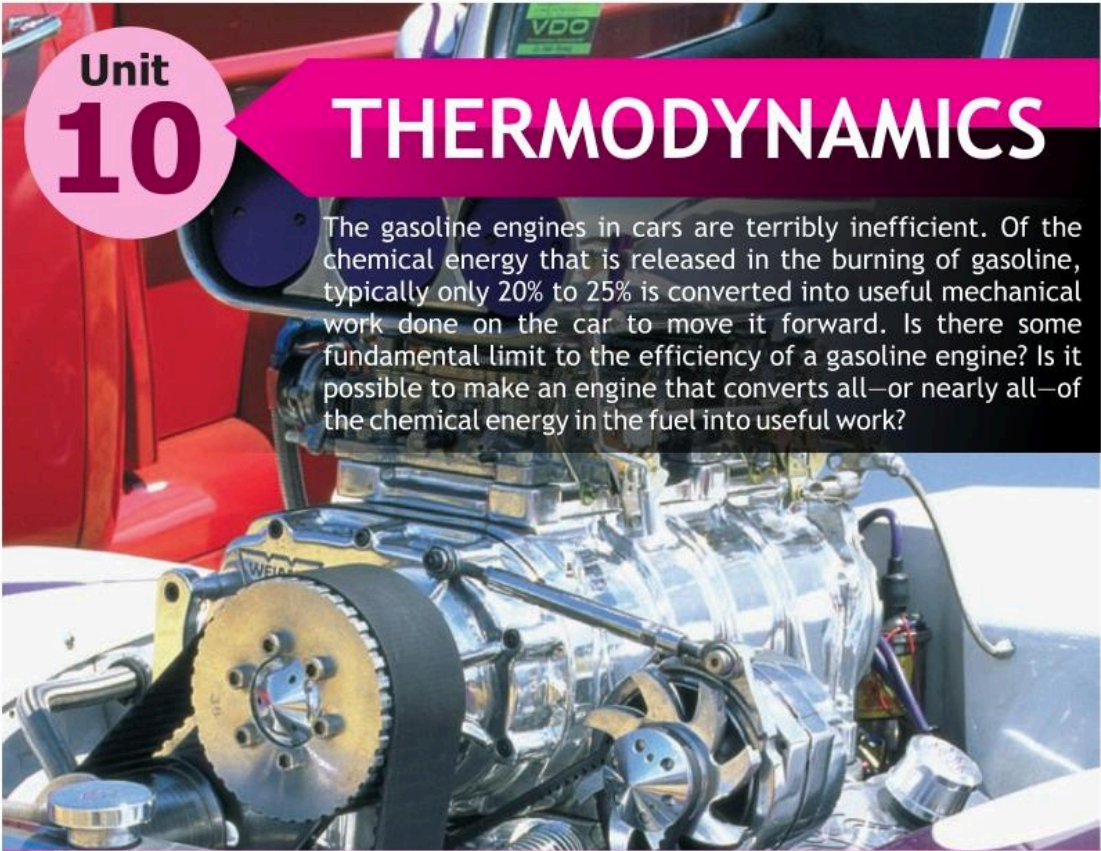




Unit 10

THERMODYNAMICS

The gasoline engines in cars are terribly inefficient. Of the chemical energy that is released in the burning of gasoline, typically only 20% to 25% is converted into useful mechanical work done on the car to move it forward. Is there some fundamental limit to the efficiency of a gasoline engine? Is it possible to make an engine that converts all—or nearly all—of the chemical energy in the fuel into useful work?

LEARNING OUTCOMES

After studying this unit the students will be able to

- ⦿ Describe that thermal energy is transferred from a region of higher temperature to a region of lower temperature.
- ⦿ Describe that regions of equal temperatures are in thermal equilibrium.
- ⦿ Describe that heat flow and work are two forms of energy transfer between systems and calculate heat being transferred.
- ⦿ Define thermodynamics and various terms associated with it.
- ⦿ Relate a rise in temperature of a body to an increase in its internal energy.
- ⦿ Describe the mechanical equivalent of heat concept, as it was historically developed, and solve problems involving work being done and temperature change.

- ⊙ Explain that internal energy is determined by the state of the system and that it can be expressed as the sum of the random distribution of kinetic and potential energies associated with the molecules of the system.
- ⊙ Calculate work done by a thermodynamic system during a volume change.
- ⊙ Describe the first law of thermodynamics expressed in terms of the change in internal energy, the heating of the system and work done on the system.
- ⊙ Explain that first law of thermodynamics expresses the conservation of energy.
- ⊙ Define the terms, specific heat and molar specific heats of a gas.
- ⊙ Apply first law of thermodynamics to derive $C_p - C_v = R$.
- ⊙ State the working principle of heat engine.
- ⊙ Describe the concept of reversible and irreversible processes.
- ⊙ State and explain second law of thermodynamics.
- ⊙ Explain the working principle of Carnot's engine.
- ⊙ Explain that the efficiency of a Carnot engine is independent of the nature of the working substance and depends on the temperatures of hot and cold reservoirs.
- ⊙ Describe that refrigerator is a heat engine operating in reverse as that of an ideal heat engine.
- ⊙ Derive an expression for the coefficient of performance of a refrigerator.
- ⊙ Describe that change in entropy is positive when heat is added and negative when heat is removed from the system.
- ⊙ Explain that increase in temperature increases the disorder of the system.
- ⊙ Explain that increase in entropy means degradation of energy.
- ⊙ Explain that energy is degraded during all natural processes.
- ⊙ Identify that systems tend to become less orderly over time.

Thermodynamics is a combination of two words, “thermo” and “dynamics”. The word thermo is related to heat while dynamics is related to the motion of particles. Therefore, we define thermodynamics as the branch of heat that deals with the laws of transformation of heat into other forms of energy such as mechanical, chemical and electrical energy and vice versa. Principally it is based on two laws of thermodynamics i.e. the first and second laws of thermodynamics. It is a practical subject that explains the working of heat engines, refrigerators and heat pumps etc.

The terms System, Surroundings, Boundary and State Variables are used in thermodynamics with specific meanings.

For Your Information

The first thermodynamic textbook was written in 1859 by William Ranking, originally trained as a physicist and a civil and mechanical engineering professor at the University of Glasgow.

10.1 THERMAL EQUILIBRIUM

When two objects at different temperatures are brought into contact with each other, energy is transferred from the hotter to the colder object until the bodies reach thermal equilibrium (that is, they are at the same temperature). These observations reveal that heat is energy transferred spontaneously due to a temperature difference. Figure 10.1 shows an example of heat transfer.

