate state (n) can be expressed as

$$S = S_n + \int_n^2 \frac{\delta Q_{rev}}{T} \quad (9.5)$$

where S_n signifies entropy of the intermediate state.

- iv) Eq. (9.4) has been derived for a reversible process. You may now ask: How will this equation modify for natural processes like free expansion

Entropy is analogous to gravitational potential energy, which is specified with respect to some reference level.

or heat flow? To discover the answer to this question, refer to Fig. 9.1 again and consider heat flow along the path 1C2, which is an irreversible process. You may like to know as to how the method of calculation of entropy is modified in this case. To this end, we assume that heat is given in infinitesimal steps so that irreversible process between states 1 and 2 can be replaced by a reversible process through infinite quasi-static equilibrium states. It means that we can use Eq. (9.4) to calculate the entropy change for each quasi-static state. Therefore, we can conclude that Eq. (9.4) is valid for irreversible processes as well for the same initial and final states. This is because entropy is a property of state and the entropy difference does not depend on how a system got into that state.

Before proceeding further, you should recapitulate what you have learnt about entropy so far in this section.

ENTROPY

Recap

- Entropy for a reversible process is defined through the relation

$$\Delta S = \frac{\delta Q_{rev}}{T}$$

where δQ_{rev} is the amount of heat given reversibly.

- For a reversible cycle, net change in entropy will be zero, i.e., entropy is conserved in a reversible process.
- Between states 1 and 2, the change in entropy for reversible process for n moles of a gas is given by:

$$S_2 - S_1 \equiv \Delta S = \int_1^2 \frac{\delta Q_{rev}}{T}$$

- We can calculate change in entropy rather than its absolute value.
- Eq. (9.4) can also be used to calculate the change in entropy even for an irreversible process.

Now we would like you to go through the following examples to grasp the concepts discussed above.

EXAMPLE 9.1: ENTROPY CALCULATION

Two blocks of iron are in thermal contact. The temperature of block A is 300K and that of block B is infinitesimally higher than 300K. The blocks are so large that 600 J of heat transferred from B to A leaves their temperatures unchanged. Calculate the entropy change of the individual blocks and also the total entropy change. Take the process to be reversible.

SOLUTION ■ Since block A is at lower temperature, it will absorb heat. You can calculate the entropy change using Eq. (9.3):

$$\text{The entropy change for block } A, \Delta S_A = \frac{\delta Q_A}{T} = \frac{600 \text{ J}}{300 \text{ K}} = 2 \text{ JK}^{-1}$$

$$\text{The entropy change for block } B, \Delta S_B = \frac{\delta Q_B}{T} = -\frac{600 \text{ J}}{300 \text{ K}} = -2 \text{ JK}^{-1}$$

The negative sign is included with ΔS_B as B loses heat. This means that entropy of a system increases when it is heated and vice versa.

$$\text{Total entropy change, } \Delta S = \Delta S_A + \Delta S_B = 2 \text{ JK}^{-1} - 2 \text{ JK}^{-1} = 0$$

That is, when heat transfer is reversible, there is no net change in entropy and you can say that entropy is conserved in a reversible process.

EXAMPLE 9.2: CHANGE IN ENTROPY OF A SYSTEM

A block of copper of mass 1.5 kg is heated from 300K to 350K. Calculate the change in entropy of the block. The specific heat capacity of copper is $389 \text{ J kg}^{-1} \text{ K}^{-1}$. Assume that heat is added irreversibly.

SOLUTION ■ Although heat has been added irreversibly, we can calculate ΔS using Eq. (9.4):

$$\Delta S = \int_{300\text{K}}^{350\text{K}} \frac{\delta Q_{\text{rev}}}{T} \quad (\text{i})$$

The heat absorbed for an infinitesimal rise in temperature is given by:

$$\delta Q_{\text{rev}} = ms\Delta T \quad (\text{ii})$$

where m is mass and s is specific heat capacity of the block. On inserting the given data in Eq. (ii), we find that

$$\delta Q_{\text{rev}} = (1.5 \text{ kg}) \times (389 \text{ J kg}^{-1} \text{ K}^{-1}) \times \Delta T$$

$$\begin{aligned} \therefore \Delta S &= \int_{300\text{K}}^{350\text{K}} \frac{(1.5 \text{ kg}) \times (389 \text{ J kg}^{-1} \text{ K}^{-1}) \times \Delta T}{T} = 583.5 \ln \left(\frac{350}{300} \right) \text{ JK}^{-1} \\ &= 583.5 \times 2.303 \times \log_{10}(1.67) \text{ JK}^{-1} = 90.0 \text{ JK}^{-1} \end{aligned}$$

You should not confuse small letter s with entropy.

You may now like to answer an SAQ to check your understanding.

SAQ 1 – Entropy change

One kg water at 27°C and 1 atm pressure is heated to 80°C at the same pressure. Calculate the change in entropy. Take specific heat capacity of water as $4.2 \times 10^3 \text{ JK}^{-1} \text{ kg}^{-1}$.

Before proceeding further, you may like to know the physical significance of entropy. So far, we have not said anything about it. We know that when heat

is added to ice, it melts and the molecular arrangement (in water) is somewhat loosened (compared to ice). If you add more heat, water may change to the vapour state. In vapour state, molecules are relatively far apart and molecular motion is quite disordered. So, we can say that **addition of heat (or increase in entropy) creates disorder**. On the other hand, when a gas condenses or a liquid solidifies (giving out heat), the molecular arrangement becomes more ordered. That is, disorder decreases when a gaseous substance changes into the solid state. From this discussion we can conclude that **entropy is a measure of disorder** in the system.

So far, we have introduced the concept of entropy and calculated entropy change in a reversible/irreversible process. You may now ask: How does such a change influence the system, its surroundings and hence the universe? The answer to this question leads us to the second law of thermodynamics. It applies to processes in our body, to combustion of fuel in an automobile, an aeroplane and a rocket as well as to working of refrigerators and other cooling machines. It enables us to specify the direction of evolution of natural processes. We now discuss it in detail.

9.3 ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

Consider that an infinitesimal amount of heat δQ flows from the surroundings at temperature T_{surr} to the system under consideration at temperature T_{sys} .

The net change in the entropies of the system and surroundings is given by

$$\Delta S = \Delta S_{sys} + \Delta S_{surr} = \delta Q \left(\frac{1}{T_{sys}} - \frac{1}{T_{surr}} \right) \geq 0 \quad (9.6)$$

Note that the equality sign holds for reversible heat flow, whereas greater than sign signifies irreversible heat flow. Since all natural processes are irreversible, you may be tempted to conclude that entropy of the universe is continuously increasing. If you think so, you are on the right track. This continuous increase of entropy in natural processes is known as the **principle of increase of entropy**. And the second law of thermodynamics may be stated as follows:

The entropy of the universe can never decrease.

Consider the construction of a building from materials that were initially dispersed in the Earth. In this process, matter goes from a completely disorganized state to a highly ordered state. That is, the entropy decreases. In Unit 7 of Block 2, you have learnt that the internal energy of a growing child or a plant increases. But the growth of a living organism from a random mix of molecules is accompanied by decrease in entropy. These examples may seem to you to contradict the first and second laws of thermodynamics. But it is not so. To understand this, let us enquire: What is responsible for life on the Earth? We can trace it to the energy generated in the Sun's core by nuclear

Recall that the second law has been stated in somewhat different but essentially equivalent forms by Kelvin-Planck and Clausius. You have learnt about these in Unit 8.



Don't forget

fusion ($H_2 \rightarrow He$ cycle). For example, plants use solar energy for photosynthesis and create food. Similarly, humans receive this energy via food chain. So, to answer the above question, you have to consider the Earth-Sun system. When you do so, you will find that the magnitude of entropy decrease associated with life on the Earth is less than the entropy increase associated with nuclear reaction in the core of the Sun. That is, the organisation of matter is governed by a tendency towards greater disorder elsewhere in the universe (Sun in this case). Thus, a more formal statement of the second law in terms of entropy reads as follows:



When an isolated system undergoes a change, its entropy cannot decrease; it increases or remains constant.

In view of the above discussion, can we say that entropy of the universe has continuously increased ever since its creation? Definitely, yes.

You must now be convinced that the second law relates (available) energy to entropy. We can use the integrated statement of these laws to obtain an expression for entropy difference for any process. This is illustrated in the next section.

9.3.1 The Combined Form of the First and Second Laws

The first law of thermodynamics establishes the existence of internal energy (U) as a function of state. Similarly, the second law introduces entropy (S) as a state function. You may now ask: Can we relate these functions? You may recall from Unit 7 that for any change of state, the change in internal energy is given by

$$dU = \delta Q - \delta W \quad (9.7)$$

Similarly, for an infinitesimal reversible process between two equilibrium states, the second law of thermodynamics tells us that

$$dS = \frac{\delta Q}{T} \quad (9.8)$$

These equations may be combined to obtain mathematical expression for the combined form of the first and the second laws of thermodynamics:

$$TdS = dU + \delta W \quad (9.9)$$

This is one of the most important thermodynamic relations. In the next unit, you will use it to derive many useful thermodynamic relations.

Proceeding further, we note that for a gaseous system, $\delta W = pdV$ so that Eq. (9.9) takes the form

$$TdS = dU + pdV \quad (9.10)$$

Note that this equation relates all five thermodynamic variables that you have learnt so far.

Using the results obtained in Unit 8, we can rewrite Eq. (9.10) in three equivalent forms:

$$TdS = nC_V dT + pdV \quad (9.11a)$$

$$TdS = nC_P dT - Vdp \quad (9.11b)$$

and
$$TdS = \frac{1}{R}(C_P pdV + C_V Vdp) \quad (9.11c)$$

where C_P and C_V , respectively, denote molar thermal capacities at constant pressure and constant volume. Note that dS denotes change in molar entropy.

Before proceeding further, you may like to answer the following SAQ.

SAQ 2 – First and second law of thermodynamics

Write the combined mathematical forms of the first and second laws of thermodynamics for a i) stretched wire, ii) surface film, and iii) paramagnetic substance.

Before proceeding further, we recapitulate the important results of this section.

ENTROPY AND THE FIRST AND SECOND LAWS

Recap

- The second law of thermodynamics states that when an isolated system undergoes a change, its entropy either increases or remains constant.
- In the most general form, the combined form of the first and the second laws of thermodynamics can be mathematically expressed as

$$TdS = dU + \delta W$$

We now use Eqs. (9.11a, b, c) to obtain expressions for changes in entropy for an ideal gas under different physical conditions.

9.4 ENTROPY CHANGE OF AN IDEAL GAS

Consider n moles of an ideal gas at temperature T in a cylinder fitted with a frictionless piston. Depending on the physical conditions, we can use one of the relations given in Eqs. (9.11a, b, c) to obtain an expression for change in entropy. Suppose that the gas is given an infinitesimal amount of heat, which induces changes in temperature and volume. We can describe such a change by Eq. (9.11a). On dividing throughout by T and substituting for p from the equation of state ($pV = nRT$), we get

$$dS = nC_V \frac{dT}{T} + nR \frac{dV}{V} \quad (9.12)$$

Let us now suppose that the initial and final states are characterized by the thermodynamic variables (V_1, T_1) and (V_2, T_2) , respectively. If we assume that C_V is independent of temperature, we can readily integrate Eq. (9.12) to obtain the same result as given in Eq. (9.2):

$$\Delta S = nC_V \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{V_2}{V_1} \right) \quad (9.13)$$

You should study the following example to learn how to apply this result.

EXAMPLE 9.3: CHANGE IN ENTROPY

Calculate the increase in entropy of 1 g of hydrogen when its temperature is raised from -173°C to 27°C and its volume becomes four times. It is given that $C_V = 2.43 \text{ cal g}^{-1} \text{ K}^{-1}$, $R = 2.01 \text{ cal mol}^{-1} \text{ K}^{-1}$ and molecular weight is 2 g mol^{-1} .

SOLUTION ■ For n moles of an ideal gas, the entropy change is calculated using Eq. (9.13). However, for 1g of the gas, you have to replace nC_V by C_V and nR by $r = R/\text{mol. weight}$:

$$r = \frac{2.01 \text{ cal mol}^{-1} \text{ K}^{-1}}{2 \text{ g mol}^{-1}} = 1.005 \text{ cal g}^{-1} \text{ K}^{-1}$$

From Eq. (9.13) we recall that change in entropy is given by

$$\Delta S = 2.303 \left[C_V \log_{10} \left(\frac{T_2}{T_1} \right) + (1.005 \text{ cal g}^{-1} \text{ K}^{-1}) \log_{10} \left(\frac{V_2}{V_1} \right) \right]$$

Here $T_1 = (-173 + 273)\text{K} = 100\text{K}$, $T_2 = (27 + 273)\text{K} = 300\text{K}$, and $C_V = 2.43 \text{ cal g}^{-1} \text{ K}^{-1}$. On inserting the given values, we get

$$\begin{aligned} \Delta S &= 2.303 \times [(2.43 \text{ cal g}^{-1} \text{ K}^{-1}) \times \log_{10} 3 + (1.005 \text{ cal g}^{-1} \text{ K}^{-1}) \times \log_{10} 4] \\ &= 2.303 \times (2.43 \times 0.4771 + 1.005 \times 0.6021) \text{ cal g}^{-1} \text{ K}^{-1} \\ &= 4.062 \text{ cal g}^{-1} \text{ K}^{-1}. \end{aligned}$$

Starting from Eq. (9.11b), you can easily convince yourself that the entropy change between states defined by (T_1, p_1) and (T_2, p_2) is given by

$$\Delta S = nC_P \ln \left(\frac{T_2}{T_1} \right) - nR \ln \left(\frac{p_2}{p_1} \right) \quad (9.14)$$

Similarly, if reference states are defined by (p_1, V_1) and (p_2, V_2) , the entropy change is given by

$$\Delta S = nC_P \ln \left(\frac{V_2}{V_1} \right) - nC_V \ln \left(\frac{p_2}{p_1} \right) \quad (9.15)$$

A gas may be made to expand or compress isothermally. When n moles of an ideal gas are made to undergo isothermal changes, Eqs. (9.13) and (9.14) predict that entropy changes are, respectively, given by

$$\Delta S_T = nR \ln \left(\frac{V_2}{V_1} \right) \quad (9.16a)$$

and
$$\Delta S_T = R \ln \left(\frac{p_1}{p_2} \right) \quad (9.16b)$$

The subscript T in ΔS_T signifies that temperature remains constant. That is, *when an ideal gas undergoes an isothermal expansion defined by ($V_2 > V_1, p_1 > p_2; T = \text{constant}$), its entropy increases.* When a gas undergoes isothermal compression, entropy will decrease.

For isobaric changes, Eqs. (9.14) and (9.15) predict that

$$\Delta S_P = nC_P \ln \left(\frac{T_2}{T_1} \right) \quad (9.17a)$$

and
$$\Delta S_P = nC_P \ln \left(\frac{V_2}{V_1} \right) \quad (9.17b)$$

These results tell us that when either temperature or volume increases during an isobaric process, the entropy increases and vice versa.

Now you should go through the following example carefully.

EXAMPLE 9.4: ENTROPY CHANGE IN TERMS OF R

One mole of an ideal gas expands isothermally to four times its initial volume. Calculate the entropy change in terms of the gas constant.

SOLUTION ■ For one mole of an ideal gas, Eq. (9.16) implies that

$$\frac{\Delta S_T}{R} = \ln(V_2 / V_1) = 2.303 \log_{10}(V_2 / V_1)$$

Since $V_2 / V_1 = 4$, the entropy change during isothermal expansion, in terms of gas constant, is given by

$$\begin{aligned} \frac{\Delta S_T}{R} &= 2.303 \log_{10} 4 \\ &= 2.303 \times 0.6020 = 1.386 \end{aligned}$$

You may like to answer the following SAQ before studying further.

SAQ 3 – Increase in entropy

Calculate the increase in entropy of one mole of argon heated from 300K to 600K at constant volume.

9.4.1 Entropy of Mixing

Refer to Fig. 9.2. Suppose that the hollow circles depict n_1 moles of oxygen and solid circles denote n_2 moles of nitrogen in two separate containers at constant temperature T and pressure p . The gases are separated by means of a stopcock. We assume that these gases behave as an ideal gas. You may now like to know: What happens when the stopcock is opened and these gases mix? To answer this question, let us assume that partial pressures of oxygen and nitrogen in the mixture are p_1 and p_2 , respectively.

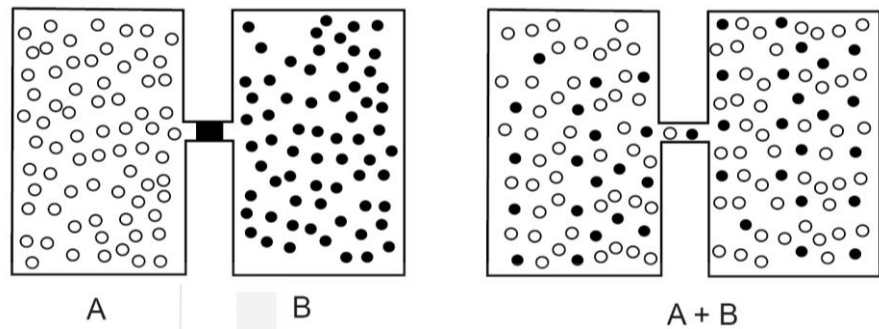


Fig. 9.2: Intermixing of two gases.