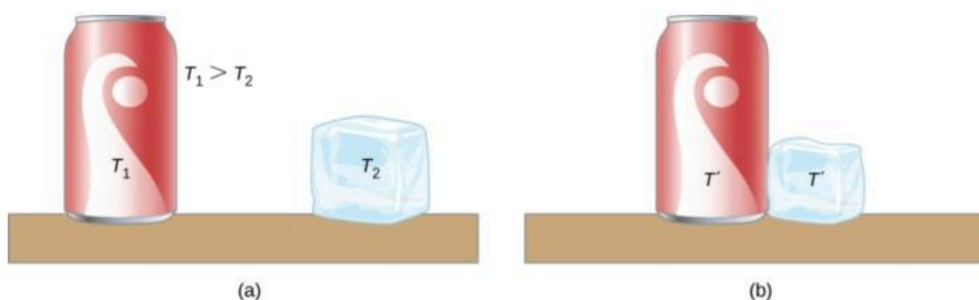


Figure 10.1 (a) Here, the soft drink has a higher temperature than the ice, so they are not in thermal equilibrium. (b) When the soft drink and ice are allowed to interact, heat is transferred from the drink to the ice due to the difference in temperatures until they reach the same temperature, T , achieving equilibrium.

In fact, since the soft drink and ice are both in contact with the surrounding air

and the bench, the ultimate equilibrium temperature will be the same as that of the surroundings.

In other words, *if two objects are in thermal equilibrium, they have the same temperature.*

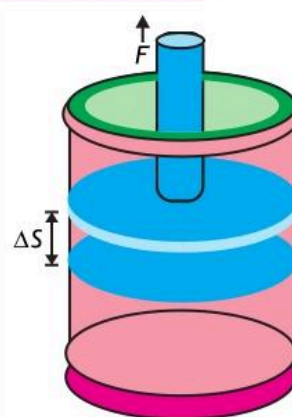
Point to Ponder

Two bodies, one hot and the other cold, are kept in vacuum. What will happen to the temperature of the hot body after sometime.

10.2 Work

Work W is defined as $\vec{F} \cdot \Delta \vec{S}$. In thermodynamics, work is said to be done by a system when the system as a whole expands. By means of the boundary, the system exerts a force on the surroundings and thereby displaces the surroundings, Figure. (10.4). The sum of all $\vec{F} \cdot \Delta \vec{S}$ over the entire boundary of the system is the work done by a system on its surroundings. Similarly, in the process of contraction of a system, work is done on the system by its surroundings. By convention the work done by a system is considered positive and the work done on the system is taken negative.

FIGURE 10.1



Work done by a system

Quiz?

The temperature of a normal healthy person is 37°C . What will be the temperature of a dead person?

10.3 INTERNAL ENERGY

The atoms or molecules of all kinds of matter are in constant motion. Atoms in solids vibrate back and forth in complex motions about their equilibrium positions. Molecules in a liquid wander around among the other molecules, having frequent collisions with them and thus exchanging energy. In gases the molecules travel about at high speeds and have frequent elastic collisions with their neighbors.

The sum of the kinetic and potential energies associated with the random motion of the atoms of the substance is the internal energy of the substance.

The kinetic energy may be in the form of translational, rotational or vibrational kinetic energy. When we heat a substance, the random motion and the energy associated with it are increased: heat energy is converted into the internal energy of the substance. Similarly, work can be performed on a substance in such a way as to increase the random motion of the atoms. Work energy is converted into the internal energy of the substance. Once heat, work or both are transferred to a substance, they are no longer distinguishable as heat energy and work energy in the substance.

Quiz?

Is the temperature of a normal healthy old man is less than that of a normal healthy young man?

A glass full of water contains ice cubes floating in it. What will happen to the water level when ice melts?

10.4 HEAT, WORK AND INTERNAL ENERGY

Heat, work and internal energy are three mutually distinct concepts. Each one of them is fundamentally related to the temperature of a body and therefore they are closely related to one another.

To raise the temperature of some water we "heat" the water by placing the water pot on a flame. Similarly, any object can be raised in temperature (heated) by placing it in thermal contact with another hotter object.

The earth is heated by the hot sun without a direct thermal contact. It is evident from the above examples that in the process of raising the temperature (heating) of a body something must have flown from the hotter body to the colder body.

This something which flows from the hotter body to the colder body till the temperatures of the two bodies become equal is called heat.

Thus heat is energy which is transferred between a substance and its surroundings or between one part of a substance to another as a result of temperature difference only.

Heat is energy in transit. It flows till the temperatures of the bodies in thermal contact are equal. Since heat is a form of energy, its SI unit is the joule J. Another common unit of energy often used for heat is the **calorie (cal)**, defined as the energy needed to change the temperature of 1.00 g of water by 1.00°C specifically, between 14.5 °C and 15.5 °C, since there is a slight temperature difference.

Kilocalorie (kcal) is the energy, needed to change the temperature of 1.00 kg of water by 1.00 °C. Since mass is most often specified in kilograms, the kilocalorie is convenient.

Besides supplying heat to a body there is another very general method of raising the temperature (heating) of a body. The method is to perform work on the body. A few examples are as follows:

- It is possible to warm up your hands by rubbing them together ;
- When we hit a nail with a hammer into wood, the nail gets hot.
- Similarly when we churn curd in a vessel, the contents are heated.
- Pumping up a tire with a hand pump heats up the pump.

In all these examples work is done on a body which warms up without heat supply. The conclusion is that heat and work both can increase the temperature of a body but they are mutually distinct forms of energy.

The difference between heat and work is that work can be exchanged between an object and its surroundings by the over all displacement of the object without requiring the difference of temperature whereas transfer of heat energy can be brought about by a temperature difference between two bodies.

Quiz?

Bore with a small drill into a hard board. The drill becomes hot to touch. Why? What happens if hard board is replaced by a soft board? Why a spark is produced when two stones collide against each other?

10.4.1 Equivalence of Heat and Work

The equivalence between heat and work was established by Count Rumford, James Joule and others. In 1798, Count Rumford, an artillery engineer observed that a great deal of heat was given off in the process of boring a gun metal. He observed that heat could be produced exhaustively by friction, i.e. by mechanical work. He showed that the heat liberated was not related with the mass of the metal bored away; but it depends on the work done against friction. This led Rumford to convince that heat is a form of energy.

In 1845, Joule carried out experiments to measure very precisely the quantity of heat produced by a certain amount of work (mechanical energy) and observed that there is a definite relationship between the mechanical work done and the

heat generated. He showed that when a given amount of work is done, the same amount of heat is always produced, no matter what may be the process of transformation.

He showed that work W done, is proportional to the quantity of heat Q

$$W \propto Q$$

$$W = J Q$$

Where J is called "Mechanical Equivalent of heat" (Joule's constant) and it is defined as:

The ratio of the work done in joules to the heat produced in calories (old unit of heat) is called the mechanical equivalent of heat J .

The mechanical equivalent of heat may also be defined as the amount of mechanical energy or work required to produce a unit quantity of heat.

The currently accepted value of mechanical equivalent of heat is

$$J = 4.18 \text{ joule per calorie.}$$

Now if we use the SI units of work and energy, then both, work W and heat Q , are measured in joules then the value of mechanical equivalent of heat is one.

Example 10.1**HEAT ENGINE WORK**

A heat engine operates with 65.0 kcal of heat supplied and exhausts 40.0 kcal of heat. How much work did the engine do?

GIVEN

Heat input $Q_H = 65.0 \text{ kcal}$

Heat rejected $Q_L = 40.0 \text{ kcal}$

Mechanical equivalent of heat $1 \text{ kcal} = 4,184 \text{ J}$

REQUIRED

Work done = $W = ?$

SOLUTION

The relationship between these quantities is found in equation,

$$W = J(Q_H - Q_L).$$

Putting values

$$= 4,184 \text{ (J/kcal)}(65.0 \text{ kcal} - 40.0 \text{ kcal})$$

$$= 4,184 \text{ (J/ kcal)} (25.0 \text{ kcal})$$

$$= 4,184 \times 25.0 \text{ (J. kcal/kcal)}$$

$$= 104,600 \text{ J} = 105 \text{ kJ}$$

105 kJ

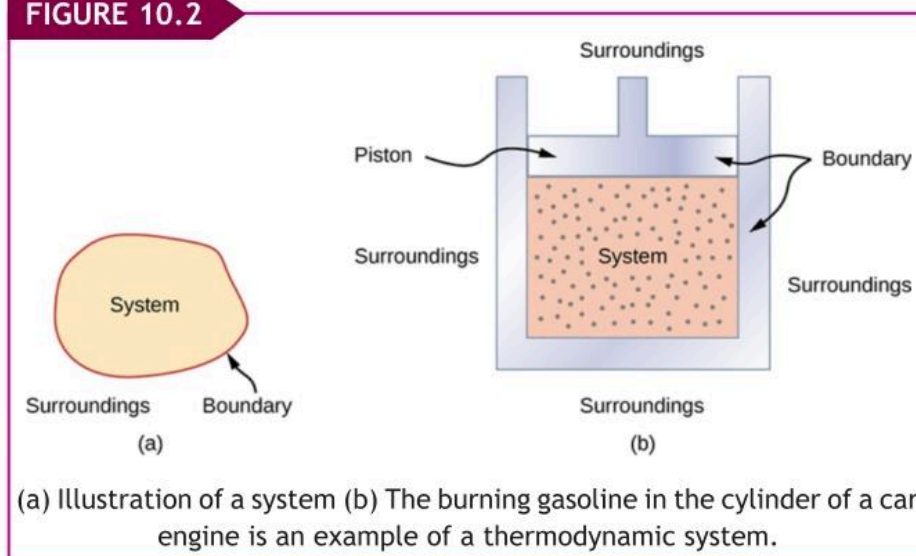
Answer

Quiz?

What is the significance of Joule's experiment for determining the value of J .

10.5 THERMODYNAMIC SYSTEM

A thermodynamic system includes anything whose thermodynamic properties are of interest. It is enclosed in its surroundings or environment; it can exchange heat with, and do work on, its environment through a **boundary**, which is the imagined wall that separates the system and the environment (Figure 10.2). In reality, the immediate surroundings of the system are interacting with it directly and therefore have a much stronger influence on its behavior and properties. For example, if we are studying a car engine, the burning gasoline inside the cylinder of the engine is the thermodynamic system; the piston, exhaust system, radiator, and air outside form the surroundings of the system. The boundary then consists of the inner surfaces of the cylinder and piston.

FIGURE 10.2

Any change or a series of changes in a thermodynamic system is called **thermodynamic process**. We need to define the following technical terms which are essential for the study of thermodynamics.

System: The quantity of matter or region of space whose behavior is being studied is called system. For example a gas enclosed in a cylinder etc.

Surroundings of the system: Everything other than the system in the universe is called the surroundings of the system Figure 10.2.

For your Information

An empty polythene bag burns or melts on a flame of a stove. However we can make a few cups of tea by placing water filled polythene bag on a flame of a stove.

Boundary of the system

The system is separated from the surroundings by its boundary. In thermodynamics, the exchange of energy between the system and the surroundings can take place through the boundary by the performance of work or the flow of heat. Figure 10.2. There are several kinds of system.

Closed system: *The system in which there is no transfer of mass across its boundary is called closed system.*

In closed system the transfer of heat energy can take place from the system to the surrounding or vice versa. For example hot food in a pressure cooker (Figure 10.3 b).

Point To Ponder

An ink dot on a white porcelain dish appears dark. When the dish is raised to a very large temperature the dot appears brighter than the surroundings. Why?

Normally, a system must have some interactions with its surroundings.

FIGURE 10.3

(a)



(b)

(a) This boiling tea kettle is an open thermodynamic system. It transfers heat and matter (steam) to its surroundings. (b) A pressure cooker is a good approximation to a closed system. A little steam escapes through the top valve to prevent explosion.

Open system: *The system in which there is a transfer of mass across its boundary is called an open system.*

In an open system the transfer of heat energy can take place from the system to the surrounding or vice versa for example boiling tea kettle (Figure 10.3 a).

Isolated system: *The system in which there is no transfer of mass and heat energy across its boundary is called an isolated system.*

In an isolated system both mass and energy cannot enter or leave the system across its boundary. Tea contained in a well insulating thermo flask is an example of an isolated system.

Thermodynamic state and thermodynamic state variables

The particular condition when a system has specified values of pressure P , volume V and temperature T etc, is called the state of the system. The variables or functions which determine the physical state of the system are called state variables and state functions of the system.

If the system is homogeneous (i.e. it has the same composition every where), then it is usually enough to specify only three parameters, namely, volume, pressure and temperature. The mathematical relationship between these parameters is known as the equation of state of the system. The exact relationship between these parameters is not known for solids, liquids and non-homogeneous substances. In the case of ideal gas, the equation of state is

$$PV = nRT$$

where n is number of moles. P, V and T are respectively the pressure, volume and temperature of the gas and R is the universal gas constant. P, V, T , are state variables. Other examples of the state variables are internal energy U and entropy S .

Point to Ponder

Why do heels crack in winter? What effect does the application of lubricants have on the heels?

10.6 REVERSIBLE AND IRREVERSIBLE PROCESSES

In thermodynamics, a process means a change in the state of a system brought about by a change in the state variables. A process occurs when a system interacts and exchanges energy with its surroundings.

Reversible Process

A process is said to be reversible if it can be retraced exactly in reverse order without producing any change in the surroundings.