The entropy of mixing is equal to the sum of the entropy changes for each gas as it expands from its initial pressure to its partial pressure in the mixture. The changes in entropies ΔS_1 and ΔS_2 for the two gases when mixing takes place at constant T can be obtained using Eq. (9.14):

$$\Delta S_1 = -n_1 R \ln \left(\frac{p_1}{p} \right) = n_1 R \ln \left(\frac{p}{p_1} \right)$$

and

$$\Delta S_2 = n_2 R \ln \left(\frac{p}{p_2} \right)$$

Hence, when the gases have mixed, the entropy of mixing is given by

$$\Delta S_{mix} = \Delta S_1 + \Delta S_2 = n_1 R \ln \left(\frac{p}{p_1} \right) + n_2 R \ln \left(\frac{p}{p_2} \right) \quad (9.18)$$

From your school curriculum in chemistry, you may recall that the partial pressures can be expressed in terms of total pressure as $p_1 = x_1 p$ and $p_2 = x_2 p$, where x_1 and x_2 are mole fractions of two gases. On substituting these values of p_1 and p_2 in Eq. (9.18), we obtain

$$\begin{aligned} \Delta S_{mix} &= n_1 R \ln \left(\frac{p}{x_1 p} \right) + n_2 R \ln \left(\frac{p}{x_2 p} \right) \\ &= -n_1 R \ln x_1 - n_2 R \ln x_2 \end{aligned} \quad (9.19)$$

Now suppose you have to compute the entropy of mixing per mole of the mixture. You can do so easily by dividing both sides of Eq. (9.19) by $n_1 + n_2$.

This gives

$$\frac{\Delta S_{mix}}{n_1 + n_2} = -R \left[\frac{n_1}{n_1 + n_2} \ln x_1 + \frac{n_2}{n_1 + n_2} \ln x_2 \right]$$

The ratios $\frac{n_1}{n_1 + n_2}$ and $\frac{n_2}{n_1 + n_2}$ define the mole fractions of two gases.

Hence, the entropy of mixing per mole of mixture is

$$\Delta S_{mix} = -R[x_1 \ln x_1 + x_2 \ln x_2] \quad (9.20)$$

Note that a negative sign occurs in the expression for entropy of mixing. Does this mean that entropy decreases in the process of mixing of two gases? If you think so, you are not correct.

Since x_1 and x_2 are less than one, the entropy of mixing will be always positive. Note that we have derived Eq. (9.20) for ideal gases. But it holds for liquids also where intermolecular forces between the components are uniform. The concept developed in this section is illustrated in the following example.

EXAMPLE 9.5: ENTROPY OF MIXING

Equal volumes of two gases are mixed under same temperature and pressure. The pressure remains unchanged but the total volume is doubled. Calculate the entropy of mixing for one mole of the mixture.

SOLUTION ■ Since the gases are initially at the same temperature and pressure, Avogadro's hypothesis tells us that equal volume will have equal number of molecules, i.e., $n_1 = n_2 = n$, say. Therefore, the mole fraction of each gas in one mole of the mixture is 0.5. Hence, the entropy of mixing is given by

$$\begin{aligned} \Delta S_{mix} &= -R[x_1 \ln x_1 + x_2 \ln x_2] \\ &= -(8.31 \text{ JK}^{-1} \text{ mol}^{-1})[0.5 \ln 0.5 + 0.5 \ln 0.5] = 5.76 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

We know that matter can change its state from solid to liquid (ice to water) and liquid to gas (water to steam) or solid to gas (dry ice, i.e., solid carbon dioxide to CO_2 gas) under appropriate conditions of temperature and pressure. Such a transformation is called **phase transition**. Conversion of ice to water is an example of first order phase transition. You will now learn to obtain expressions for entropy changes accompanying a phase transition.

9.4.2 Entropy Change of Phase Transition

We know that at atmospheric pressure, water boils at 100°C . But on hill stations, boiling begins below 100°C . In a physics laboratory also, you can make water boil below 100°C through a simple activity. Put some boiling water in a flask and allow it to cool. Then pour some water over the flask. You will observe that water begins to boil again even though it is below 100°C . It means that phase transition is determined by pressure. However, it is accompanied by absorption or evolution of heat. For an isobaric-isothermal process, the quantity of heat evolved or absorbed by a system defines enthalpy, H . Hence, the entropy change for an isothermal-isobaric process can be calculated using the relation

$$\Delta S = \frac{\delta Q_{rev}}{T} = \frac{\Delta H}{T} \quad (9.21)$$

You can use this result to compute the entropy change accompanying the transition of a solid to a liquid or a liquid to a vapour and vice versa.

When n mole of a solid melts to the liquid phase, the entropy of fusion is given by

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{fusion}} \quad (9.22)$$

where ΔH_{fusion} is molar enthalpy of fusion and T_{fusion} is the melting point.

Similarly, for n mole of a substance, the entropy of evaporation is given by

$$\Delta S_{evap} = \frac{\Delta H_{evap}}{T_{evap}} \quad (9.23)$$

where ΔH_{evap} is molar enthalpy of vaporisation and T_{evap} is the boiling point.

In the following example, we have illustrated the use of some of these relations to compute entropy changes.

EXAMPLE 9.6: ENTROPY OF VAPORISATION

The enthalpy of vaporisation of ethanol is 43.5 kJ mol^{-1} at its normal boiling point of 351.5 K . Compute the entropy of vaporisation. The enthalpy of fusion of ethanol is 4.6 kJ mol^{-1} at its normal melting point of 156 K . Calculate the entropy of fusion.

SOLUTION ■ From Eq. (9.23), we recall that entropy of vaporisation is given by

$$\Delta S_{evap} = \frac{\Delta H_{evap}}{T_{evap}} = \frac{43500 \text{ J mol}^{-1}}{351.5 \text{ K}} = 124 \text{ JK}^{-1} \text{ mol}^{-1}$$

From Eq. (9.22), we note that entropy of fusion is given by

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{fusion}} = \frac{4600 \text{ J mol}^{-1}}{156 \text{ K}} = 29.5 \text{ JK}^{-1} \text{ mol}^{-1}$$

You will note that $\Delta S_{evap} \gg \Delta S_{fusion}$. This difference shows that entropy increases as a system becomes less restricted. When a solid melts, its atoms become less ordered in their locations and motion. When a liquid vaporises, molecules gain considerably greater freedom of movement.

We would now like you to solve an SAQ.

SAQ 3 – Entropy of solidification

The melting point of water at 1 atm pressure is 273.16 K and the specific latent heat of melting is 334.4 Jg^{-1} . Calculate the entropy of solidification for one mole of water.

Before proceeding further, we would like you to recapitulate what you have learnt in this section.

Recap

ENTROPY CHANGE, ENTROPIES OF MIXING, FUSION AND EVAPORATION

- When n moles of an ideal gas undergo an isothermal transformation, the change in entropy is given by:

$$\Delta S_T = nR \ln \left(\frac{V_2}{V_1} \right) = nR \ln \left[\frac{p_1}{p_2} \right]$$

- For an isobaric process, change in entropy of a gas made up of n moles is given by:

$$\Delta S_P = nC_P \ln \left(\frac{V_2}{V_1} \right) = nC_P \ln \left[\frac{T_2}{T_1} \right]$$

- The entropy of mixing per mole of mixture of two gases is always positive:

$$\Delta S_{mix} = -R[x_1 \ln x_1 + x_2 \ln x_2]$$

where x_1 and x_2 are mole fractions.

- For one mole of a substance, the entropy of fusion is given by:

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{fusion}}$$

and the entropy of evaporation is: $\Delta S_{evap} = \frac{\Delta H_{evap}}{T_{evap}}$.

Having established that entropy is a thermodynamic property of a system, we now discuss its significance in various reversible processes and draw corresponding T - S diagrams. These diagrams are often useful in engineering. As you know, the simplest and the most important reversible cycle is the **Carnot cycle**. You have learnt how to obtain an expression for the efficiency of a Carnot engine in Unit 8. Here we will show how the same result can be obtained more elegantly using a T - S diagram.

9.5 REPRESENTATION OF CARNOT CYCLE ON ENTROPY-TEMPERATURE DIAGRAM

Refer to Fig. 9.3. It is a schematic representation of the Carnot cycle on the T - S diagram.

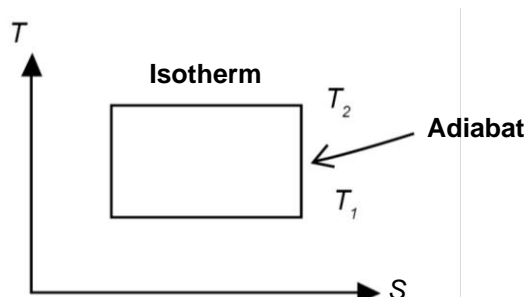


Fig. 9.3: Representation of Carnot cycle on T - S diagram.

You will recall that Carnot cycle consists of four reversible processes:

i) isothermal expansion, ii) adiabatic expansion, iii) isothermal compression, and iv) adiabatic compression.

You will note that the isotherms are horizontal straight lines for a given temperature, whereas the adiabats are vertical straight lines corresponding to constant S ($\delta Q = 0 = dS$). So, Carnot cycle is a rectangle on the T - S diagram. To obtain the expression for net entropy change in one cycle, let us consider n moles of an ideal gas is enclosed in a cylinder.

Step I: The gas absorbs heat Q_1 reversibly at temperature T_1 and expands isothermally. (The pressure decreases from p_1 to p_2 .) Using Eq. (9.3), we can write the increase in entropy of the gas as

$$\Delta S_1 = \frac{Q_1}{T_1} \quad (9.24a)$$

Step II: The gas expands adiabatically (but pressure falls from p_2 to p_3). We know that no heat exchange takes place between the system and its surroundings in an adiabatic process. Therefore, according to the first law of thermodynamics, expansion occurs at the expense of internal energy of the system. This, in turn, implies drop in temperature of the gas. Suppose that temperature drops from T_1 to T_2 . Since no heat transfer occurs, entropy does not change and we can write

$$\Delta S_2 = 0 \quad (9.24b)$$

Step III: The gas at temperature T_2 is now compressed isothermally. In this process, work is done on the gas and it gives up heat Q_2 to the environment. Then change in entropy is given by

$$\Delta S_3 = -\frac{Q_2}{T_2} \quad (9.24c)$$

Step IV: Finally, the gas is compressed adiabatically to its original volume and pressure. As a result, the gas attains its state and its entropy is conserved during the process:

$$\Delta S_4 = 0 \quad (9.24d)$$

Since Carnot cycle is reversible, there will be no net change in its entropy, i.e., $\Delta S = 0$ and we can write

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = 0$$

On using Eqs. (9.24a to d), we get

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

$$\text{or} \quad \frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad (9.25)$$

This result shows that the ratio of the heat absorbed to the heat given out in a reversible cycle is equal to the ratio of the temperatures of the source and the sink. Since efficiency is ratio of work done and heat absorbed, we can write:

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

Using Eq. (9.25) we can write:

$$\eta = 1 - \frac{T_2}{T_1} \quad (9.26)$$

Note that the expression for efficiency of Carnot engine has been obtained more conveniently using T - S diagram as compared to the indicator diagram.

9.6 ENTROPY AT ABSOLUTE ZERO: THIRD LAW OF THERMODYNAMICS

From experience we know that the basic difficulty with all cooling processes is that it becomes gradually more difficult to achieve and maintain lower and lower temperatures. For example, the cooler a liquid is, the harder it becomes to maintain its temperature or pump it out to produce further cooling.

Suppose that temperature T_{f1} , say 10% of the initial temperature T_i is achieved in one mechanical step. The second step will produce a temperature T_{f2} which is approximately 10% of T_{f1} . This means that even by an infinite number of adiabatic processes, it would not be possible to attain absolute zero. From this we may conclude that

The absolute zero is not attainable by any number of mechanical processes.



Don't forget

Like the second law, the third law can also be stated in terms of entropy. But before giving that statement, we would like you to relook at Eq. (8.5). It can be re-written as

$$S = S_n + \int_n^f \frac{\delta Q_{rev}}{T} \quad \text{where } f \text{ is the final state.}$$

It helps us to determine the change in entropy of a system during a reversible process. But absolute entropy remains indeterminate because of the presence of an additive constant (S_n). You may now ask: Can we determine this constant? The answer to this question constitutes another statement of the third law. It defines the entropy of a system as its temperature tends to absolute zero.

Nernst observed that at low temperatures entropy change of a system is very small when we go from one equilibrium state to another. It is because near absolute zero, all systems are highly ordered and the entropy of all states (of every substance) is almost constant. This prompted Nernst to state the third law as follows:

The entropy changes associated with any reversible isothermal process tend to zero as temperature approaches absolute zero.



Don't forget

Mathematically, this is expressed as:

$$\lim_{T \rightarrow 0} \Delta S \rightarrow 0 \quad (9.27)$$

This fact beautifully manifests in the case of liquid helium-II and superconductors. To understand this, we recall Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$$

You will recognise that $\frac{dp}{dT}$ defines the slope of the melting curve. Eq. (9.27) predicts that the curve should become horizontal ($\Delta S = 0$) as $T \rightarrow 0$.

In 1912, Planck extended this idea by proposing that near absolute zero, entropy of every substance is so small that it can be taken as essentially zero. He stated the third law of thermodynamics as follows:



The entropy of every substance is zero at the absolute zero.

Mathematically, this is expressed as:

$$\lim_{T \rightarrow 0} S \rightarrow 0 \quad (9.28)$$

Today, this law is supported by ample experimental evidences and finds wide applications in low temperature physics. We now discuss some important consequences of the third law.

9.6.1 Consequences of the Third Law

i) Behaviour of thermodynamic potentials

We know that $G = H - TS$ and $F = U - TS$. According to the third law of thermodynamics, as $T \rightarrow 0, S \rightarrow 0$ so that the product $TS \rightarrow 0$. That is, when temperature approaches absolute zero, Gibbs potential equals enthalpy and Helmholtz potential equals internal energy. Physically, it means that there is perfect order and entire energy is available for work.

ii) Iso-thermal volume and pressure expansion coefficients

The changes in entropy of a system due to small changes in pressure during a process near absolute zero may be expressed as

$$\Delta S = \int \left(\frac{\partial S}{\partial p} \right)_T dT \quad (9.29)$$

But according to the third law of thermodynamics, as $T \rightarrow 0, \Delta S \rightarrow 0$. So we can say that

$$\lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial p} \right)_T \rightarrow 0$$

Using Maxwell's relation $\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p$, we can write:

$$\lim_{T \rightarrow 0} \left(\frac{\partial V}{\partial T} \right)_p \rightarrow 0 \quad (9.30)$$

By definition, $\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$ is the coefficient of volume expansivity, α . So,

$$\lim_{T \rightarrow 0} \alpha \rightarrow 0 \quad (9.31)$$

Similarly, you can convince yourself that

$$\lim_{T \rightarrow 0} \left(\frac{\partial p}{\partial T} \right)_V = 0 \quad (9.32)$$

iii) Heat capacities near absolute zero

Recall that specific heat capacity at constant pressure is defined as

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

Hence, at constant pressure, we can take

$$dS = \frac{C_p dT}{T}$$

By integrating it between finite temperature limits, we can write

$$S(T_1) - S(T) = \int_T^{T_1} \frac{C_p dT}{T} \quad (9.33)$$

In the limit $T \rightarrow 0$, the third law implies that the integral on the right hand side of Eq. (9.33) should be finite. That is, it should not diverge as $T \rightarrow 0$.

Thus, we must have

$$\lim_{T \rightarrow 0} C_p = 0 \quad (9.34)$$

Similarly, it can be shown that as $T \rightarrow 0$

$$\lim_{T \rightarrow 0} C_V = 0 \quad (9.35)$$

It shows that in the limit $T \rightarrow 0$, the specific heat capacities attain the same value. This prediction of the third law is borne out by experiments rather well. Let us recapitulate what you have learnt in this section

THIRD LAW OF THERMODYNAMICS

Recap

Entropy of a system at absolute zero is zero and the system is in perfect order. It essentially implies non-attainability of absolute zero temperature.

Let us now summarise what you have learnt in this unit.

9.7 SUMMARY

Concept	Description
Entropy	<ul style="list-style-type: none"> Entropy is defined through the relation $dS = \frac{\delta Q_{rev}}{T}$ Entropy is an extensive variable and a state function.
Second law of thermodynamics in terms of entropy	<ul style="list-style-type: none"> Entropy is a measure of disorder in the system; more chaotic the system, greater will be its entropy. The second law of thermodynamics is essentially the principle of increase of entropy. It states that, when a closed system undergoes a change, its entropy cannot decrease; it either increases or remains constant. Mathematically, it may be expressed as $\Delta S \geq 0$
Entropy change of an ideal gas	<ul style="list-style-type: none"> The entropy change of an ideal gas made up of n moles can be calculated using the relations $\begin{aligned} \Delta S &= nC_V \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{V_2}{V_1} \right) \\ &= nC_P \ln \left(\frac{V_2}{V_1} \right) + nC_V \ln \left(\frac{p_2}{p_1} \right) \\ &= nC_P \ln \left(\frac{T_2}{T_1} \right) - nR \ln \left(\frac{p_2}{p_1} \right) \end{aligned}$
Third law of thermodynamics	<ul style="list-style-type: none"> Third law of thermodynamics states that equilibrium entropies of all systems and the entropy changes in all reversible isothermal processes tend to zero as temperature approaches absolute zero.

9.8 TERMINAL QUESTIONS

- A huge copper block at 1000K is joined to another huge copper block at 500K by a copper rod. The rate of heat conduction is 10^4 Js^{-1} . Calculate the increase in entropy of the universe due to this process.
- Eddington proposed that entropy is the arrow of time. Comment.
- m g of water at temperature T_1 is mixed with an equal mass of water at temperature T_2 . Show that the change in entropy is

$$2mC_P \ln \left(\frac{T_{av}}{\sqrt{T_1 T_2}} \right) \text{ where } T_{av} = \frac{T_1 + T_2}{2} \text{ is average temperature.}$$

- 20 g of ice at 0°C is converted into water at the same temperature. Calculate the change in entropy. [Given: Latent heat of fusion (L) = 80 cal/g].

- Calculate the change in entropy when 10 g of ice at 0°C is converted into steam. [Given: latent heat of fusion of ice = 80 cal/g; latent heat of fusion of steam = 540 cal/g].
- Write the third law of thermodynamics in terms of entropy differences.

9.9 SOLUTIONS AND ANSWERS

Self-assessment Questions

- The change in entropy when 1 kg water is heated from 27°C (= 300K) to 80°C (= 353K) is given by

$$\Delta s = \int_{300}^{353} \frac{mcdT}{T} = mc \ln \left(\frac{353}{300} \right)$$

On substituting the given values, we get

$$\begin{aligned} \Delta s &= (1\text{kg}) \times (4.2 \times 10^3 \text{Jkg}^{-1}\text{K}^{-1}) \ln \left(\frac{353}{300} \right) \\ &= (4.2 \times 10^3 \text{Jkg}^{-1}\text{K}^{-1}) \times 0.163 \text{JK}^{-1} = 6.84 \times 10^2 \text{JK}^{-1} \end{aligned}$$

- a) $TdS = dU - Fdl$; b) $TdS = dU - \sigma dA$ and c) $TdS = dU - BdM$

- $\Delta S_V = nC_V \ln \left(\frac{T_2}{T_1} \right) = C_V \ln 2$

Since $C_V = \frac{3}{2}R$, we find that

$$\Delta S_V = \frac{3}{2} \times (8.314 \text{JK}^{-1} \text{mol}^{-1}) \ln 2 = 8.64 \text{JK}^{-1}$$

- $\Delta S_{melt} = \frac{m\Delta\ell}{T_{melt}} = \frac{18\text{g} \times 334.4\text{Jg}^{-1}}{273.16\text{K}} = \frac{6019.2\text{J}}{273.16\text{K}} = 22 \text{JK}^{-1}$

Terminal Questions

- By carrying out the heat transfer reversibly, we can calculate that

$$\Delta S = (q/T_1) - (q/T_2) = 10^4 \text{Js}^{-1} [(1/500\text{K}) - (1/1000\text{K})] = 10 \text{JK}^{-1}\text{s}^{-1}$$

Thus, the entropy of the universe increases by 10 JK⁻¹ per second.

- The statement is justified. If you calculate entropy of the universe at two different times, the point of higher entropy would correspond to the point of later time. This statement is further justified by the fact that the universe has been expanding uniformly ever since its creation. Even if one observed the motion of galaxies, these are found receding with respect to any point of observation. This means that the entropy of the universe is increasing continuously, as does time.
- Since the masses of water being mixed are equal, the temperature of the mixture will be the arithmetic mean of T_1 and T_2 :

$$T_{\text{mix}} = \frac{T_1 + T_2}{2} = T_{\text{av}}$$

Since the process is isobaric, the change in entropy of water sample whose temperature rises from T_1 to T_{av} is given by:

$$\Delta S_1 = \frac{\delta Q}{T} = m C_P \ln\left(\frac{T_{av}}{T_1}\right) \quad (\text{i})$$

Similarly, the change in entropy of water sample whose temperature falls from T_2 to T_{av} is:

$$\Delta S_2 = m C_P \ln\left(\frac{T_{av}}{T_2}\right) \quad (\text{ii})$$

Hence, the net change in entropy is:

$$\Delta S = \Delta S_1 + \Delta S_2 = m C_P \ln\left(\frac{T_{av}}{T_1}\right) + m C_P \ln\left(\frac{T_{av}}{T_2}\right) \quad (\text{iii})$$

Since $\ln a + \ln b = \ln(ab)$, you can write it as $\Delta S = m C_P \ln\left(\frac{T_{av}^2}{T_1 T_2}\right)$

$$= m C_P \ln\left(\frac{T_{av}}{\sqrt{T_1 T_2}}\right)^2 = 2m C_P \ln\left(\frac{T_{av}}{\sqrt{T_1 T_2}}\right) \text{ since } \ln x^n = n \ln x. \quad (\text{iv})$$

In (iii), T_{av} is the arithmetic mean. $\sqrt{T_1 T_2}$ is geometric mean of T_1 and T_2 . We know that the arithmetic mean of two unequal positive numbers is greater than their geometric mean. So, the argument of logarithmic function is greater than one and the entropy of the system increases:

$$\Delta S > 0 \quad (\text{v})$$

You will recognise that entropy change is not necessarily accompanied by heat flow. That is why, entropy increases in free expansion, intermixing of gases and so on.

4. Total heat is $dQ = mL = 20 \times 80 = 1600$ cal and $T = 0^\circ\text{C} = 273\text{K}$.

$$\text{The increase in entropy } dS = \frac{dQ}{T} = \frac{1600}{273} = 5.86 \text{ cal/K}$$

5. It is given that latent heat of fusion of ice = 80 cal/g, and Latent heat of fusion of steam = 540 cal/g.

Step I: Ice changes into water at 0°C (isothermal change)

$$\Delta S_1 = \frac{mL_1}{T_1} = \frac{10 \times 80}{273} \text{ cal/K} = 2.93 \text{ cal/K}$$

Step II: Water changes its temperature from 0°C to 100°C .

$$\Delta S_2 = \int_{273}^{373} \frac{mcdT}{T} = mc \ln\left(\frac{373}{273}\right) = 10 \times 1 \times \ln\left(\frac{373}{273}\right) = 3.12 \text{ cal/K}$$

Step III: Water at 100°C changes into steam at 100°C .

$$\Delta S_3 = \frac{10 \times 540}{373} = 14.48 \text{ cal/K}$$

$$\therefore \text{Net change in entropy} = 2.93 + 3.12 + 14.48 = 20.53 \text{ cal/K}$$

6. In terms of entropy, third law of thermodynamics can be expressed as

$$\lim_{T \rightarrow 0} S \rightarrow 0$$



A pressure cooker cooks vegetables faster at high altitude. (Picture source: <https://pixabay.com/photos/nature-landscape-mountains-4408716/>)

THE THERMODYNAMIC POTENTIALS

Structure

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STUDY GUIDE

In Unit 9, you have learnt the concept of entropy and used it to state the second law of thermodynamics, which emphasises that entropy increases in all natural processes. In this unit, you will learn that a change in a thermodynamic system under specific constraints requires a new function, called *free energy*. We will introduce the concept of *Helmholtz free energy*, F and *Gibbs free energy*, G . In deriving various thermodynamic relations, we shall make extensive use of partial differentiation. Therefore, you should refresh your previous knowledge of this topic. We firmly believe that you must not memorise thermodynamic relations. Instead, you should learn how to obtain these based on mnemonic diagrams. This will make your learning an enjoyable experience. Quite a few numerical problems, solved examples and SAQs based on Maxwell's relations have been given in the unit. Do practice solving these for better understanding. In case, you are not able to solve on your own, read the section again before looking for the solutions provided at the end of the Unit.

“Thermodynamic irreversibility is due to cosmological expansion.”

***Peter T.
Landeberg***

10.1 INTRODUCTION

Helmholtz free energy is also denoted by the symbol A in literature.

So far, we have discussed three thermodynamic functions – temperature (T), internal energy (U), and entropy (S). You may recall that temperature helped us in formulating the equation of state of a thermodynamic system and internal energy enabled us to develop a mathematical formulation of the first law of thermodynamics. The concept of entropy was used to mathematically formulate second law of thermodynamics, which emphasises that entropy increases in all natural processes. From experience, we know that every system has an inherent tendency to approach equilibrium and the first and second laws of thermodynamics do not provide us any information about this. This suggests that there is a need to supplement these laws when we wish to get information about the condition of thermodynamic equilibrium of a system. In Sec. 10.2, you will learn that a change under specific constraints requires a new function, called *free energy*, which is a function of state. We introduce *enthalpy*, H ; *Helmholtz free energy*, F and *Gibbs free energy*, G . The functions U , H , F and G are collectively called *thermodynamic potentials* or *free energies*. You will note that each free energy has its own pair of natural variables. Moreover, these carry a treasure trove of information about the system.

Thermodynamic potentials are very handy in obtaining Maxwell's relations, which are used to derive all important thermodynamic relations. Their usefulness lies in the fact that they frequently relate quantities which seem unrelated. As a result, these relations enable us to link experimental data obtained in different ways or replace a difficult measurement by an easier one. We can also use these to obtain values of one property, which may be straightforward, from calculations or measurement of another property. In brief, these relations are very general and extremely useful as they enormously simplify thermodynamic analysis. You will learn how to derive Maxwell's relations in Sec. 10.3. You will also learn how to obtain TdS -equations and energy equations using Maxwell's relations. We have also discussed applications of Maxwell's relations to derive Clausius-Clapeyron equation in Sec. 10.4. In Sec.10.5, you will learn about Joule-Thomson effect which is used to produce low temperatures.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ define thermodynamic potentials;
- ❖ derive Maxwell's relations from thermodynamic potentials;
- ❖ apply Maxwell's relations to obtain the TdS -equations and energy equations;
- ❖ obtain Clausius-Clapeyron equation from Maxwell's relations;
- ❖ discuss Joule-Thomson effect and how it can be used to produce low temperatures; and
- ❖ define inversion temperature and discuss its importance for liquefaction of gases.

10.2 THERMODYNAMIC POTENTIALS

Consider a gas contained in a cylinder fitted with frictionless piston. The thermodynamic behaviour of this gas can be described in terms of any two variables out of p , V and T ; the third one is automatically fixed in view of the equation of state. Such a system is said to be a **two-coordinate system**. But even for description of such a system, we need several functions of state: p , V , T , S , U and H . (Of these, U and H have dimensions of energy.) In principle, we can construct several functions of state by combining these functions. However, only a few of these may have physical significance. In particular, we define Helmholtz and Gibbs free energies, which also have dimensions of energy like internal energy and enthalpy. As you proceed, you will learn that knowledge of the behaviour of two-coordinate system can be obtained from any one of these four free energies. These are defined as follows:

- Internal energy : U
- Enthalpy : $H = U + pV$
- Helmholtz energy : $F = U - TS = H - pV - TS$
- Gibbs energy : $G = U - TS + pV = F + pV$

(10.1)

It is interesting to mention here that U , H , F and G are collectively referred to as thermodynamic potentials or free energies. Of these, Helmholtz energy is particularly important as it provides a vital connection between thermodynamics and statistical mechanics. That is, it provides a bridge between macroscopic and microscopic viewpoints. You will know these details in Block 4 of this course. Gibbs free energy finds wide applications in the study of phase transitions.

The physical significance of thermodynamic potentials becomes clearer from their differential forms. You will learn about these now.

Differentials of Potential Functions

Let us consider a gaseous system undergoing an infinitesimal reversible process. From Eq. (9.10), you would recall that change in internal energy can be written as

$$dU = TdS - pdV \quad (10.2)$$

Also, a small change in enthalpy, defined as $H = U + pV$, can be written in terms of changes in internal energy, volume and pressure as

$$dH = dU + pdV + Vdp$$

On combining this result with Eq. (10.2), we can write

$$dH = TdS + Vdp \quad (10.3)$$

Likewise, using the definition of Helmholtz free energy ($F = U - TS$), we can write

$$dF = dU - (TdS + SdT)$$

On combining this result with Eq. (10.2), we get

$$dF = -SdT - pdV \quad (10.4)$$

This equation defines the dependence of F on independent variations of T and V . These thermodynamic variables, therefore, constitute the natural pair for Helmholtz energy and we can write $F = F(T, V)$. Note that the right-hand side of Eq. (10.4) comprises two terms and each of these terms consists of a pair of thermodynamic variables such that their product has dimensions of energy.

It readily follows from Eq. (10.4) that entropy and pressure, respectively, of constant V and constant T systems are given by

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \quad (10.5a)$$

and
$$p = -\left(\frac{\partial F}{\partial V}\right)_T \quad (10.5b)$$

These relations show that once F is known for a system under consideration, we can obtain complete information about its thermal properties. Further, Eq. (10.5a) shows that the Helmholtz energy decreases with rise in temperature, since entropy of any substance is always positive definite. The higher the entropy of a substance, greater would be the rate of decrease of F . That is why at higher temperatures, the rate of fall of F with temperature is maximum for gases and minimum for solids. Similarly, Eq. (10.5b) shows that an increase in volume decreases Helmholtz energy; the rate of fall being greater at higher pressures.

Starting from the definition of Gibbs energy ($G = F + pV$) and using Eq. (10.4), you can easily convince yourself that an infinitesimal change in G is given by (SAQ 1):

$$dG = -SdT + Vdp \quad (10.6)$$

Note that T and p constitute the pair of natural variables for Gibbs energy and we can write $G = G(T, p)$. Further, we can write

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \quad (10.7a)$$

and
$$V = \left(\frac{\partial G}{\partial p}\right)_T \quad (10.7b)$$

You should now solve an SAQ before proceeding further.

SAQ 1 – Gibbs energy

Derive Eq. (10.6).

Proceeding further, let us suppose that only one of the free energies is known explicitly. You may then logically ask: Can we get complete information about the system from it? The answer to this question is in the affirmative. We illustrate this by considering the Helmholtz free energy.

To express U, H and G in terms of F , we have to start from their respective definitions. For example, by substituting for S from Eq. (10.5a), the internal energy can be expressed as

$$U = F + TS = F - T \left(\frac{\partial F}{\partial T} \right)_V = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{F}{T} \right) \right]_V = \left[\frac{\partial (F/T)}{\partial (1/T)} \right]_V \quad (10.8)$$

since $\frac{d}{dT} \left(\frac{1}{T} \right) = -\frac{1}{T^2} dT$.

Eq. (10.8) is known as the **Gibbs-Helmholtz equation**. It finds great use in thermo-chemistry.

Similarly, on substituting for S and p from Eqs. (10.5a) and (10.5b) respectively, you can write

$$H = F + TS + pV = F - T \left(\frac{\partial F}{\partial T} \right)_V - V \left(\frac{\partial F}{\partial V} \right)_T \quad (10.9)$$

and $G = F + pV = F - V \left(\frac{\partial F}{\partial V} \right)_T = -V^2 \left[\frac{\partial}{\partial V} \left(\frac{F}{V} \right) \right]_T = \left[\frac{\partial (F/V)}{\partial (1/V)} \right]_T \quad (10.10)$

Eqs. (10.8), (10.9) and (10.10) clearly show that the entire information about a thermodynamic system can be obtained once we know Helmholtz free energy. You may now logically ask: Can we say the same for other thermodynamic potentials? The answer to this question is in affirmative. However, we will not establish this result. To convince yourself, you should answer the following SAQ.

SAQ 2 – Thermodynamic potentials

- a) Obtain first order derivatives of H and G which justify the following statements:
- At constant entropy, the rate of increase of enthalpy with pressure is greater for a gas than that for a solid.
 - Under isothermal conditions, the Gibbs energy increases more rapidly with pressure for a gas than for a liquid or a solid.
- b) Prove that

i) $p = - \left(\frac{\partial U}{\partial V} \right)_T + T \left(\frac{\partial S}{\partial V} \right)_T$

ii) $H = \left[\frac{\partial (G/T)}{\partial (1/T)} \right]_p$

Before proceeding further, let us recapitulate what you have learnt in this unit so far.

Recap

THERMODYNAMIC FREE ENERGIES

- The behaviour of any pVT system can be explained in terms of four thermodynamic free energies:
 - Internal energy, U
 - Enthalpy, $H = U + pV$
 - Helmholtz energy, $F = U - TS$
 - Gibbs energy, $G = F + pV$
- Each thermodynamic free energy is associated with a natural pair of variables:

$$U = U(S, V); H = H(S, p); F = F(T, V) \text{ and } G = G(T, p)$$

Now that you have learnt about free energies, you can use these to obtain several thermodynamic relations. We first illustrate it by deriving Maxwell's relations. As you proceed, you will learn that these relations derive their usefulness from the fact that they frequently relate quantities, which apparently seem unrelated. Moreover, Maxwell's relations simplify thermodynamic analysis considerably without compromising with elegance.