In the reverse process, the system passes through the same changes as in the direct process through the same states as in the direct process, but the thermal and mechanical effects at each stage are exactly reversed. If heat is absorbed in the direct process, it will be given out in the reverse process. Similarly, if work is done by the system in the direct process, work will be done on the system in the reverse process.

In practice, no actual change is exactly reversible. However, very slowly occurring processes can be considered reversible. For example, liquification and evaporation of a substance, performed slowly, are practically reversible. Slow compression of a gas in a cylinder is a reversible process as the compression can be changed into expansion by slowly decreasing the pressure on the piston to reverse the operation.

Irreversible Process

A process which cannot be retraced in the backward direction by reversing the controlling factors is said to be irreversible.

All changes which occur suddenly or which involve friction or dissipation of energy through conduction, convection and radiation are irreversible. An example of highly irreversible process is an explosion.

Cyclic Process

A series of processes which bring the system back to the initial state is called a cycle and the process is called a cyclic process.

The system which goes through a succession of cyclic process is often called, heat engines.

10.7 FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is based on the idea that energy can neither be created nor destroyed in any thermodynamics system. So it is a particular form of the law of conservation of energy, which deals only with the heat energy.

This law states that every thermodynamic system possesses a state variable (U) called the internal energy.

In any thermodynamic process, when heat energy (ΔQ) is added to a system, this energy appears as an increase in the internal energy (ΔU) stored in the system plus the work done (ΔW) by the system on its surroundings.

$$\Delta Q = \Delta U + \Delta W \quad (10.1)$$

ΔQ is taken positive when heat enters the system and negative when it leaves the system. ΔU is taken positive when temperature of the system rises while it is negative when temperature of the system decreases.

It is emphasized that the first law expresses three related ideas in a single mathematical formulation:

- (1) The existence of an internal energy U as a state variable.
- (2). The principle of conservation of energy.
- (3). The definition of heat as energy in transit.

The sum of all the kinetic (translational, rotational and vibrational) and potential energies associated with the random motion of the atoms of a substance or system is the internal energy (U) of the substance.

Point to Ponder

The earth is receiving heat from the sun continuously. In this case, the earth will be as hot as a furnace in no time. As such thing does not happen, what compensatory measures does earth have to maintain the temperature?

According to the first law of thermodynamics (Eq: 10.1)

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

It means that the change in the internal energy of a system is equal to the energy flowing in as heat minus the energy flowing out as work. In other words the change in the internal energy of the system is measured by the energy retained by the system. This energy absorbed by the system changes the translational, vibrational and rotational kinetic energy of the molecules. It also changes the potential energy of the molecules due to intermolecular forces.

The change in the internal energy of a system depends only upon the initial and final states of the system and not on the path taken between these two states. If the state of a thermodynamics system is changed from state (A) to state (B) then the change in internal energy of the system is

$$\Delta U = U_B - U_A$$

Putting this value in equation (10.1) we have

$$U_B - U_A = \Delta Q - \Delta W$$

Where (U_A) and (U_B) are the initial and final internal energies of the system.
 If a system under goes a cyclic process i.e. it attains its initial state after undergoing a certain process then $U_B = U_A$
 Put this in above equation we get $U_A - U_A = \Delta Q - \Delta W$

$$\begin{aligned} 0 &= \Delta Q - \Delta W \\ \Delta Q &= \Delta W \end{aligned} \quad (10.2)$$

Thus in cyclic process all the heat energy absorbed by the system is used in doing some useful work by the system.

Quiz?

Two blocks of ice when pressed together, combine to form a single piece. Explain how this happen?

10.7.1 Applications of the first law thermodynamics

First law of thermodynamics finds many practical applications. They are all based on the principle that using the system the three forms of energy: internal energy ; heat ; and work can be inter-converted.

The system is then often called the working substance. The mathematical formulation of the law $\Delta Q = \Delta U + \Delta W$ suggests the followings processes that can be used for practical applications :

- The processes in which any one of the three terms of the equation is zero.
- The processes in which any one of the state variables P , V , T , of the system are held constant.

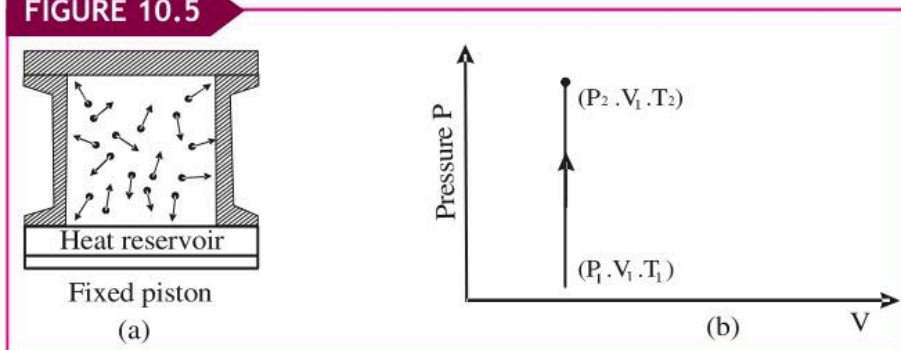
(a) **Isochoric Process:** *The thermodynamics process during which the volume of the system remains constant is called isochoric process.*

We consider the gas contained in a cylinder having a conducting base and non- conducting walls and with a fixed piston at the end as shown in the Figure (10.5.a). Let heat ΔQ be imparted to the gas. The gas is then heated at constant volume. The pressure of the gas increases from P_1 to P_2 while its temperature increases from T_1 to T_2 . Since the system neither expands nor contracts, work is neither done by the system nor on the system i.e $\Delta W = 0$
 Using the first law of thermodynamics equation (10.1) we have

$$\begin{aligned} \Delta Q &= \Delta U + \Delta W \\ \Delta Q &= \Delta U \end{aligned} \quad (10.3)$$

This means that in an isochoric process the entire amount of heat supplied to the gas is converted to the internal energy of the gas. The pressure and temperature of the gas will increase. On the contrary, removal of heat from a system under isochoric condition will cause an equivalent decrease in the internal energy. The system will cool down and the pressure will fall.

FIGURE 10.5



The graph of isochoric process is called an “isochor”, which is a straight line, parallel to the pressure axis as shown in the Figure (10.5 b).

(b) Isobaric Process: *The thermodynamics process during which the pressure is kept constant is called an isobaric process.*

Isobaric expansion of a system is often used to convert heat into work. Practically all heat engines depend on the transformation of heat into work. We consider the gas contained in a cylinder having a conducting base and non-conducting walls and frictionless piston of cross-sectional area (A) as shown in the Figure (10.6a).