10.3 MAXWELL'S RELATIONS

You have read about exact differentials in Block 2. We will now use this concept for deriving Maxwell's relations, which connect the partial derivatives of p, V, T and S for a simple compressible substance. These are extremely useful relations. These can be readily applied to determine the changes in a property that cannot be measured directly, by simply measuring the changes in p, V and T .

Suppose z is a function of state which depends on two independent state variables x and y and we can write $z = z(x, y)$. Then an infinitesimal change dz in z due to changes in x and y can be expressed as

$$\begin{aligned} dz &= \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \\ &= Mdx + Ndy \end{aligned} \quad (10.11a)$$

where we have put $M = \left(\frac{\partial z}{\partial x} \right)_y$ and $N = \left(\frac{\partial z}{\partial y} \right)_x$. If we differentiate M with respect to y , keeping x fixed, and N with respect to x , keeping y fixed, we get

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial}{\partial y} \left(\frac{\partial z}{\partial x} \right)_y \right)_x$$

and

$$\left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right)_y$$

We know that the order of differentiation does not affect the value of a perfect differential, that is $\left(\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right)_y$. So, we can write

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad (10.11b)$$

We are now in a position to use Eqs. (10.11a) and (10.11b) to obtain Maxwell relations from thermodynamic potentials. But before doing so, let us summarise what you have learnt in this section.

If dz is an exact differential

$$dz = M dx + N dy$$

where z, M and N are functions of x and y , then

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

To obtain Maxwell's relations using thermodynamic free energies, you can choose any one of the free energies as a function of any two thermodynamic variables out of p, V, S and T . Let us first choose T and V as independent variables. Recall that the free energy associated with these variables is F . It means that we have to refer to Eq. (10.4) and compare it with Eq. (10.11a). You will note that these equations have exactly the same form. In fact, these will be identical if you identify F with z , $-S$ with M , $-p$ with N , T with x and V with y . (This means that F, S and p are now functions of T and V .) Therefore, using Eq. (10.11b), we can write:

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

or
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad (10.12a)$$

Similarly, if we choose T and p as independent variables, we have to consider Gibbs free energy and refer to Eq. (10.6). Then on comparing it with Eq. (10.11a), we note that these equations will become identical if we replace G with z , $-S$ with M , and V with N . Moreover, T is identified with x and p with y . Then using Eq. (10.11b), you will obtain

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \quad (10.12b)$$

Similarly, if we choose S and V and S and p as independent variables, we have to work with Eqs. (10.2) and (10.3), respectively.



Don't forget!

Maxwell's relations can be written from the following statement:

$$\frac{\partial(p, V)}{\partial(x, y)} = \frac{\partial(T, S)}{\partial(x, y)}$$

where x and y can be pairs out of

$$(T, V), (T, p), (S, V)$$

and (S, p) .

The variables occurring at exactly the same position in the numerator as well as the denominator are cancelled out and put as suffix but if they occur in crossed positions, we put a negative sign while cancelling them.

Following the procedure outlined above, you can easily convince yourself that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (10.12c)$$

and
$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \quad (10.12d)$$

From Maxwell's relations, you will note that:

- i) Cross multiplication of the variables involved in the partial derivatives always gives the form: $(TS) = (pV)$, which has the dimensions of energy.
- ii) The independent variable of the partial differentiation on the left-hand side appears as a constant on the right-hand side and vice-versa.
- iii) The sign is positive if T appears with p in a partial derivative (remember 'p' for positive).
- iv) We can study pressure and volume variation of entropy in terms of partial derivatives involving extensive and intensive thermodynamic variables

A detailed study of Maxwell's relations leads to a satisfactory explanation of many interesting physical phenomena. For example, let us consider the first Maxwell relation. It can be used to explain the co-existence of two phases of a substance in equilibrium. Similarly, the second relation can be used to explain anomalous expansion of water when it is heated from 0°C to 4°C.

You can perform a very simple activity. Take Indian rubber and stretch it before touching with your lips. Do you experience some heat? We can seek explanation of this and such other phenomena in Maxwell's relations. You will learn about these a little later.

Before you go over to the next section, you should learn how to apply Maxwell's relations. We explain it by solving an example.

EXAMPLE 10.1: MAXWELL'S RELATIONS

Calculate the pressure at which water would boil at 160°C, if the change in specific volume when 1 g of water converted into steam is 1676 cc. Given $1 \text{ cal} = 4.2 \times 10^7 \text{ erg}$, $1 \text{ atm} = 10^6 \text{ dyne cm}^{-2}$ and specific latent heat of vaporization of steam is 540 cal g^{-1} .

SOLUTION ■ From Maxwell's first relation [Eq. (10.12a)], we can write

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

Multiplying both sides by T , we get $T\left(\frac{\partial S}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V$

But we know that $\delta Q = TdS$

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

Here $\delta Q = ml = 540 \text{ cal} = 540 \times 4.2 \times 10^7 \text{ erg}$,

$T_1 = 100^\circ\text{C} = 373 \text{ K}$, $T_2 = 160^\circ\text{C} = (160 + 273) \text{ K} = 433 \text{ K}$,

$\Delta T = (433 - 373) \text{ K} = 60 \text{ K}$ and $\Delta V = (1676 - 1) \text{ cm}^3 = 1675 \text{ cm}^3$.

Substituting these values in the above relation, we get

$$\begin{aligned} \Delta p &= \frac{\partial T}{T} \left(\frac{\delta Q}{\partial V}\right) = \frac{60 \text{ K} \times 540 \times 4.2 \times 10^7 \text{ erg}}{373 \text{ K} \times 1675 \text{ cm}^3} \\ &= 2.177 \times 10^6 \text{ dyne cm}^{-2} = 2.177 \text{ atm} \end{aligned}$$

Therefore, the required pressure at which water would boil at $160^\circ\text{C} = 2.177 + 1 = 3.177 \text{ atm}$.

This is the working principle of a pressure cooker.

We now summarise the important results of Maxwell's relations.

MAXWELL'S RELATIONS

Recap

- Maxwell's relations help us to study variation of entropy with volume and pressure in terms of partial derivatives involving extensive and intensive variables.
- Four important Maxwell's relations are:

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

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

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

and
$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

In the Study Guide of this unit, we emphasized that you should not memorise any thermodynamic relation. We now illustrate how you can conveniently write these down based on a simple sentence.

Do not forget what we have explained in the box ahead.

Memorise the sentence: **Good Physicists Have Studied Under Very Fine Teachers.**

Note that the first letter of each word in this sentence highlights a thermodynamic variable or free energy.

So, we draw a rectangle called mnemonic diagram, whose upper right and lower left corners have been clipped.

Starting from the upper left corner in the figure, place the first letter of each word successively proceeding clockwise, as shown in Fig. 10.1.

Note that each energy function is flanked by its respective set of natural variables.

To write expressions for dG , dH , dU and dF in terms of changes in their natural variables, we choose the energy corner as origin and note the position of natural variables.

If a variable is below or to the left of the origin, a negative sign precedes it. Thus, we can write

$$dG = () dp - () dT$$

The variable in the brackets is chosen such that it ensures dimensions of energy for the product. So, in the instant case, we can write

$$dG = Vdp - SdT$$

You should practice writing expressions for other free energies. Once you have written using the analogy with the relations

$$dz = Mdx + Ndy$$

and $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

You can obtain Maxwell's relations in the sequence given in the text by working with (T, V) ; (T, p) ; (S, V) and (S, p) with their respective free energies.

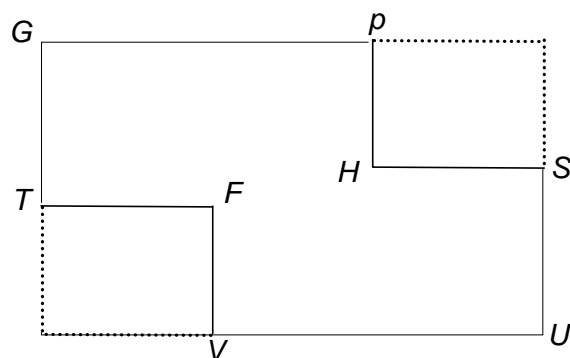


Fig. 10.1: Mnemonic diagram.



10.4 DEDUCTIONS FROM MAXWELL'S RELATIONS

The heat transfer in an infinitesimal reversible process is given by $\delta Q = TdS$. Let us see how Maxwell's relations enable us to calculate heat transfer under different physical conditions.

10.4.1 TdS -Equations

TdS -equations enable us to relate the entropy of a substance with directly measurable quantities, provided its equation of state and heat capacities are known. Depending on the choice of independent variables, we obtain three TdS -equations. To derive the first TdS -equation, let us take T and V as independent variables and express entropy of a substance as

$$S = S(T, V)$$

An infinitesimal change in T and/or V may induce a corresponding change in entropy. We can mathematically express it as

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

Multiplying throughout by T , we get

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

You would recall that for a gas made up of n moles, $T\left(\frac{\partial S}{\partial T}\right)_V = nC_V$.

Further, using Eq. (10.12a) we replace $\left(\frac{\partial S}{\partial V}\right)_T$ by $\left(\frac{\partial p}{\partial T}\right)_V$. This gives

$$TdS = nC_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV \quad (10.13a)$$

Eq. (10.13a) is called the **first TdS -equation**. Note that

- i) all quantities occurring on the right-hand side of Eq. (10.13a) can be measured, and
- ii) the second term defines pressure variation with temperature for an isochoric process.

So, once we know the equation of state, we can easily determine the pressure variation with temperature at constant volume. (This is explained for a van der Waals' gas in Example 10.2.) However, we can express it as a ratio of two measurable quantities: isothermal compressibility and volume expansivity. We illustrate it now:

Recall that volume expansivity $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ and isothermal compressibility

$$\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \text{ so that } \frac{\alpha}{\beta_T} = -\frac{\left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial V}{\partial p} \right)_T} = -\left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial V} \right)_T.$$

The cyclic relation between variables (p, V, T) is

$$\left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial T}{\partial p} \right)_V = -1$$

Using the cyclic relation between thermodynamic variables (p, V, T) we can write

$$\frac{\alpha}{\beta_T} = \left(\frac{\partial p}{\partial T} \right)_V$$

On combining this result with Eq. (10.13a), we can rewrite the first TdS equation as

$$TdS = nC_V dT + T \frac{\alpha}{\beta_T} dV \quad (10.13b)$$

Note that Eqs. (10.13a, b) express variation in entropy in terms of physically measurable quantities. We now illustrate the use of the first TdS equation through an example.

EXAMPLE 10.2: APPLICATION OF MAXWELL'S RELATION

One mole of a van der Waals' gas undergoes a reversible isothermal expansion from a volume v_i to a volume v_f . Calculate the amount of heat transferred in this process.

SOLUTION ■ For one mole, we can write the first TdS equation as

$$TdS = C_V dT + T \left(\frac{\partial p}{\partial T} \right)_V dv \quad (i)$$

where S, C_V and V , respectively, denote molar entropy, molar heat capacity at constant volume, and molar volume of the gas. For one mole of a van der Waals' gas, we can write the equation of state as:

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \quad (ii)$$

From this, you can easily write: $\left(\frac{\partial p}{\partial T} \right)_V = \frac{R}{V-b}$ (iii)

Using this result in (i), we get: $Tds = C_V dT + \frac{RT}{V-b} dV$ (iv)

Since the gas undergoes an isothermal expansion, $dT = 0$. Therefore, the first term on the right-hand side of Eq. (iv) drops out. Further, we know that the heat transferred $\delta Q = Tds$. Hence on integrating (iv) over volume between given initial and final values, we get

$$\delta Q = RT \int_{v_i}^{v_f} \frac{dV}{V-b} = RT \ln \left[\frac{V_f - b}{V_i - b} \right] \quad (v)$$

To obtain the second TdS -equation, we take entropy as a function of T and p .

Then we can write:

$$TdS = T \left(\frac{\partial S}{\partial T} \right)_p dT + T \left(\frac{\partial S}{\partial p} \right)_T dp$$

In terms of heat capacity at constant pressure, we can write

$$TdS = nC_p dT + T \left(\frac{\partial S}{\partial p} \right)_T dp$$

If we now use Eq. (10.12b), we get

$$TdS = nC_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp \quad (10.14a)$$

This is the *second* TdS -equation. In terms of volume expansivity α , we can rewrite it as

$$TdS = nC_p dT - TV\alpha dp \quad (10.14b)$$

Similarly, by taking p and V as independent variables and writing $S = S(p, V)$, we get

$$T dS = T \left(\frac{\partial S}{\partial p} \right)_V dp + T \left(\frac{\partial S}{\partial V} \right)_p dV$$

To put it in a more meaningful form, we split the bracketed terms on the RHS of this equation and rewrite it as

$$T dS = T \left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial T}{\partial p} \right)_V dp + T \left(\frac{\partial S}{\partial T} \right)_p \left(\frac{\partial T}{\partial V} \right)_p dV$$

For n moles of the gas, we can write

$$T dS = nC_V \left(\frac{\partial T}{\partial p} \right)_V dp + nC_p \left(\frac{\partial T}{\partial V} \right)_p dV \quad (10.15)$$

This is the *third* TdS -equation. You may now like to work out an SAQ on TdS -equations.

SAQ 3 – TdS -equations

The pressure on 0.015 litre of mercury at 0°C is increased reversibly isochorically and isothermally from one to 1001 atm. Use Eq. (10.14b) to calculate the heat transfer. It is given that α for mercury = $178 \times 10^{-6} \text{K}^{-1}$. Take $1 \text{atm} = 10^5 \text{Nm}^{-2}$. (Assume that V remains constant.)

EXAMPLE 10.3: APPLICATION OF TdS -EQUATIONS

Write TdS equation for a surface film defined by $TdS = dU - \sigma dA$.

SOLUTION ■ By comparing the TdS equation for surface film with for a hydrostatic system, we note that p and V have been replaced by $-\sigma$ and A , respectively.

Using these variables in the first and second TdS -equations, we can write

$$TdS = C_A dT - T \left(\frac{\partial \sigma}{\partial T} \right)_A dA$$

and
$$TdS = C_\sigma dT + T \left(\frac{\partial A}{\partial T} \right)_\sigma d\sigma$$

Here C_A and C_σ are heat capacities of the film at constant area and at constant surface tension, respectively.

If the film is stretched isothermally and the area increases by dA , the heat transferred to the film is

$$\delta Q_T = TdS = -T \left(\frac{\partial \sigma}{\partial T} \right)_A dA$$

It is an experimentally established fact that surface tension is a function of temperature only. Therefore, we can write

$$\delta Q_T = -T \frac{d\sigma}{dT} dA$$

Since $\frac{d\sigma}{dT}$ is negative for liquids, δQ_T will be positive if $dA > 0$.

Before proceeding further, let us recapitulate what you have learnt in this section so far.

TdS -EQUATIONS

- A TdS -equation helps us to relate changes in entropy in terms of molar heat capacities, volume expansivity and compressibility.
- For a hydrostatic system, the TdS -equations are

$$TdS = nC_V dT + T \left(\frac{\partial p}{\partial T} \right)_V dV$$

$$T dS = nC_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp$$

$$T dS = nC_V \left(\frac{\partial T}{\partial p} \right)_V dp + nC_p \left(\frac{\partial T}{\partial V} \right)_p dV$$

10.4.2 Energy Equations

Just as Maxwell's relations enable us to know heat transfer, we can also use these to study how internal energy changes with volume, temperature or pressure. The resulting relations are known as **energy equations**. To derive first of these, we divide Eq. (10.2) by dV .

This gives $\frac{dU}{dV} = T \frac{dS}{dV} - p$

If T is held constant, the derivatives in the above equation will have to be treated as partial derivatives, so that you can write

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

Using first Maxwell's relation (Eq. (10.12a)), we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p \quad (10.16)$$

Eq. (10.16) is the so-called **first energy equation**.

To illustrate its use, we consider a simple example. For an ideal gas, we know that

$$p = \frac{nRT}{V} \quad \text{and} \quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V}$$

Substituting this in Eq. (10.16), we have

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{nRT}{V} - p = 0$$

This result shows that internal energy of an ideal gas is independent of its volume. So we may say that for an ideal gas U depends on only T . But, in general, U is a function of both T and V . You will understand this by solving the following SAQ.

SAQ 4 – Energy equation

Using Eq. (10.16), show that for one mole of a van der Waals' gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}.$$

The pressure dependence of internal energy can be obtained by dividing Eq. (10.2) by dp and using Eq.(10.12b). The result is the so-called **second energy equation**:

$$\left(\frac{\partial U}{\partial p}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_p - p \left(\frac{\partial V}{\partial p}\right)_T \quad (10.17)$$

Before proceeding further, we would like you to work out an SAQ.

SAQ 5 – Energy equation

Obtain Eq. (10.17) and show that for on ideal gas, internal energy is independent of pressure that U is independent of p .

10.4.3 Clausius-Clapeyron Equation

From the first Maxwell's relation (Eq. (10.12a)) we recall that in isothermal expansion, the heat absorbed per unit volume is equal to the product of the absolute temperature and the rate of increase of pressure with temperature in an isochoric process. Now, let us consider a cylinder which contains a liquid in equilibrium with some of its vapour. (The pressure is called the saturated vapour pressure. It does not depend on the quantities of liquid and vapour present.) If we allow the system to expand at constant temperature, the vapour pressure will stay constant but liquid will evaporate to fill the extra space with vapour. Then we can write $\delta Q = \ell dm$, where ℓ is specific latent heat of evaporation. The change in volume will be equal to $(v_{vap} - v_{liq}) dm$ where v_{vap} and v_{liq} are the specific volumes for the vapour and the liquid, respectively. So, we can rewrite Eq. (10.12a) as

$$\frac{1}{T} \left(\frac{\delta Q}{\delta V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V \quad (10.18a)$$

or
$$\left(\frac{\delta Q}{\delta V} \right)_T = \frac{\ell}{v_{vap} - v_{liq}} = T \left(\frac{\partial p}{\partial T} \right)_V \quad (10.18b)$$

Alternatively, if we hold the volume constant and increase the temperature by dT , the liquid will evaporate till the mixture reaches a new equilibrium state and hence a new saturated vapour pressure. Then we may identify

$$\left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial p}{\partial T} \right)_{sat}$$

On combining this result with Eq. (10.18b), we can write

$$\left(\frac{\partial p}{\partial T} \right)_{sat} = \frac{\ell}{T [v_{vap} - v_{liq}]} \quad (10.19)$$

This is known as *Clausius-Clapeyron equation*. It is one of the most important formulae in thermodynamics and gives the rate at which vapour pressure must change with temperature for two phases to coexist in equilibrium. (Inversely, you can study the effect of pressure on the boiling point of a liquid.) We can also obtain Eq. (10.19) from the equality of Gibbs Free energies in two co-existing phases. Since $v_{vap} > v_{liq}$ always, $(\partial p / \partial T)_{sat}$ will be positive implying that increase in pressure raises boiling point and vice versa. This explains why vegetables cook faster in a pressure cooker. This also explains why it is difficult to cook food at high altitudes than at the sea level. To give you a feel for the numbers, we may mention that at the top of the Mount Everest, an altitude of about 8 km above the sea level, water boils at about 80°C.

Though we have derived Eq. (10.19) for the evaporation process, the arguments can be extended to any phase change (solid-liquid, liquid-vapour and solid-vapour transition) involving latent heat. That is, Eq. (10.19) applies to all *first order* phase changes in which entropy and volume are

First order phase transition involves change of phase of the matter accompanied by absorption or release of latent heat at constant temperature.

discontinuous at the transition temperature. (You will get an opportunity to arrive at the Clausius-Clapeyron equation based on Gibbs energy in TQ 6.)

The phase diagrams for CO_2 and H_2O are shown in Figs. 10.2a and b, respectively. These curves represent a unique relationship which must hold for two phases to coexist. Note that the three curves intersect at one point. The point (on p - T diagram) where all three phases coexist is known as the *Triple Point*. For CO_2 , $T_{tp} = -56.6^\circ\text{C}$ or 216.4 K and $p_{tp} = 5.11$ atm whereas for water, the triple point is defined by $T_{tp} = 0.0075^\circ\text{C}$ or 273.0075 K and $p_{tp} = 4.58$ atm.

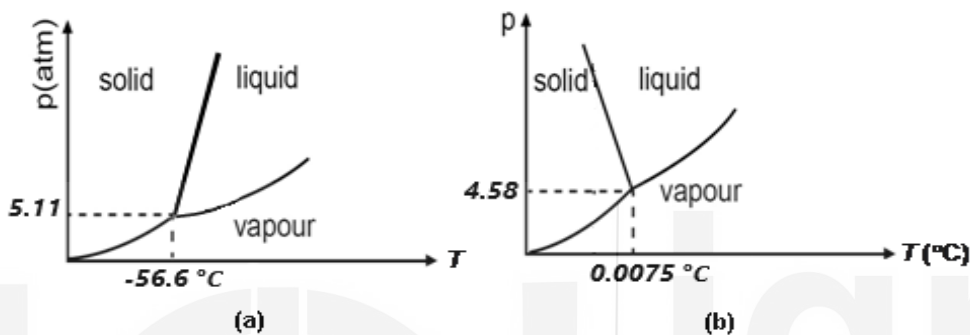


Fig.10.2: The phase diagrams for (a) carbon-di-oxide, and (b) water.

From Fig. 10.2(a) we note that the slope of the solid-liquid curve is positive. This means that most substances expand on melting and dp/dT is positive. So melting point of such materials will increase when pressure is raised. On the other hand, the solid-liquid curve for water (Fig. 10.2b) has a negative slope implying that water expands on freezing and its melting point decreases when pressure increases. Note that water is an exception in that at the triple point, it passes from vapour \rightarrow solid \rightarrow liquid phase when pressure is increased.

It may be remarked here that the Clausius-Clapeyron equation is obeyed by systems to a high degree of accuracy and over a wide range of experimental conditions. This constitutes strong evidence in favour of the second law of thermodynamics.

Now you should study the following example carefully.

EXAMPLE 10.4: CLAUSIUS-CLAYPERON EQUATION

Calculate the change in the melting point of ice at 0°C when pressure is increased by 2 atm. How much pressure is required to lower the melting point by 1°C ? Given, latent heat of fusion is 79.6 cal g^{-1} and the specific volumes of water and ice are 1.001 cm^3 and 1.0908 cm^3 , respectively.

SOLUTION ■ From Eq. (10.19), we can write

$$\left(\frac{\partial p}{\partial T}\right)_{\text{sat}} = \frac{\ell}{T[v_{\text{water}} - v_{\text{ice}}]}$$

On substituting $\ell = 79.6 \times 4.186 \times 10^7 \text{ erg g}^{-1}$, $v_{\text{water}} = 1.0001 \text{ cm}^3$,
 $v_{\text{ice}} = 1.0908 \text{ cm}^3$ and $T = 273.16 \text{ K}$, we get

$$\frac{dp}{dT} = \frac{79.6 \times 4.186 \times 10^7 \text{ erg g}^{-1}}{(273.16 \text{ K}) \times (1.0001 - 1.0908) \text{ cm}^3} = -13.45 \times 10^7 \text{ dyne cm}^{-2} \text{ K}^{-1}$$

Since $dp = 2 \text{ atm} = 2.026 \times 10^6 \text{ dyne cm}^{-2}$, the change in melting point is given by

$$dT = -\frac{2.026 \times 10^6 \text{ dyne cm}^{-2}}{13.45 \times 10^7 \text{ dyne cm}^{-2} \text{ K}^{-1}} = -0.015 \text{ K} = -0.015^\circ \text{C}$$

This result shows that the melting point of ice decreases with pressure; the drop per atmosphere being 0.0075°C . Thus, when enough pressure is applied, ice melts. This fact is of significance in the game of ice skating as well as in the study of glaciers.

The increase in pressure required to lower the melting point of ice by 1°C is $1 \text{ K} / 0.0075 \approx 133 \text{ atm}$.

10.5 JOULE-THOMSON EFFECT

From the discussion of van der Waals' equation in Block 1, you may recall that in arriving at his equation, van der Waals assumed that gas molecules have finite size and experience molecular attraction. To verify these assumptions, Joule performed a simple experiment wherein he allowed a gas to undergo free expansion. He argued that if intermolecular forces do exist, some work will be done against these when a gas expands. And since this work can only be done at the expense of the internal energy of the gas, its temperature should drop producing a cooling effect. However, he could observe no cooling effect.

Soon after, Joule carried out a series of experiments in collaboration with Thomson. They made a gas to **expand adiabatically through a porous plug from a constant higher pressure to a constant lower pressure**. They showed that when temperature of the gas was below a certain temperature, known as inversion temperature, it did show cooling effect. This is known as **Joule-Thomson effect**. The findings of Joule-Thomson experiment are summarized below:

- All gases showed a change in temperature after passing through the porous plug.
- At ordinary temperatures, all gases, except hydrogen and helium, showed cooling effect. In fact, these gases showed slight heating, which was completely unexpected.
- At low enough temperatures, all gases showed cooling effect.
- The fall in temperature was directly proportional to the pressure difference on the two sides of the porous plug. However, for a given difference of

pressure, the drop in temperature was more if the initial temperature of the gas was less.

- For every gas, no change in temperature was observed when it was made to expand at the temperature of inversion, denoted as T_i . When the initial temperature of a gas was below the temperature of inversion, it cooled after adiabatic expansion through the porous plug.

Joule-Thomson coefficient is defined as

$$\mu = \frac{\Delta T}{\Delta p} \quad (10.20)$$

Without going into details, we will just quote the result for a van der Waals' gas:

$$\mu = \frac{1}{C_p} \left(\frac{2a}{RT} - b \right) \quad (10.21)$$

We know that Δp is greater than zero since gas is made to expand from a constant higher pressure to a constant lower pressure. So, Eq. (10.21) suggests that cooling or heating in Joule-Thomson expansion will be determined by the competition between terms characterizing intermolecular forces represented by a and finite size of gas molecules represented by b .

If intermolecular forces are strong, i.e. $a \gg b$, then $\left(\frac{2a}{RT} - b \right) > 0$.

Hence, $\Delta T > 0$ and the gas will cool and vice versa. However, there will be neither cooling nor heating if

$$\frac{2a}{RT_i} = b \quad (10.22)$$

T_i is referred to as *inversion temperature*. It signifies that when a gas undergoes Joule-Thomson expansion below its *inversion temperature*, it will cool down. But if the temperature before expansion is above its *inversion temperature*, it will warm up.

The inversion temperatures for some typical gases are given in Table 10.1.

Table 10.1: Inversion temperatures of some gases

Gas	He	H ₂	N ₂	A	O ₂	CO ₂	Air
T_i (K)	23.6	195	621	723	893	1500	603

Note that for H₂ and He, T_i is well below the room temperature (273K) and that is why they show warming at ordinary temperatures.

From Eq. (10.21) we further note that for a perfect gas, $a = b = 0$. It means that Joule-Thomson coefficient for a perfect gas would be zero.

We now sum up what you have learnt in this unit.

10.6 SUMMARY

Concept	Description
Thermodynamic potentials	<ul style="list-style-type: none"> ■ When a system can be subjected to work by pressure only, there exist four thermodynamic potential functions: internal energy U; enthalpy $H = U + pV$; Helmholtz function $F = U - TS$; and Gibbs function $G = U - TS + pV$. ■ Infinitesimal changes in thermodynamic potentials are given by $dU = TdS - pdV, \quad dH = TdS + Vdp$ $dF = -SdT - pdV, \quad dG = -SdT + Vdp$
Maxwell's relations	<ul style="list-style-type: none"> ■ The four Maxwell's relations are $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$ $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$ $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$ $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$
TdS-equations	<ul style="list-style-type: none"> ■ Three TdS-equations relate changes in entropy to change in temperature, volume or pressure: $TdS = nC_V dT + T \left(\frac{\partial p}{\partial T}\right)_V dV$ $TdS = nC_p dT - T \left(\frac{\partial V}{\partial T}\right)_p dV$ $TdS = nC_V \left(\frac{\partial T}{\partial p}\right)_V dp + nC_p \left(\frac{\partial T}{\partial V}\right)_p dV$
Energy equations	<ul style="list-style-type: none"> ■ Energy equations specify the variation of internal energy with volume and pressure: $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p$ $\left(\frac{\partial U}{\partial p}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_p - p \left(\frac{\partial V}{\partial p}\right)_T$

Joule-Thomson coefficient

■ Joule-Thomson coefficient is defined as

$$\mu = \frac{\Delta T}{\Delta p} = \frac{1}{C_p} \left(\frac{2a}{RT} - b \right) = \frac{b}{C_p} \left(\frac{T_i}{T} - 1 \right)$$

where $T_i = \frac{2a}{Rb}$ is the temperature of inversion of the gas. Every gas undergoing Joule-Thomson expansion at a temperature below the inversion temperature cools down and vice versa.

10.7 TERMINAL QUESTIONS

1. For a magnetic system, the infinitesimal change in internal energy may be expressed as

$$dU = TdS + VB dM$$

Here B is the applied magnetic field and M is the intensity of magnetisation. If $M = \frac{m'}{V}$ where m' is the magnetic moment, you can write

$$dU = TdS + B dm'$$

Now, starting from the above equation, write for the magnetic system

- the four Maxwell's relations,
 - the second TdS -equation.
2. A gas obeys the equation $p(V - b) = RT$, where b is constant. Show that
- U is a function of only T ,
 - $p(V - b)^\gamma = \text{constant}$ for the gas undergoing a reversible adiabatic process.
3. For an ideal gas show that
- coefficient of volume expansion is a function of only temperature.
 - the isothermal compressibility is a function of only pressure.
4. Water boils at a temperature of 101°C at a pressure of 78.8 cm of Hg. If 1 g of water occupies 1601 cm^3 on evaporation, calculate the latent heat of steam. Given $1 \text{ cal} = 4.2 \times 10^7 \text{ erg}$ and $g = 980 \text{ cm s}^{-2}$.
5. Calculate the specific volume of solid sulphur from the following data: Melting point of sulphur = 115°C ; latent heat of fusion of sulphur = 9.3 cal g^{-1} , volume of 1 g of liquid sulphur = 0.513 cm^3 ; rate of change of melting point with pressure is $0.025^\circ\text{C atm}^{-1}$. ($1 \text{ atm} = 10^6 \text{ dyne cm}^{-2}$)
6. When two phases of a substance co-exist in equilibrium at constant temperature and pressure, their specific Gibbs free energies are equal. Using this fact, obtain Clausius-Clapeyron equation.

10.8 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. We know that $G = F + pV$

$$\therefore dG = dF + pdV + Vdp = -SdT - pdV + pdV + Vdp$$

$$\text{or } dG = -SdT + Vdp, \text{ which is Eq. (10.6).}$$

$$2. \text{ a) i) From Eq. (10.3), we can write } V = \left(\frac{\partial H}{\partial p} \right)_S$$

For a fixed mass, a gas occupies more space (volume) than a solid. So, at constant entropy, the rate of increase of enthalpy with pressure is greater for a gas than a solid.

$$\text{ii) From Eq. (10.7b), we recall that } V = \left(\frac{\partial G}{\partial p} \right)_T$$

As explained above, we can say that at constant temperature, Gibbs energy increases with pressure more rapidly for a gas than that for a liquid or a solid.

$$\text{b) i) From Eq. (10.5b), we know that } p = - \left(\frac{\partial F}{\partial V} \right)_T$$

On substituting for F from Eq. (10.1), we get

$$p = - \left[\frac{\partial}{\partial V} (U - TS) \right]_T = - \left(\frac{\partial U}{\partial V} \right)_T + T \left(\frac{\partial S}{\partial V} \right)_T$$

This relation signifies that pressure exerted by a system arises out of two contributions: isothermal variations of internal energy and entropy with volume. While the first term dominates in case of solids, the second term is more prominent in elastic polymers such as rubber. The variation of entropy of a system with volume may also contribute to pressure when its energy remains constant. This is exactly what happens in the case of an ideal gas at constant temperature.

$$\text{ii) We know that } G = H - TS \text{ and } S = - \left(\frac{\partial G}{\partial T} \right)_p. \text{ Therefore, we can}$$

$$\text{invert this relation to write } H = G - T \left(\frac{\partial G}{\partial T} \right)_p$$

On multiplying and dividing by T^2 , we rewrite it as

$$= T^2 \left[\frac{G - T \left(\frac{\partial G}{\partial T} \right)_p}{T^2} \right] = T^2 \left[\frac{G}{T^2} - \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_p \right] = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{G}{T} \right) \right]_p$$

$$\text{But } \left[\frac{\partial}{\partial T} \left(\frac{1}{T} \right) \right]_p = -\frac{1}{T^2}. \text{ Hence, we get the desired result:}$$

$$H = \left[\frac{\partial (G/T)}{\partial (1/T)} \right]_p$$

3. Since the process is reversible and isothermal ($dT = 0$), from Eq. (10.14) we have

$$\delta Q = TdS = -T \left(\frac{\partial V}{\partial T} \right)_p dp = -TV\alpha dp \quad (i)$$

$$\therefore Q = -\int TV\alpha dp = -T \int V\alpha dp \quad (\because T \text{ is a constant})$$

Since V and α remain constant during the process, we can write

$$Q = -TV\alpha \int dp = -TV\alpha(p_f - p_i) \quad (ii)$$

where p_i and p_f are the initial and the final pressures.