Let V_1 , T_1 and P be the volume, temperature and pressure of the gas. When the gas is heated, a certain amount of heat energy ΔQ is transferred into the system. The gas expands and moves the piston outward. If the displacement of the piston is kept very small, the pressure of the gas will not change much and can be considered constant. After expansion the values of temperature and volume of the gas become T_2 and V_2 . If the piston moves through a small displacement ΔY in the upward direction, the work done by the gas against the environment is

$$\begin{aligned}\Delta W &= (\text{Force}) (\text{distance}) \\ \Delta W &= F \cdot \Delta Y\end{aligned}\quad (i)$$

Where F is the force exerted on the piston during expansion: $F = P A$

Thus equation (i) becomes

$$\begin{aligned}\Delta W &= P A \Delta Y \\ \Delta W &= P (V_2 - V_1) = P \Delta V\end{aligned}$$

Where V_1 is the initial volume, V_2 is the final volume and ΔV is the increase in volume of the gas. Hence, the work done by the gas which expands at constant pressure is

$$\Delta W = P\Delta V \quad (10.4)$$

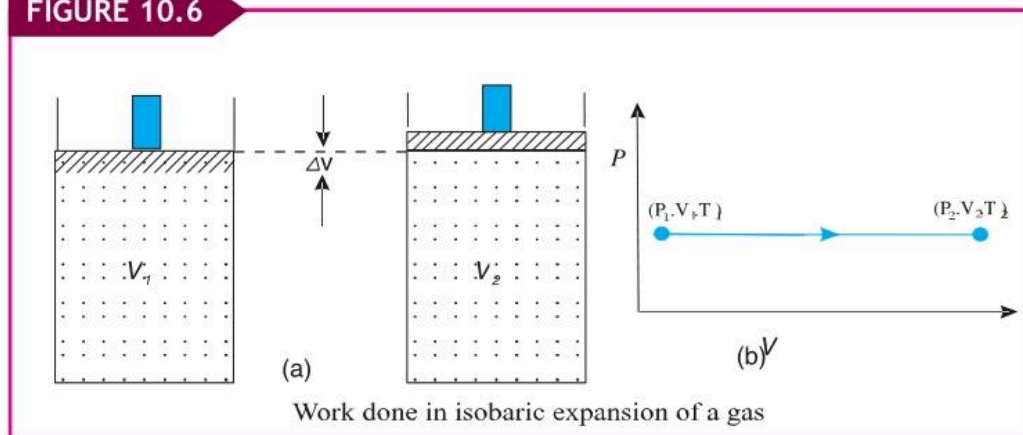
Using the first law of thermodynamics equation (10.1) we have

$$\begin{aligned} \Delta Q &= \Delta U + \Delta W \\ \Delta Q &= \Delta U + P\Delta V \end{aligned} \quad (10.5)$$

The work performed by the expanding or contracting gas comes from one or both sources: heat supplied to the gas and the internal energy of the gas.

The graph of isobaric process is called an “isobar”, which is a straight line, parallel to the volume axis as shown in the Figure (10.6b).

FIGURE 10.6



(c) Isothermal Process

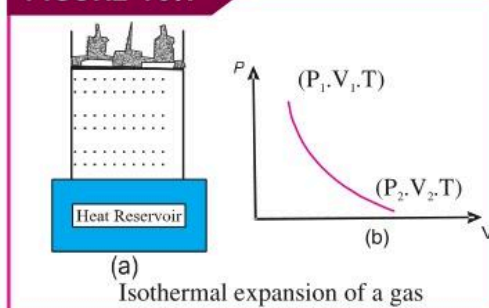
The thermodynamics process which is carried out in such a way that a system undergoes changes but its temperature remains constant is called an isothermal process.

For sake of simplicity, we shall assume the system contain an ideal gas.

The internal energy of an ideal gas does not depend on the volume but depends only on the temperature of the gas. To perform an isothermal process on a gas, we consider the gas to be contained in a cylinder having a conducting base and non-conducting walls and with a movable piston at the end as shown in the Figure. (10.7a). The base of the cylinder is placed on a heat reservoir at temperature T_1 . A reservoir is a body of large heat capacity that maintains the temperature of the gas at T_1 .

Let the gas be then allowed to expand slowly by decreasing the pressure on the piston. Due to this expansion, the gas tends to cool down. But heat is conducted from the heat reservoir to the gas so that the temperature of the system remains constant and is equal to the temperature of the reservoir. The whole process from an initial state P_1, V_1, T , to a final state P_2, V_2, T , is represented by a continuous curve which is called an “isotherm” as shown in the Figure (10.7.b).

FIGURE 10.7



During isothermal expansion some work ΔW is done by the gas in pushing up the piston in the cylinder. Since the temperature remains constant, there is no change in the internal energy of the gas, that is, $\Delta U = 0$

According to the first law of thermodynamics, $\Delta Q = \Delta U + \Delta W$

$$\Delta Q = 0 + \Delta W$$

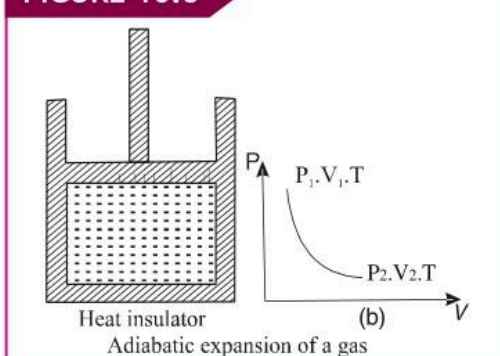
$$\Delta Q = \Delta W$$

This shows that if the gas expands and does external work, an equal amount of heat has to be supplied in order to maintain its temperature constant. Conversely, if the gas contracts, work is being done on it and equal amount of heat has to be allowed to leave the gas.

(d) Adiabatic Process: *The thermodynamics process during which no heat enters or leaves a system is called an adiabatic process.*

For every adiabatic process $\Delta Q = 0$. A truly adiabatic process is an ideal one which cannot be realized. However, the flow of heat may be prevented either by surrounding the system with a thick layer of heating insulating material such as cork, asbestos, or by performing the process very quickly. The flow of heat requires finite time, so any process performed quickly enough will

FIGURE 10.8



be practically adiabatic. Figure 10.8

To perform an adiabatic process on a gas, we consider the gas to be contained in a completely insulated cylinder with a movable piston at the end as shown in the Figure.(10.8.a). Since no heat energy can enter or leave the system during an expansion or compression therefore $\Delta Q = 0$.

If the gas is allowed to expand suddenly decreasing the pressure on the piston, the gas will be cooled, so that its temperature will decrease. Therefore the internal energy of the gas will decrease. Similarly if the gas is compressed by suddenly increasing the pressure on the piston, the gas will be heated, so that temperature will increase. Therefore the internal energy of the gas will increase. According to the first law of thermodynamics

$$\begin{aligned}\Delta Q &= \Delta U + \Delta W \\ 0 &= \Delta U + \Delta W \\ \text{or} \quad \Delta U &= - \Delta W\end{aligned}$$

Thus an increase in the internal energy of the system in an adiabatic process is equal to the work done on the system. We can write the above equation as

$$\Delta W = - \Delta U \quad (10.6)$$

This means that if the system does the work, then in adiabatic process, the work is done at the cost of internal energy.

The curve shown in Figure.(10.8b) is the graphic representation of an adiabatic expansion of an ideal gas. Such a curve is known as “adiabat”.

Quiz?

The rate of formation of ice on ponds decreases gradually as more and more ice is formed. Why?

Example 10.2

INTERNAL ENERGY

In a certain process, 400 J of heat energy is supplied to a system and at the same time 150 J of work is done by the system. What is the increase in internal energy of the system?

GIVEN

Heat energy supplied to the system, $\Delta Q = 400\text{J}$
Work done by the system, $\Delta W = 150\text{J}$

REQUIRED

increase in internal energy of the system $\Delta U = ?$

SOLUTION

Using the first law of thermodynamics

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

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

$$\Delta U = 400\text{J} - 150\text{J} = 250\text{J}$$

$$= 250\text{J}$$

Answer**Assignment 1:**

An ideal gas absorbs $5.00 \times 10^3 \text{ J}$ of energy while doing $2.00 \times 10^3 \text{ J}$ of work on the environment during a constant pressure process. (a) Compute the change in the internal energy of the gas. (b) If the internal energy now drops by $4.50 \times 10^3 \text{ J}$ and $7.50 \times 10^3 \text{ J}$ is expelled from the system, find the change in volume, assuming a constant pressure process at $1.01 \times 10^5 \text{ Pa}$.

$$(3.00 \times 10^5 \text{ J}, -2.97 \times 10^{-2} \text{ m}^3)$$

For Your Information

However, thermodynamics also applies to living systems, such as our own bodies. This forms the basis of the biological thermodynamics (**Figure**).

$$\Delta U = Q - W + \text{food energy}$$

$$\Delta U = \text{stored food energy}$$

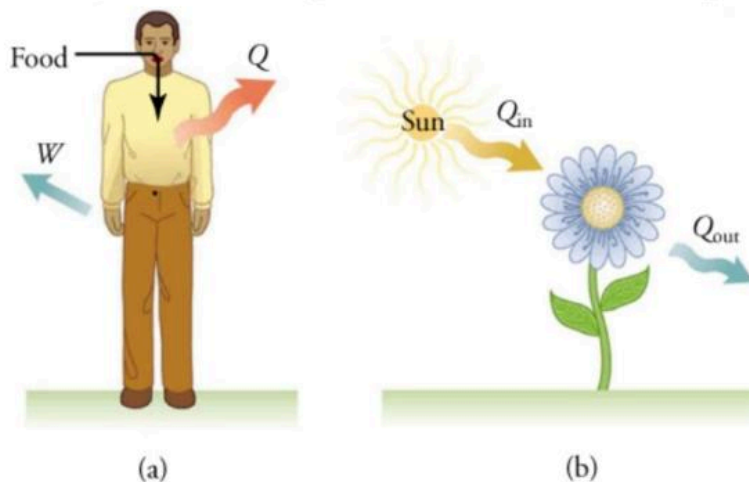


Figure (a) The first law of thermodynamics applies to metabolism. Heat transferred out of the body (Q) and work done by the body (W) remove internal energy, whereas food intake replaces it. (Food intake may be considered work done on the body.) (b) Plants convert part of the radiant energy in sunlight into stored chemical energy, a process called *photosynthesis*.

Life itself depends on the biological transfer of energy. Through photosynthesis, plants absorb solar energy from the sun and use this energy to convert carbon dioxide and water into glucose and oxygen. Photosynthesis takes in one form of energy—light—and converts it into another form—chemical potential energy (glucose and other carbohydrates). *Human metabolism* is the conversion of food into energy given off by heat, work done by the body's cells, and stored fat. Metabolism is an interesting example of the first law of thermodynamics in action. Eating increases the internal energy of the body by adding chemical potential energy.

10.8 MOLAR SPECIFIC HEAT OF A GAS

Specific heat of a body is defined as the quantity of heat required to raise the temperature of 1 kg of the substance by 1K.

The quantity of heat required to raise the temperature of one mole of gas by 1 K is called molar specific heat or molar specific heat capacity of that gas.

If ΔQ is the amount of heat required to raise the temperature of n moles of a substance by ΔT then

$$\begin{aligned}\Delta Q &\propto n\Delta T \\ \Delta Q &= C_M n \Delta T \\ C_M &= \frac{1}{n} \frac{\Delta Q}{\Delta T}\end{aligned}\tag{10.7}$$

where, C_M is a constant of proportionality and is known as molar specific heat or molar specific heat capacity.

The SI unit of molar specific heat or molar specific heat capacity is joule per mole per Kelvin which is expressed as $\text{J mole}^{-1} \text{K}^{-1}$.

The temperature of a gas may be changed under variety of conditions.

The volume may be kept constant or the pressure may be kept constant or both may be varied in some definite manner. Thus for a gas two specific heats are defined. The molar specific heat at constant volume C_v and the molar specific heat at constant pressure C_p .

10.8.1 Constant volume molar specific heat of a gas C_v

The amount of heat required to raise the temperature of one mole of a gas by 1 K while keeping its volume constant is called the constant volume molar specific heat C_v of that gas.

Consider n moles of an ideal gas which is confined in a cylinder fitted with a fixed piston as shown in the Figure. 10.9.

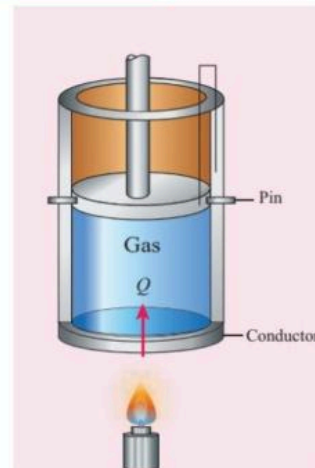
When the gas is heated, its volume remains constant. All the heat supplied goes to increase the kinetic energy of the molecules due to which the temperature of the gas increases.

If ΔQ_v is the amount of heat supplied to n moles of a ideal gas and ΔT is the rise in temperature, then by the definition of the molar specific heat we have

$$\Delta Q_v = n C_v \Delta T \quad (10.8)$$

Where C_v is the molar specific of a gas at constant volume.