We are given that $T = (0 + 273)\text{K} = 273\text{K}$, $V = 0.015$ litre,
 $\beta = 178 \times 10^{-6}\text{K}^{-1}$, $p_f = 1001$ atm, and $p_i = 1$ atm,

On substituting these values in Eq. (ii), we get

$$Q = -(273\text{K}) \times (0.015 \text{ litre}) \times (178 \times 10^{-6}\text{K}^{-1}) \times (1000 \text{ atm}) \\ = -0.729 \text{ litre atm}$$

Since $1 \text{ litre} = 10^{-3} \text{ m}^3$, and $1 \text{ atm} = 10^5 \text{ Nm}^{-2}$ we can express this result as

$$Q = -0.729 \times (10^{-3} \text{ m}^3) \times 10^5 \text{ Nm}^{-2} = -72.9 \text{ Nm} = -72.9 \frac{\text{J}}{4.2 \text{ Jcal}^{-1}} \\ = -17.4 \text{ cal}$$

The negative sign signifies that heat flows out of the system during the above process.

4. For one mole of a van der Waals' gas, we have $p = \frac{RT}{V-b} - \frac{a}{V^2}$

and $\left(\frac{\partial p}{\partial T} \right)_p = \frac{R}{V-b}$

From Eq. (10.12), we have $\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p$

On substituting for p and $(\partial p / \partial T)_v$, we get

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

5. From Eq. (10.2) we recall that $dU = TdS - pdV$

Dividing both sides by dp , we can write for constant T

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

On using Eq. (10.13), we get

$$\left(\frac{\partial U}{\partial p} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_p - p \left(\frac{\partial V}{\partial p} \right)_T$$

For an ideal gas,

$$pV = nRT$$

or $V = \frac{nRT}{p}$, so that $\left(\frac{\partial V}{\partial T} \right)_p = \frac{nR}{p}$ and $\left(\frac{\partial V}{\partial p} \right)_T = -\frac{nRT}{p^2}$

$$\therefore \left(\frac{\partial U}{\partial p} \right)_T = -\frac{nRT}{p} - p \left(-\frac{nRT}{p^2} \right) = 0$$

This result shows that internal energy of an ideal gas is independent of pressure.

Terminal Questions

1. a) We have $dU = TdS + Bdm'$

If we compare this with Eq. (10.2a), we see that p has been replaced by B and V by $-m'$. Using this idea, we may write the analogues of Eq. (10.2) for magnetic system as follows:

$$dU = T dS + B dm'$$

$$dH = T dS - m' dB$$

$$dF = -S dT + B dm'$$

$$dG = -S dT - m' dB$$

Now applying the conditions (10.13), we have the following four Maxwell's relations

$$\left(\frac{\partial T}{\partial m'} \right)_S = \left(\frac{\partial B}{\partial S} \right)_{m'}$$

$$\left(\frac{\partial T}{\partial B} \right)_S = -\left(\frac{\partial m'}{\partial S} \right)_B$$

$$\left(\frac{\partial S}{\partial m'} \right)_T = -\left(\frac{\partial B}{\partial T} \right)_{m'}$$

$$\left(\frac{\partial S}{\partial B} \right)_T = \left(\frac{\partial m'}{\partial T} \right)_B$$

- b) The TdS -equation may also be obtained by replacing p by B and V by $-m'$. Thus, from Eq. (10.14a), we have $T dS = V C_{Bd}dT + T \left(\frac{\partial m'}{\partial T} \right)_B dB$

2. a) $p(V-b) = RT$ and so, $p = \frac{RT}{V-b}$ and $\left(\frac{\partial p}{\partial T} \right)_V = \frac{R}{V-b}$

We know from Eq. (10.16), that

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p = \frac{RT}{V-b} - p = p - p = 0$$

So, u is a function of only T .

- b) We know from Eqs. (10.13 and 10.14) that $TdS = C_V dT + T \left(\frac{\partial p}{\partial T} \right)_V dV$

$$\text{and } TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp$$

For a reversible adiabatic process, $TdS = 0$

$$\therefore C_V dT = -T \left(\frac{\partial p}{\partial T} \right)_V dV \quad \text{and} \quad C_p dT = T \left(\frac{\partial V}{\partial T} \right)_p dp$$

$$\text{or } C_V dT = -\frac{RT}{V-b} \quad \text{and} \quad C_p dT = \frac{RT}{p} dp$$

$$\text{Hence, } \frac{C_p dT}{C_V dT} = \frac{\frac{RT}{p} dp}{-\frac{RT}{V-b} dV} = -\frac{V-b}{p} \frac{dp}{dV} = \gamma$$

$$\text{so that } -\gamma \frac{dV}{V-b} = \frac{dp}{p}$$

On integrating both sides, we can write

$$-\gamma \ln(V-b) = \ln p + K$$

where K is constant of integration. We can rewrite it as

$$\ln(p(V-b)^\gamma) = K$$

On taking antilog of both sides, we get $p(V-b)^\gamma = K'$

3. i) The coefficient of volume expansion or volume expansivity is given as

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad \text{For an ideal gas, } pV = RT$$

$$\therefore \left(\frac{\partial V}{\partial T} \right)_p = \frac{R}{p} \quad \text{or} \quad \beta = \frac{1}{V} \frac{R}{p} = \frac{1}{T}$$

That is coefficient of volume expansion of an ideal gas is an inverse function of temperature only.

- ii) The expression for thermal compressibility is written as

$$\alpha = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left(-\frac{RT}{p^2} \right) = \frac{1}{p}$$

This shows that the isothermal compressibility of an ideal gas is a function of pressure only.

4. From Clausius Clapeyron equation, we know that

$$\frac{dp}{dT} = \frac{\ell}{T(v_2 - v_1)} \quad \Rightarrow \quad \ell = T(v_2 - v_1) \frac{dp}{dT}$$

$$\text{Here } T = 373\text{K}, \quad v_2 - v_1 = 1600\text{cm}^3 \text{ g}^{-1}$$

$$dp = (78.8 - 76.0) \text{ cm} \times (13.6 \text{ g cm}^{-3}) \times (980 \text{ cm s}^{-2}) = 37318 \text{ dyne cm}^{-2}$$

and $dT = 1\text{K} = 1^\circ\text{C}$

$$\therefore \ell = \frac{(373\text{K}) \times 1600\text{cm}^3\text{g}^{-1} \times (37318\text{dyne cm}^{-2})}{1\text{K}} = 22.27 \times 10^9 \text{ ergg}^{-1}$$

$$= \frac{22.27 \times 10^9 \text{ ergg}^{-1}}{4.2 \times 10^7 \text{ ergcal}^{-1}} = 530.2 \text{ cal g}^{-1}$$

5. From Clausius-Clapeyron equation, we know that

$$\frac{dp}{dT} = \frac{\ell}{T(v_2 - v_1)}$$

$$\text{or } (v_2 - v_1) = \frac{\ell}{T} \frac{dT}{dp}$$

$$\text{Here } \frac{dT}{dp} = 0.025 \text{ K atm}^{-1}, \ell = 9.3 \text{ cal g}^{-1} \text{ and } T = 388 \text{ K}$$

$$\therefore (v_2 - v_1) = \frac{9.3 \text{ cal g}^{-1}}{388 \text{ K}} \times 0.025 \text{ K atm}^{-1} = 0.252 \text{ cm}^3$$

Since the volume of liquid sulphur is $v_2 = 0.513 \text{ cm}^3$, the volume of solid sulphur is given by

$$v_1 \equiv V_s = (0.513 - 0.252) \text{ cm}^3 = 0.261 \text{ cm}^3.$$

6. The specific Gibbs free energy of two phases must always be equal for coexistence of first order phase transitions: $g_1 = g_2$ (i)

If we change the temperature and pressure by ΔT and Δp , respectively, there will be a corresponding change in specific Gibbs free energies as well. But the condition for two phases to co-exist and be stable is given by

$$g_1 + \Delta g_1 = g_2 + \Delta g_2 \quad (\text{ii})$$

From Eqs. (i) and (ii), we can write $\Delta g_1 = \Delta g_2$.

That is, the change in the specific Gibbs free energy of one phase in equilibrium with another phase is equal to the change in specific Gibbs free energy of the other phase. For one-component system, which can exist in two phases, the specific Gibbs energy is given by

$dg = -sdT + vdp$. So, on substituting for Δg_1 and Δg_2 , we get

$$v_1 \Delta p - s_1 \Delta T = v_2 \Delta p - s_2 \Delta T$$

$$\text{or } \frac{\Delta p}{\Delta T} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\Delta s}{\Delta v}$$

where Δs and Δv , respectively, denote changes in specific entropy and specific volume when the system goes from one phase to another. If the specific latent heat (absorbed) required to accomplish change from phase 1 to phase 2 is ℓ , we can write

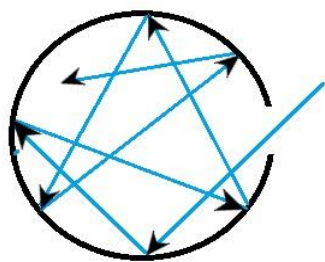
$$s_2 - s_1 = \frac{\ell}{T}$$

Hence, the required relation for changes in pressure and temperature in stable phase equilibrium is

$$\frac{dp}{dT} = \frac{\ell}{T(v_2 - v_1)}$$

This is the Clausius-Clapeyron equation. It gives the rate at which pressure must change with temperature for two phases to remain in equilibrium.

(Note: For details about the phase transitions, you should consult books mentioned in Further Readings at the end of this block.)



A typical black body.

THEORY OF RADIATION

Structure

- | | |
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| <ul style="list-style-type: none"> 11.1 Introduction <ul style="list-style-type: none"> Expected Learning Outcomes 11.2 Definitions and Concepts 11.3 Spectral Distribution of Radiant Energy 11.4 Planck's Law | <ul style="list-style-type: none"> 11.5 Deductions from Planck's Law <ul style="list-style-type: none"> Rayleigh-Jeans Law Wien's Law Stefan's Law 11.6 Summary 11.7 Terminal Questions 11.8 Solutions and Answers Appendix 11A: Number of Allowed Modes of Standing Waves in an Enclosure |
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STUDY GUIDE

The blackbody radiation presented huge challenge to theoretical physicists of late nineteenth and early twentieth century. Lord Rutherford described it as one of the two darkest clouds on the horizon of theoretical physics. All efforts based on classical theory assumed that the energy of a system could be taken as continuous variable but these failed to explain the experimental results in entirety. It required the genius of Planck to provide satisfactory explanation of observed results for all wavelengths. He made a drastic deviation from classical concept about energy of a system in that it should not be treated as a continuous variable. He proposed that energy can change only in concrete steps in units of what is now known as Planck's constant. You will learn to obtain expression for Planck's formula and show that all other laws of radiation are contained in it.

The derivations given in this unit require good knowledge of geometrical series, calculus and acquaintance with special functions. So, you are advised to re-read Block 1 on kinetic theory of gases before studying this unit. To make the unit self-contained and for completeness, we have given all mathematical steps. But you will enjoy the subject more if you solve these steps by yourself. Therefore, keep a pen/pencil as well as a notebook ready with you. Also, answer SAQs and solve TQs or other numerical problems to gain greater proficiency.

“An experiment is a question which science poses to Nature and a measurement is the recording of Nature's answer.”

Max Planck

11.1 INTRODUCTION

In your school physics, you have learnt that all bodies emit thermal radiation. And the intensity, wavelength and rate of emission depend on temperature. For instance, at room temperature, most of the energy is radiated in the far infra-red region, whereas at 6000K, which corresponds to the temperature of the outer surface of the Sun, it lies in the visible region. You have also learnt that the mode of energy transmission from the Sun to the Earth is **radiation**. In fact, radiation is the main mechanism for energy transfer in our solar system, interstellar space and the galaxies. It implies that energy transfer by radiation does not require intervening medium to participate actively.

It is now well accepted that thermal radiations are electromagnetic in nature. Moreover, these produce a sensation of warmth. An enclosure maintained at a constant temperature can be imagined to be filled with electromagnetic radiation, which is in thermal equilibrium with its walls. The electromagnetic radiation in a cavity is called **blackbody radiation** corresponding to a well-defined temperature. In the beginning, the laws of thermodynamics in conjunction with the law of equipartition of energy were used to study the behaviour of blackbody radiation. However, these efforts proved only partly successful.

In this unit, you will get the correct insight into the nature of blackbody radiation and its spectral distribution. We begin by discussing some important terms and concepts related to blackbody radiation in Sec. 11.2. This is followed by a discussion of spectral distribution of radiant energy in Sec. 11.3. Planck proposed the concept of quanta as carriers of energy in emission or absorption of blackbody radiation and explained all observed results available then rather well. In Sec. 11.4, you will learn how to derive Planck's formula of blackbody radiation following the approach used by Planck. (For the number of modes per unit volume in the frequency range ν to $\nu+d\nu$, he used the expression obtained by Rayleigh and Jeans.) In Sec. 11.5, you will learn that all other laws of radiation (Wien's law, Rayleigh-Jeans law and Stefan-Boltzmann's law) are contained in Planck's law.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ explain the concepts of blackbody radiation, spectral distribution and energy density;
- ❖ discuss Planck's theory of black body radiation;
- ❖ obtain Planck's formula for spectral distribution of black body radiation; and
- ❖ derive Rayleigh-Jeans law, Wien's law and Stefan's law from Planck's law.

11.2 DEFINITIONS AND CONCEPTS

To discuss distribution of energies in blackbody radiation, we have to introduce some basic definitions:

Spectral energy density (u_λ) is defined with respect to a particular wavelength λ as a measure of the energy per unit volume per unit range of wavelength. It means that $u_\lambda d\lambda$ denotes the energy per unit volume in the wavelength range from λ to $\lambda + d\lambda$. Therefore, a sum of spectral energy densities for all wavelengths from 0 to ∞ per unit volume gives the total energy density:

$$u = \int_0^{\infty} u_\lambda d\lambda \quad (11.1)$$

Note that the total energy density is measured in units of Jm^{-3} .

Spectral emissive power (e_λ) of a body corresponding to wavelength λ is a measure of energy radiated per second per unit surface area per unit wavelength. Therefore, $e_\lambda d\lambda$ denotes the energy emitted by unit area in one second in the wavelength range from λ to $\lambda + d\lambda$. A sum of spectral emissive powers for all wavelengths from 0 to ∞ gives total emissivity:

$$e = \int_0^{\infty} e_\lambda d\lambda \quad (11.2)$$

Note that emissivity is measured in $\text{Jm}^{-2} \text{s}^{-1}$ or Wm^{-2} .

Spectral absorptivity (a_λ) denotes the fraction of incident energy of a particular wavelength absorbed by unit surface area of a body in one second.

If a body absorbs all radiations incident on it, $a_\lambda = 1$, then the body is said to be a **perfect blackbody**. This nomenclature is based on the colour that we see due to selective absorption of light. Do you know that the text of this unit appears black because letters in it absorb all light falling on them? Why does a flower have colour or why does the paper of your unit appear white?

Note that e and e_λ characterise the properties of a body as emitter whereas a_λ describes the properties of the body as an absorber of radiation. However, these three physical quantities depend on temperature and the nature of the surface of the body.

When radiation of a particular wavelength λ is incident on a body, it may be partially reflected, partially absorbed and partially transmitted. But a blackbody absorbs all radiations incident on it. Then we can write

$$r_\lambda + a_\lambda + t_\lambda = 1$$

where r_λ , a_λ and t_λ , respectively, characterise energy reflection, absorption and transmission coefficients of the body corresponding to wavelength λ . If $r_\lambda = t_\lambda = 0$, then $a_\lambda = 1$. That is, the body is perfectly black for a given wavelength. In practice, no surface or body satisfies this ideal definition strictly. Even lamp black and platinum black respectively absorb nearly 96% and 98% of visible light. So, a_λ is always less than unity.

11.3 SPECTRAL DISTRIBUTION OF RADIANT ENERGY

In your school physics, you have learnt Stefan's law of blackbody radiation. It states that **the rate of emission of radiant energy by unit area of a perfect blackbody is directly proportional to the fourth power of its absolute temperature**. Mathematically, we express it as

$$E = \sigma T^4 \quad (11.3)$$

where σ is called **Stefan's constant** and has value $5.672 \times 10^{-8} \text{ Jm}^{-2}\text{K}^{-4}\text{s}^{-1}$. Stefan's law in the above form refers to the amount of heat emitted by the body by virtue of its temperature, irrespective of what it receives from the surroundings. Therefore, it is natural to extend the scope of this law to represent the exchange of heat and be stated as follows:

For a blackbody at absolute temperature T surrounded by another blackbody at absolute temperature T_0 , the amount of net heat lost by the blackbody at higher temperature per unit time can be expressed as

$$E = \sigma(T^4 - T_0^4) \quad (11.4)$$

This law is known as **Stefan-Boltzmann law**.

Note that Stefan-Boltzmann law relates total energy density of black body radiation with temperature; it does not give any information about the distribution of energy in different parts of the spectrum.

Now refer to Fig. 11.1, which shows observed results of spectral energy density of a black body at different temperatures.