FIGURE 10.9



Specific heat capacity at constant volume

10.8.2 Constant pressure molar specific heat of a gas C_p

The amount of heat required to raise the temperature of one mole of a gas by 1 K while keeping its pressure constant is called the constant pressure molar specific heat C_p of that gas.

Consider n moles of an ideal gas which is confined in a cylinder fitted with a movable piston as shown in the Figure.10.10.

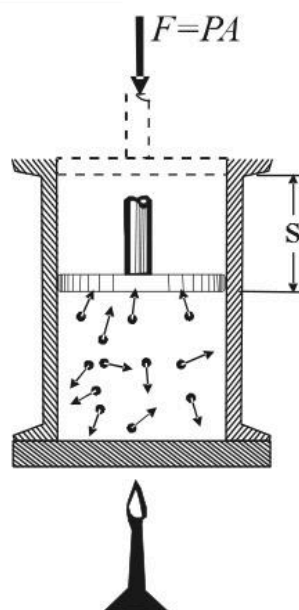
When the gas is heated in this way its temperature rises and at the same time it expands by pushing the piston upward against the constant external pressure. The gas does work on piston.

If ΔQ_p is the amount of heat supplied to n moles of a ideal gas and ΔT is the rise in temperature, then by the definition of the molar specific heat we have

$$\Delta Q_p = n C_p \Delta T \quad (10.9)$$

Where C_p is the molar specific of a gas at constant pressure.

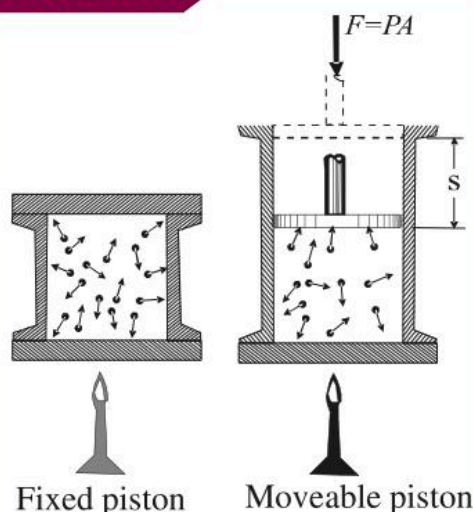
FIGURE 10.10



10.8.3 Relation between molar specific heat at constant pressure and molar specific heat at constant volume.

When gas is heated at constant volume, there is no work done by the gas against the surroundings. The heat received is converted entirely into the internal energy, in the form of molecular kinetic energy, thus raising the temperature (Figure 10.11.a). On the other hand, when the gas is heated at constant pressure, the gas will expand on being heated. It does work against the surroundings (Figure 10.11.b). Hence heat must be supplied to change the internal energy of the gas and to perform external work. Since the change of internal energy is the same in

FIGURE 10.10



both cases, the specific heat at constant pressure C_p is greater than the specific heat at constant volume C_v i.e. $C_p > C_v$ because external work is also performed when the gas expands at constant pressure.

If ΔQ_v is the amount of heat supplied and ΔT is the rise in temperature, then by the definition of the constant volume molar specific heat we have

$$\Delta Q_v = n C_v \Delta T$$

The pressure of the gas increases during the process, but no work is done, because the volume is kept constant. $\Delta W_v = 0$

From the first law of thermodynamics :

$$\Delta Q_v = \Delta U + \Delta W_v$$

$$\Delta Q_v = \Delta U + 0$$

$$\Delta Q_v = \Delta U \quad (i)$$

Compare equation (10.8) and equation (i) we get

$$\Delta U = n C_v \Delta T \quad (ii)$$

If ΔQ_p is the heat supplied and ΔT is the rise in temperature, then

$$\Delta Q_p = n C_p \Delta T \quad (iii)$$

The work done by the gas against the constant external pressure is given by

$$\Delta W_p = \text{Force} \times \text{distance}$$

$$\Delta W_p = F \Delta Y$$

$$\Delta W_p = PA \Delta Y = P \Delta V \quad \therefore F = PA$$

For an ideal gas, the general gas equation is $P \Delta V = nR \Delta T$

Therefore $\Delta W_p = P \Delta V = nR \Delta T$ (iv)

From first law of thermodynamics

$$\Delta Q_p = \Delta U + \Delta W_p \quad (v)$$

Substitute the expressions for ΔQ_p , ΔU and ΔW_p from equation (10.9), (ii) and (iv) respectively in the Equation (v) we get

$$nC_p \Delta T = nC_v \Delta T + nR \Delta T$$

On simplifying, we get

$$C_p - C_v = R \quad (10.10)$$

Where R is the universal gas constant and its value is $R = 8.315 \text{ J mol}^{-1} \text{ K}^{-1}$

Point to Ponder

A foot ball is inflated in a warm room. It is used out of door on a cold day. What happens to the ball? Why?

Example 10.3

INTERNAL ENERGY OF THE NITROGEN GAS

What is the change in internal energy of 200 g of nitrogen as it is heated from 10 °C to 30 °C at constant volume? (For nitrogen gas $C_v = 20.815 \text{ J mole}^{-1} \text{ K}^{-1}$).

GIVEN

Mass of nitrogen gas $m = 200 \text{ g}$
 Initial temperature of nitrogen gas $T_i = 10^\circ \text{C}$
 Final temperature of nitrogen gas $T_f = 30^\circ \text{C}$
 Change in temperature $\Delta T = T_f - T_i = 30^\circ \text{C} - 10^\circ \text{C}$
 $= 20^\circ \text{C} = 20 \text{ K}$

REQUIRED

Change in internal energy $\Delta U = ?$

SOLUTION

Molecular mass of nitrogen gas $M = 28 \text{ g per mole}$

$$\text{Number of moles, } n = \frac{m}{M} = \frac{200 \text{ g}}{28 \text{ g per mole}} = 7.143 \text{ mole}$$

The heat added is converted entirely into the internal energy of the nitrogen gas.

$$\Delta U = nC_v \Delta T$$

$$\Delta U = 7.143 \text{ mole} \times 20.815 \text{ J mole}^{-1} \text{ K}^{-1} \times 20 \text{ K}$$

$$\Delta U = 2973.6 \text{ J}$$

Answer

10.9 HEAT ENGINE

A heat engine is a device that converts heat energy into mechanical work. Steam engine, petrol engine and diesel engine, are all the examples of heat engines. A heat engine consists of the following parts:

Heat Source or heat reservoir

It is a very large reservoir or source of heat energy, and is at a higher temperature T_1 . Its temperature remains practically unchanged during any transfer of heat into or out of it. It is also called high temperature reservoir (HTR).

Heat Sink or cold reservoir

It is a very large body or reservoir at a lower temperature T_2 . Its temperature remains practically constant during any transfer of heat into or out of it. It is also called low temperature reservoir (LTR).