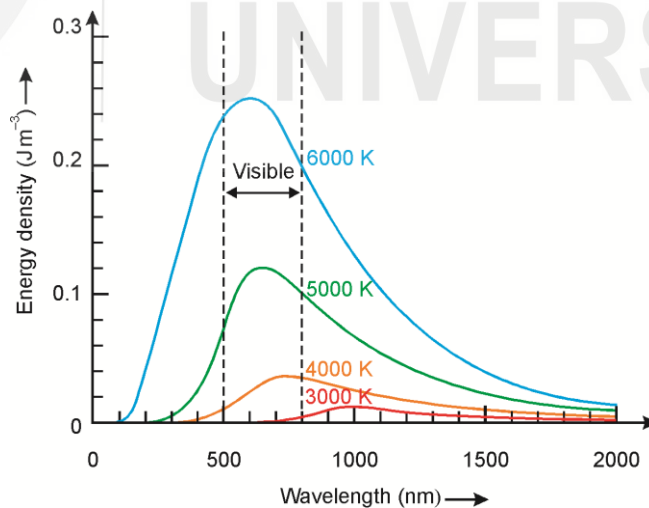


Fig. 11.1: Plot of spectral energy density of a black body with wavelength at different temperatures.

You will note in Fig. 11.1 that:

- For a given wavelength λ , u_λ increases with temperature.
- For each temperature, the spectral energy density plot shows a maximum. It shifts to shorter wavelengths with increase in temperature.

- The spectral energy density becomes zero as wavelength tends to either zero or infinity.

To explain experimental results, Wien and Rayleigh and Jeans used thermodynamic reasoning with the principle of equipartition of energy, wherein energy is considered a continuous variable. However, they could not explain the results satisfactorily in the entire range of the spectrum. In fact, their efforts succeeded either in the higher or in the lower energy regions. This raised doubts about the applicability/utility of the principle of equipartition of energy to understand the physics of blackbody radiation.

Planck then conjectured, albeit heuristically, that **emission and absorption of radiation is a discontinuous process**. To derive Planck's formula, we have preferred discussion of developments in chronological order as this approach is more informative and learner-friendly. It will give you a feel of how scientists handle difficult unknown situations, particularly when their results do not conform to experimental results. (This law was later derived by Indian physicist Prof. S.N. Bose by treating radiation as an assembly of photons, which obey Bose-Einstein statistics. You will learn about it in Block 4.)

11.4 PLANCK'S LAW

Planck presented the following formula for energy density empirically to fit the experimental results on blackbody spectrum:

$$u_\nu d\nu = \frac{8\pi\nu^2}{c^3} \left(\frac{h\nu}{\exp(h\nu/k_B T) - 1} \right) d\nu \quad (11.5)$$

We can rewrite it as:

$$u_\nu d\nu = n_\nu \varepsilon_\nu d\nu = \frac{8\pi\nu^2 \varepsilon_\nu}{c^3} d\nu \quad (11.6)$$

where

$$\varepsilon_\nu = \left(\frac{h\nu}{\exp(h\nu/k_B T) - 1} \right) \quad (11.6a)$$

is the average energy of an oscillator, and

$$n_\nu d\nu = \frac{8\pi\nu^2}{c^3} d\nu \quad (11.6b)$$

defines the number of modes per unit volume in the frequency range ν to $\nu + d\nu$. (The calculation of the number of modes is given in Appendix 11A)

Eq. (11.6b) can also be written as

$$N_\nu d\nu = \frac{8\pi V\nu^2}{c^3} d\nu \quad (11.6c)$$

to define the number of modes in volume V in the frequency range ν to $\nu + d\nu$.

You should now go through the following example.

EXAMPLE 11.1: Calculation of Number of Modes

Calculate the number of modes of oscillations in a chamber of volume 100 cm^3 in the frequency range $4.02 \times 10^{14}\text{ Hz}$ to $4.03 \times 10^{14}\text{ Hz}$.

SOLUTION ■ It is given that $V = 100\text{ cm}^3 = 10^{-4}\text{ m}^3$, $\nu = 4.02 \times 10^{14}\text{ Hz}$, $d\nu = 0.01 \times 10^{14}\text{ Hz}$ and $c = 3 \times 10^8\text{ ms}^{-1}$. On substituting these values in the expression given in Eq. (11.6c), we get

$$N_{\nu}d\nu = \frac{8 \times 3.14 \times (4.02 \times 10^{14}\text{ Hz})^2 \times (10^{-4}\text{ m}^3) \times (0.01 \times 10^{14}\text{ Hz})}{(3 \times 10^8\text{ ms}^{-1})^3} = 1.5 \times 10^{13}$$

By substituting $\varepsilon_{\nu} = k_B T$ in Eq. (11.6), you will obtain Rayleigh-Jeans law, which was derived by them based on the law of equipartition. (It suggests that ε_{ν} is the average energy of a mode of oscillation in Planck's theory.) But Planck was convinced about the inappropriateness of the classical theories and he made a drastic deviation. He postulated that

- the exchange of energy between matter (walls) and radiation (cavity) could take place only in bundles of a certain size; and
- the quantum of exchange is directly proportional to its frequency. That is, the energy of an oscillator having frequency ν could only be an integral multiple of $h\nu$, where h is a constant.

These postulates marked a fundamental departure from the contemporary ideas. The constant h is now known as *Planck's constant*. Its value is $6.62618 \times 10^{-34}\text{ Js}$. (Planck was awarded Nobel Prize in Physics in 1918 for his work on blackbody radiation.)

Before proceeding further, it would be appropriate to clarify the significance of Planck's postulates with an example. Suppose two litre of milk is to be distributed between two persons. Since milk is an infinitely indivisible entity, you can divide it between two persons in an infinite number of ways. Next you are asked to distribute milk in units of a litre. Now both the persons can receive either 0, 1 or 2 litre meaning thereby that the number of ways reduces to three. The number of ways will be five if the unit (quantum) of distribution is half-a-litre. From this example, you can convince yourself how discretisation introduces a drastic change. Planck achieved similar result in the case of blackbody radiation by introducing the concept of energy quanta in energy exchange.

Planck argued that blackbody radiation chamber be considered to be filled up not only with radiation but also with a perfect gas, whose molecules exchanged energy via resonators of molecular dimensions. (Matter-radiation interaction was necessary to introduce the notion of temperature.) The resonators were assumed to absorb energy from the radiation and transfer the same wholly or partially to gas molecules when they collided with them. This helped to establish thermodynamic equilibrium. (You may think that the

process is somewhat roundabout but this was the only one possible and consistent with accepted ideas at that time.)

Let us now suppose that the total number of Planck resonators is N and their total energy is E . The average energy of Planck resonators is given by

$$\frac{hv}{[\exp(hv/k_B T) - 1]} \text{ rather than } k_B T.$$

Before proceeding further, go through the following example.

EXAMPLE 11.2: MEAN ENERGY

An oscillator vibrates with frequency 1.51×10^{14} Hz at $T = 1800$ K. Compare the values of its average energy by treating it as (a) a classical oscillator and (b) Planck's oscillator. Take $h = 6.62 \times 10^{-34}$ Js $^{-1}$, and $k_B = 1.38 \times 10^{-23}$ JK $^{-1}$.

SOLUTION ■ (a) The average energy of a classical oscillator is given by

$$\begin{aligned} \bar{\varepsilon} &= k_B T = (1.38 \times 10^{-23} \text{ JK}^{-1}) \times (1800 \text{ K}) \\ &= 2.48 \times 10^{-20} \text{ J} \end{aligned}$$

(b) The average energy of Planck's oscillator is given by

$$\bar{\varepsilon} = \frac{hv}{e^{hv/k_B T} - 1} = \frac{k_B T (hv/k_B T)}{e^{hv/k_B T} - 1}$$

$$\begin{aligned} \text{We note that } \frac{hv}{k_B T} &= \frac{(6.62 \times 10^{-34} \text{ Js}) \times (1.51 \times 10^{14} \text{ s}^{-1})}{(1.38 \times 10^{-23} \text{ JK}^{-1}) \times (1800 \text{ K})} \\ &= \frac{9.99 \times 10^{-20} \text{ J}}{2.48 \times 10^{-20} \text{ J}} = 4.03 \end{aligned}$$

$$\text{Hence, } \bar{\varepsilon} = \frac{(2.48 \times 10^{-20} \text{ J}) \times (4.03)}{e^{4.03} - 1} = \frac{9.99 \times 10^{-20} \text{ J}}{53.6} = 1.81 \times 10^{-20} \text{ J}$$

Note that the average energy of Planck's oscillator is less than that of a classical oscillator.

You should now answer an SAQ.

SAQ 1 – Mean energy

Obtain expression for mean energy of a Planck's oscillator in the limit $\nu \rightarrow 0$.

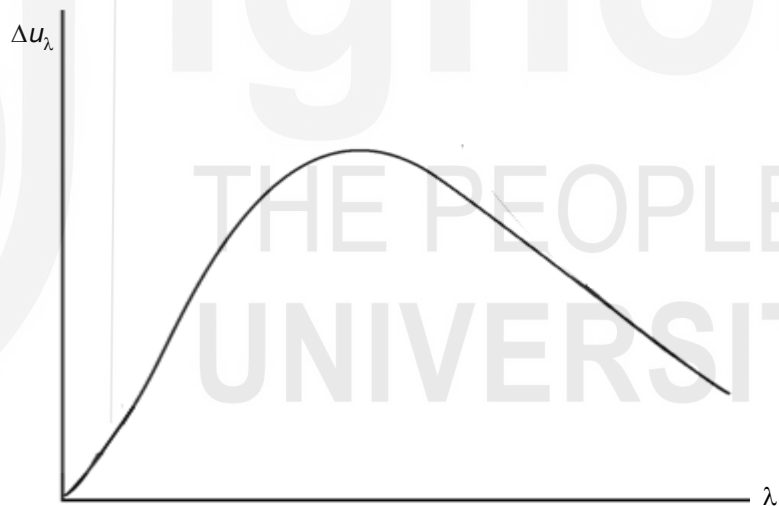
While answering SAQ 1 you have noted that in the limit $\nu \rightarrow 0$, the mean energy of a Planck's oscillator is $k_B T$. The implication of this result is that

when $h\nu$ is small compared to $k_B T$, the discrete nature of energy does not show up.

In terms of wavelength, we can express Planck's formula using the relation $\nu = c/\lambda$ in Eq. (11.5). Note that $|d\nu| = \left| -\frac{c}{\lambda^2} d\lambda \right|$ and we use the fact that $u_\lambda d\lambda$ corresponds to $u_\nu d\nu$. Hence, Planck's law in terms of wavelength can be expressed as

$$\begin{aligned} u_\lambda d\lambda &= \frac{8\pi h}{c^3} \left(\frac{c}{\lambda} \right)^3 \left(\frac{1}{\exp(hc/\lambda k_B T) - 1} \right) \left| -\frac{c}{\lambda^2} d\lambda \right| \\ &= \frac{8\pi hc}{\lambda^5} \left(\frac{1}{\exp(hc/\lambda k_B T) - 1} \right) d\lambda \end{aligned} \quad (11.7)$$

Now refer to Fig. 11.2. It shows a plot of Planck's law based on Eq. (11.7). Since Planck's law explained the observed results of blackbody radiation for all wavelengths available then, the validity of the concept of discreteness of energy was established. In fact, this revolutionary idea, led to the birth of a new branch of physics known as **quantum mechanics**.



11.2: Plot of Planck's law based on Eq. (11.7).

11.5 DEDUCTIONS FROM PLANCK'S LAW

We now show that Planck's law provides us with the most general description of blackbody radiation. That is, you are justified to think that all other laws of blackbody radiation are its special cases. We first show that Rayleigh-Jeans law and Wien's law are its limiting cases in the region of longer and shorter wavelengths, respectively.

11.5.1 Rayleigh-Jeans Law

To begin with, we obtain the expression for Rayleigh-Jeans law. For $\lambda \gg hc/k_B T$, the exponential term in Eq. (11.7) can be approximated as

$$\exp(hc/\lambda k_B T) \approx 1 + \frac{hc}{\lambda k_B T} + \dots$$

$$\text{so that } \exp(hc/\lambda k_B T) - 1 = \frac{hc}{\lambda k_B T}$$

Hence, for $\lambda \gg hc/k_B T$, Eq. (11.7) reduces to

$$u_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \times \left(\frac{\lambda k_B T}{hc} \right) d\lambda = \frac{8\pi k_B T}{\lambda^4} d\lambda \quad (11.8)$$

This is Rayleigh-Jeans law.

11.5.2 Wien's Law

For $\lambda \ll hc/k_B T$, the exponential term in Eq. (11.7) will be significantly greater than unity. Therefore, we can ignore 1 in comparison to the exponential in Eq. (11.7). Then Eq. (11.7) reduces to

$$u_\lambda d\lambda = \left(\frac{8\pi hc}{\lambda^5} \right) \exp(-hc/\lambda k_B T) d\lambda \quad (11.9)$$

This is Wien's law.

11.5.3 Stefan's Law

By integrating Eq. (11.7) for photons of all wavelengths, we obtain the expression for total energy density:

$$u(T) = \int_0^\infty u_\lambda d\lambda = 8\pi hc \int_0^\infty \frac{d\lambda}{\lambda^5 [\exp(hc/\lambda k_B T) - 1]} \quad (11.10)$$

To evaluate this integral, we introduce a change of variable and define

$$x = \frac{hc}{\lambda k_B T} \text{ so that } \lambda = \frac{hc}{x k_B T} \text{ and } d\lambda = -\frac{hc}{x^2 k_B T} dx. \text{ Note that the limits of}$$

integration will change as $-\infty$ to 0. Using these results in Eq. (11.10), we get

$$u(T) = 8\pi hc \int_0^\infty \frac{\left(-\frac{hc}{x^2 k_B T} \right) dx}{\left(\frac{hc}{x k_B T} \right)^5 [\exp(x) - 1]}$$

If we now change the limits of integration as 0 to ∞ , the negative sign will be automatically absorbed. Hence, we can write

$$u(T) = \frac{8\pi k_B^4 T^4}{c^3 h^3} \int_0^\infty \frac{x^3 dx}{\exp(x) - 1}$$

The procedure to solve the integral in this expression is quite involved.

You should just remember that it has the value $\Gamma(4) \zeta(4) = \pi^4 / 15$. (Here $\Gamma(4) = 6$ is gamma function of order 4 and $\zeta(4) = \pi^4 / 90$ is zeta function of order 4.) So, we can write the expression for total energy density at temperature T as

$$u(T) = \frac{8\pi^5 k_B^4}{15h^3 c^3} T^4$$

$$\text{or } u(T) = aT^4 \quad (11.11)$$

$$\text{where } a = \frac{8\pi^5 k_B^4}{15h^3 c^3} = 7.56 \times 10^{-16} \text{ Jm}^{-3} \text{ K}^{-4}.$$

The interior of the Sun can be assumed to consist of photon gas at constant temperature 3×10^6 K. It means that the energy density radiated by the Sun is given by

$$\begin{aligned} u &= (7.56 \times 10^{-16} \text{ Jm}^{-3} \text{ K}^{-4}) \times (3 \times 10^6 \text{ K})^4 \\ &= 6.1 \times 10^{10} \text{ Jm}^{-3} \end{aligned}$$

The volume of the Sun is known to be nearly equal to $1.4 \times 10^{27} \text{ m}^3$. It means that the total energy of photons inside the Sun is

$$E = uV = 8.6 \times 10^{37} \text{ J}$$

If photons are assumed to **effuse** through a small cavity-like opening in the surface of the Sun, the net rate of flow of radiation per unit area of the opening will be given by

$$R = \frac{1}{4} u c = \frac{2\pi^5 k_B^4}{15h^3 c^2} T^4$$

We can rewrite it as

$$R = \sigma T^4 \quad (11.12)$$

$$\text{where } \sigma = \frac{2\pi^5 k_B^4}{15h^3 c^2} = 5.672 \times 10^{-8} \text{ Jm}^{-2} \text{ K}^{-4} \text{ s}^{-1} \text{ is Stefan's constant.}$$

There is another law of radiation: Wien's displacement law:

$\lambda_{\text{max}} T = 2.897 \times 10^{-6} \text{ mK}$. We can use it to calculate the temperature of the surface of celestial bodies.

Though obtaining this expression from Planck's law involves cumbersome mathematics, we have put it as a TQ. You should try to obtain this expression rather than looking at the solution at the first attempt itself.

Let us now summarise what you have learnt in this unit.

11.6 SUMMARY

Concept	Description
Blackbody	<ul style="list-style-type: none"> ■ A blackbody absorbs all radiations incident on it, regardless of their frequency. A small hole in a large enclosure or cavity is a practical approximation to an ideal black body.
Spectroscopic analysis of blackbody radiation	<ul style="list-style-type: none"> ■ Spectroscopic analysis of black body radiation shows that <ul style="list-style-type: none"> • for a given wavelength λ, u_λ increases with temperature; • for each temperature, the spectral energy density versus wavelength curve shows a maximum, which shifts to shorter wavelengths as temperature increases; and • the energy density goes to zero as $\lambda \rightarrow 0$ or as $\lambda \rightarrow \infty$.
Planck's hypothesis	<ul style="list-style-type: none"> ■ According to Planck: <ul style="list-style-type: none"> • The exchange of energy between matter (walls) and radiation (cavity) takes place in bundles of a certain size; and • The quantum of exchange is directly proportional to its frequency. That is, the energy of an oscillator having frequency ν is an integral multiple of $h\nu$, where h is a constant. It is now referred to as Planck's constant and its value is 6.67×10^{-34} Js.
Planck's law	<ul style="list-style-type: none"> ■ According to Planck's law, the energy density of blackbody radiation is given by $u_\nu d\nu = \frac{8\pi\nu^2}{c^3} \left(\frac{h\nu}{\exp(h\nu/k_B T) - 1} \right) d\nu$ <p>In terms of wavelength, we can express it as</p> $u_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \left(\frac{1}{\exp(hc/\lambda k_B T) - 1} \right) d\lambda$
Wien's law	<ul style="list-style-type: none"> ■ For $\lambda \ll hc/k_B T$, Planck's law reduces to Wien's law: $u_\lambda d\lambda = \left(\frac{8\pi hc}{\lambda^5} \right) \exp(-hc/\lambda k_B T) d\lambda$
Rayleigh-Jeans law	<ul style="list-style-type: none"> ■ For $\lambda \gg hc/k_B T$, Planck's law reduces to Rayleigh-Jeans law: $u_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \times \left(\frac{\lambda k_B T}{hc} \right) d\lambda = \frac{8\pi k_B T}{\lambda^4} d\lambda$

Stefan's law

- Stefan's law gives total energy density of all photons in blackbody spectrum. It states that total rate of emission of radiant energy per unit area is related to energy density as fourth power of temperature:

$$E = \sigma T^4$$

where σ is known as Stefan's constant. Its value is $5.672 \times 10^{-8} \text{ Jm}^{-2}\text{K}^{-4}\text{s}^{-1}$.

Stefan-Boltzmann law states that when a blackbody at absolute temperature T is surrounded by another blackbody at absolute temperature T_0 , the amount of net heat lost by the blackbody at higher temperature per unit time can be expressed as

$$E = \sigma(T^4 - T_0^4) .$$

11.7 TERMINAL QUESTIONS

- Calculate the number of modes in a chamber of volume 1m^3 in the frequency range $0.6 \times 10^{14}\text{Hz}$ to $0.61 \times 10^{14}\text{Hz}$.
- Calculate the average energy of a Planck oscillator of frequency $0.6 \times 10^{14}\text{Hz}$ at 2000K . How does it compare with the energy of a classical oscillator?
- Calculate the number of modes of vibration in a 100cm^3 chamber in the wavelength region (a) $500.0\text{nm} - 500.2\text{nm}$ and (b) frequency range $1.5 \times 10^{14}\text{Hz}$ to $1.51 \times 10^{14}\text{Hz}$.
- Calculate the number of photons in 1cm^3 cavity containing black-body radiation at 1000K .
- Using (Eq. 11.7), obtain Wien's displacement law.

11.8 SOLUTIONS AND ANSWERS

Self-Assessment Questions

- In the limit $v \rightarrow 0$, the Planck factor reduces to $k_B T$:

$$\frac{hv}{[\exp(hv/k_B T) - 1]} \rightarrow \frac{hv}{\left(1 - \frac{hv}{k_B T} + \dots - 1\right)} = k_B T .$$

Terminal Questions

- Using Eq. (11.6a), we can write

$$N_\nu d\nu = \frac{8\pi V}{c^3} \nu^2 d\nu$$

$$V = 1\text{m}^3; \nu = 0.6 \times 10^{14}\text{Hz} \quad d\nu = 0.1 \times 10^{14}\text{Hz} \quad c = 3 \times 10^8\text{ms}^{-1}.$$

$$\begin{aligned} N_\nu d\nu &= \frac{8 \times 3.14 \times 1}{(3 \times 10^8)^3} \times (0.6 \times 10^{14})^2 \times (0.1 \times 10^{14}) \\ &= \frac{25.12 \times 0.36 \times 10^{28} \times 0.01 \times 10^{14}}{27 \times 10^{24}} \\ &= \frac{0.090432 \times 10^{42}}{27 \times 10^{24}} \\ &= \frac{90.432 \times 10^{15}}{27} \\ &= 3.35 \times 10^{15} \end{aligned}$$

2. We recall that average energy of photons is

$$\begin{aligned} \bar{\epsilon} &= \frac{h\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} \\ &= \frac{6.6 \times 10^{-34} \times 0.6 \times 10^{14}}{\exp\left(\frac{6.6 \times 10^{-34} \times 0.6 \times 10^{14}}{1.38 \times 10^{-23} \times 2000}\right) - 1} \\ &= \frac{3.96 \times 10^{-20}}{\exp\left(\frac{3.96 \times 10^{-20}}{2.6 \times 10^{-20}}\right) - 1} = \frac{3.96 \times 10^{-20}}{e^{1.523} - 1} \\ \bar{\epsilon} &= \frac{3.96 \times 10^{-20}}{4.59 - 1} = \frac{3.96 \times 10^{-20}}{3.59} \approx 1.10 \times 10^{-20}\text{J} \end{aligned}$$

The energy of a classical oscillator is

$$\begin{aligned} &= k_B T = 1.38 \times 10^{-23} \times 2000 \\ &= 2.76 \times 10^{-20}\text{J} \end{aligned}$$

∴ The energy of a Planck's oscillator is nearly half of classical oscillator.

3. a) The number of modes per unit volume in the wavelength region λ to $\lambda + d\lambda$ is given by

$$N(\lambda) = \frac{8\pi V}{\lambda^4} d\lambda$$

Therefore, the number of modes within wavelength range λ to $\lambda + d\lambda$ in a chamber of volume V is

$$\begin{aligned} N(\lambda) &= \frac{8 \times 3.14 \times (100 \text{ cm}^3)}{(5 \times 10^{-5} \text{ cm})^4} \times (2 \times 10^{-8} \text{ cm}) \\ &= \frac{50.24 \times 10^{-6}}{625 \times 10^{-20}} \\ &= 8.014 \times 10^{12} \end{aligned}$$

- b) The number of modes in the frequency range ν to $\nu + d\nu$ in chamber of volume V is given by

$$N(\nu) = V \frac{8\pi\nu^2}{c^3} d\nu$$

Here $\nu = 1.5 \times 10^{14}$ Hz, $d\nu = 0.01 \times 10^{14}$ Hz, $c = 3 \times 10^{10}$ cm s⁻¹ and $V = 100$ cm³. Hence on substituting the values, we get

$$\begin{aligned} N(\nu) &= \frac{8 \times 3.14 \times (100 \text{ cm}^3) \times (1.5 \times 10^{14} \text{ s}^{-1})^2}{(3 \times 10^{10} \text{ cms}^{-1})^3} \times (0.01 \times 10^{14} \text{ s}^{-1}) \\ &= \frac{56.52 \times 10^{42} \text{ cm}^3 \text{ s}^{-3}}{27 \times 10^{30} \text{ cm}^3 \text{ s}^{-3}} \\ &= 2.09 \times 10^{12} \end{aligned}$$

4. According to Planck, the energy density of the radiation in the frequency range ν and $\nu + d\nu$ is given by

$$u_\nu d\nu = \frac{8\pi h}{c^3} \frac{\nu^3}{\exp(h\nu/k_B T) - 1} d\nu$$

Since $u_\nu d\nu = h\nu dn_\nu$, the number density of photons in the frequency range ν and $\nu + d\nu$ is

$$dn_\nu = \frac{8\pi}{c^3} \frac{\nu^2 d\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}$$

To obtain the expression of the total number density of photons, we integrate this expression to get

$$n = \frac{8\pi}{c^3} \int \frac{\nu^2 d\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} \quad (i)$$

We now put $\frac{h\nu}{k_B T} = x$.

Then Eq. (i) can be rewritten as

$$n = \frac{8\pi}{c^3} \left(\frac{k_B T}{h} \right)^3 \int_0^\infty \frac{x^2 dx}{e^x - 1} = \frac{16\zeta(3)\pi(k_B T)^3}{c^3 h^3}$$

The Riemann Zeta function $\zeta(3) = 1.202$.

On substituting the given values

$c = 3 \times 10^8 \text{ ms}^{-1}$, $h = 6.6 \times 10^{-34} \text{ Js}$, $k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$ and $T = 1000 \text{ K}$, we get

$$n = \frac{16 \times 1.202 \times \pi (1.38 \times 10^{-23})^3 (10^3)^3}{(3 \times 10^8)^3 (6.6 \times 10^{-34})^3} = 2.0456 \times 10^{16} \text{ m}^{-3}$$

5. The wavelength at which maximum occurs can be obtained from Eq. (11.7) using the condition

$$\left[\frac{\partial u_\lambda}{\partial \lambda} \right]_{\lambda=\lambda_{\max}} = 0$$

This leads to

$$\begin{aligned} \frac{\partial u_\lambda}{\partial \lambda} &= 8\pi hc \frac{\partial}{\partial \lambda} \left[\frac{\lambda^{-5}}{\exp(hc/\lambda k_B T) - 1} \right] \\ &= 8\pi hc \left[\frac{-5\lambda^{-6}(\exp(hc/\lambda k_B T) - 1) - \lambda^{-5} \left(-\frac{hc}{\lambda^2 k_B T} \exp(hc/\lambda k_B T) \right)}{(\exp(hc/\lambda k_B T) - 1)^2} \right] \end{aligned}$$

$$= \frac{8\pi hc}{\lambda^5} \frac{1}{(\exp(hc/\lambda k_B T) - 1)} \left[-\frac{5}{\lambda} + \frac{hc}{\lambda^2 k_B T} \frac{\exp(hc/\lambda k_B T)}{(\exp(hc/\lambda k_B T) - 1)} \right]$$

$$= u_\lambda \left[-\frac{5}{\lambda} + \frac{hc}{\lambda^2 k_B T} \frac{\exp(hc/\lambda k_B T)}{(\exp(hc/\lambda k_B T) - 1)} \right]$$

Suppose the value of u_λ is maximum for $\lambda = \lambda_{\max}$.

Therefore, we equate the right-hand side of the above expression equal to zero and put $\lambda = \lambda_{\max}$. This gives

$$\left[-\frac{5}{\lambda_{\max}} + \frac{hc}{\lambda_{\max}^2 k_B T} \frac{\exp(hc/\lambda_{\max} k_B T)}{(\exp(hc/\lambda_{\max} k_B T) - 1)} \right] = 0$$

$$\text{or } \frac{hc}{\lambda_{\max} k_B T} \frac{\exp(hc/\lambda_{\max} k_B T)}{[\exp(hc/\lambda_{\max} k_B T) - 1]} = 5 \quad (\text{i})$$

We now introduce a new variable by defining $x = hc/\lambda_{\max} k_B T$. Then we can rewrite Eq. (i) in an elegant form:

$$x \frac{\exp(x)}{\exp(x) - 1} = 5$$

$$\text{or } x = 5(1 - e^{-x}) \quad (\text{ii})$$

This is a transcendental equation and can be solved either graphically or numerically. The exact value of x is 4.965.

Hence, we can write

$$x = \frac{hc}{\lambda_{\max} k_B T} = 4.965$$

$$\text{or } \lambda_{\max} T = b = \frac{hc}{k_B \times 4.965} \quad (\text{iii})$$

This is *Wien's displacement law*. On substituting for h, c and k_B , we get

$$\lambda_{\max} T = 2.897 \times 10^{-6} \text{ mK}$$

APPENDIX 11A: NUMBER OF ALLOWED MODES OF STANDING WAVES IN AN ENCLOSURE

Rayleigh considered blackbody radiation in an enclosure, a hollow cubical box of side L , say, to consist of a number of electromagnetic waves which travelled in all possible directions. As a result, these made multiple reflections at the walls of the enclosure. Their subsequent superposition led to formation of standing waves and the walls of the enclosure acted as nodes.

The standing waves in such a system are described by the wave equation

$$\nabla^2 \psi(x, y, z, t) = \frac{1}{v} \frac{\partial^2 \psi(x, y, z, t)}{\partial t^2} \quad (11A.1)$$

where v is velocity of the standing waves.

Since the walls of the enclosure act as nodal points, we can say that the amplitude ψ of the waves will be zero at $x, y, z = 0$ and $x, y, z = L$. Then we take the solution of Eq. (11A.1) to be of the form

$$\psi(x, y, z, t) = C \exp(-i\omega t) \sin\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi y}{L}\right) \sin\left(\frac{\ell\pi z}{L}\right) \quad (11A.2)$$

where (m, n, ℓ) are integers and ω is the angular frequency of the wave. Note that each combination of (m, n, ℓ) defines a mode of oscillation of the waves in the enclosure.

On combining Eqs. (11A.1) and (11A.2) and simplifying the resultant expression, we get

$$\frac{\pi^2}{L^2} (m^2 + n^2 + \ell^2) = \frac{\omega^2}{v^2}$$

$$\text{or } m^2 + n^2 + \ell^2 = \frac{\omega^2}{\pi^2} \cdot \frac{L^2}{v^2} = \left(\frac{2vL}{v}\right)^2 = \left(\frac{2L}{\lambda}\right)^2 \quad (11A.3)$$

where $\lambda = v/\nu$ defines the wavelength of the standing waves of frequency ν .

It may be remarked here that Eq. (11A.3) gives the number of allowed modes of vibration inside the enclosure for different, positive and integral values of m, n and ℓ . The total number of modes of vibration will be specified by the total number of possible sets (m, n, ℓ) .

If we now put $\frac{2L}{\lambda} = p$, Eq. (11A.3) can be rewritten as

$$m^2 + n^2 + \ell^2 = p^2 \quad (11A.4)$$

Geometrically, this result suggests that p is the radius of a sphere in (m, n, ℓ) space and the number of allowed modes can be obtained by plotting m, n, ℓ and counting the number of points corresponding to positive integral values. These will lie in the positive octant of a sphere of radius p , as shown in Fig. 11A.1. (In other octants, at least one value, either m, n or ℓ will be

negative.) Note that in Fig. 11A.1, the allowed set of values of m, n and l form a mesh of small cubes.

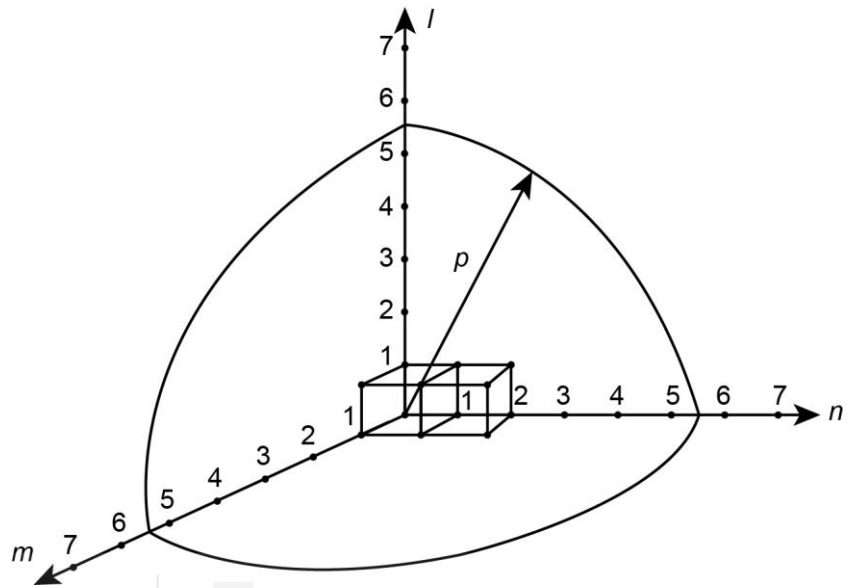


Fig. 11A.1: Calculation of the number of allowed modes of standing waves in an enclosure filled with blackbody radiation.

For sufficiently large values of ρ , each point will correspond in one unit cube in this octant. Therefore, the total number of allowed modes of vibration will be equal to the volume of the octant and we can write

$$N = \frac{1}{8} \left(\frac{4\pi}{3} \rho^3 \right) = \frac{1 \times 4}{8 \times 3} \pi \left(\frac{2L}{\lambda} \right)^3 = \frac{4\pi L^3}{3\lambda^3}$$

Hence, the number of modes of wavelengths between λ and $\lambda + d\lambda$ is obtained by differentiating this expression for total number of modes. Thus,

$$|N_\lambda d\lambda| = \left| \frac{4\pi V}{3} (-3\lambda^{-4}) d\lambda \right| = \frac{4\pi V}{\lambda^4} d\lambda \tag{11A.5}$$

Here $V = L^3$ is volume of the enclosure.

You may recall that we are dealing with electromagnetic waves, which are transverse in nature and for a given value of wave vector, there will be two independent polarisation states. We, therefore, have to multiply Eq. (11A.5) by two. That is, the correct number of allowed modes will be twice as many:

$$N_\lambda d\lambda = \frac{8\pi V}{\lambda^4} d\lambda \tag{11A.6}$$

You can easily convince yourself that for blackbody radiation, the number of modes in the frequency range ν and $\nu + d\nu$ can be expressed as

$$N_\nu d\nu = \frac{8\pi V}{c^3} \nu^2 d\nu \tag{11A.7}$$

The fact that the number of allowed modes was to be multiplied by two was pointed out by Jeans.