Working Substance

Normally gas is used as a working substance for a heat engine. In principle, a heat engine is a device through which a working substance is taken through a cyclic process. The process is performed in such a way that some heat Q_1 is absorbed from a high temperature reservoir (HTR or source) at temperature T_1 maximum work W is done on the surroundings and heat Q_2 is rejected to a low temperature reservoir (LTR or sink) at temperature T_2 . As shown in the Figure 10.12.

Consider a heat engine that operates in a cycle. Therefore, after completing one cycle the internal energy of the system reaches its original value. So the net change in internal energy is zero for a complete cycle i.e $\Delta U = 0$

Now using first law of thermodynamics we have $\Delta Q = \Delta U + \Delta W$

$$\Delta Q = 0 + \Delta W$$

$$\Delta W = \Delta Q$$

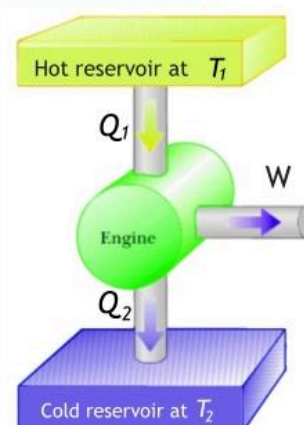
Let Q_1 be the heat energy absorbed by heat engine from a high temperature reservoir and Q_2 be the heat energy rejected by the engine to low temperature reservoir then for one complete cycle the work done by the engine is

$$\Delta W = \Delta Q$$

$$\Delta W = Q_1 - Q_2 \quad (10.11)$$

The thermal efficiency η of a heat engine is defined as the ratio of the net work

FIGURE 10.12



Schematic representation of a heat engine

T_2

W done by the engine in each cycle to the heat Q_1 absorbed in each cycle

$$\text{Thermal efficiency} = \frac{\text{Work done by the engine}}{\text{Heat absorbed by the engine}}$$

$$\eta = \frac{\Delta W}{Q_1} \quad (10.12)$$

Put the value of ΔW from equation 10.11, we have

Therefore

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

$$\eta = 1 - \frac{Q_2}{Q_1} \quad (10.13)$$

If $Q_2 = 0$ i.e. no heat were exhausted by the engine so that all the heat Q_1 absorbed were converted to work

$$\eta = 1 - \frac{0}{Q_1} = 1 - 0 = 1$$

$$\eta = 1 \times \frac{100}{100} = 100\%$$

Experiments show that it is impossible to construct a 100 % efficient heat engine. In the operation of a heat engine, such as steam engine, gasoline engine or diesel engine some heat Q_2 must be rejected to heat sink (LTR).

We can state this fact as follows: It is impossible to construct a heat engine which will produce no effect other than the extraction of heat from a reservoir and the performance of an equal amount of work. This statement is, in fact, one form of the statements of the second law of thermodynamics.

Quiz?

What is the function of spark plug in a petrol engine?

There is no spark plug in a diesel engine, then how does fuel burn in it?

Example 10.4

HEAT ENGINE

A reversible engine works between two temperatures whose difference is 100°C . If it absorbs 746 J of heat from the source and rejects 546 J to the sink, calculate the temperature of the source and the sink.

GIVEN

Difference between temperatures,

$$T_1 - T_2 = 100^\circ\text{C} = 100\text{K}$$

Heat absorbed, $Q_1 = 746\text{J}$ Heat rejected, $Q_2 = 546\text{J}$ **REQUIRED**Temperature of the source = $T_1 = ?$ Temperature of the sink = $T_2 = ?$ **SOLUTION**

The efficiency of a reversible heat engine is given by the formula:

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

Substitute the given values in the above equation, we get:

$$\eta = \frac{746\text{ J} - 546\text{ J}}{746\text{ J}} = \frac{100\text{ K}}{T_1}$$

$$\Rightarrow \frac{200\text{ J}}{746\text{ J}} = \frac{100\text{ K}}{T_1}$$

$$\Rightarrow T_1 = \frac{746\text{ K}}{2} = 373\text{ K} = (373 - 273)^\circ\text{C}$$

$$T_1 = 100^\circ\text{C}$$

Since, $T_1 - T_2 = 100^\circ\text{C}$

$$\Rightarrow T_2 = T_1 - 100^\circ\text{C} = 100^\circ\text{C} - 100^\circ\text{C}$$

$$T_1 = 100^\circ\text{C} \text{ \& } T_2 = 0^\circ\text{C}$$

Answer**Assignment 2:****THE EFFICIENCY OF AN ENGINE**

During one cycle, an engine extracts $2.00 \times 10^3\text{ J}$ of energy from a hot reservoir and transfers $1.50 \times 10^3\text{ J}$ to a cold reservoir. (a) Find the thermal efficiency of the engine. (b) How much work does this engine do in one cycle? (c) What average power does the engine generate if it goes through four cycles in 2.50 s? (0.250, or 25.0%, $5.00 \times 10^2\text{ J}$, $8.00 \times 10^2\text{ W}$)

10.10 SECOND LAW OF THERMODYNAMICS

The first law of thermodynamics is a generalization of the law of conservation of energy. It tells us that heat and mechanical work are mutually interconvertible.

But the second law of thermodynamics tells us how heat energy can be converted

into useful work. The second law of thermodynamics can be stated in a number of forms each emphasizing one or another aspect of the law but they can be proved to be equivalent. Two often quoted statements are the following:

10.10.1 Lord Kelvin Statement

It is impossible to construct a heat engine, operating continuously in a cycle, which takes heat from a heat source at higher temperature and performs an equivalent amount of work without rejecting any heat to a heat sink at low temperature.

According to this statement, a heat source at high temperature and a heat sink at low temperature are essentials for the conversion of heat into mechanical work. Heat cannot be completely converted into useful work during a complete cycle. A heat engine absorbs an amount of heat from the heat source, converts a part of heat energy into mechanical work and rejects the remaining part of heat to the sink.

Therefore, the work performed by the heat engine will be less than the heat energy absorbed. In other words output is always less than the input or efficiency of a heat engine is always less than 100%.

10.10.2 Rudolf Clausius Statement

It is impossible to cause heat to flow from a cold body to a hot body without the expenditure of work. The first law of thermodynamics tells us of the equivalence of heat and work: they are merely different forms of energy. The second law is concerned with the conversion of heat into work. For a cyclic process the first law forbids getting more work out of an engine than the heat put into it. The second law asserts that the work performed will be less than the heat absorbed.

10.11 CARNOT HEAT ENGINE

A heat engine is a closed system that exchanges only heat and work with its surrounding and that operates in cycles. All cyclic heat engines derive heat from a heat source and convert some of it into useful work, and rejects the remainder to a heat sink. As a matter of fact, all engines possess

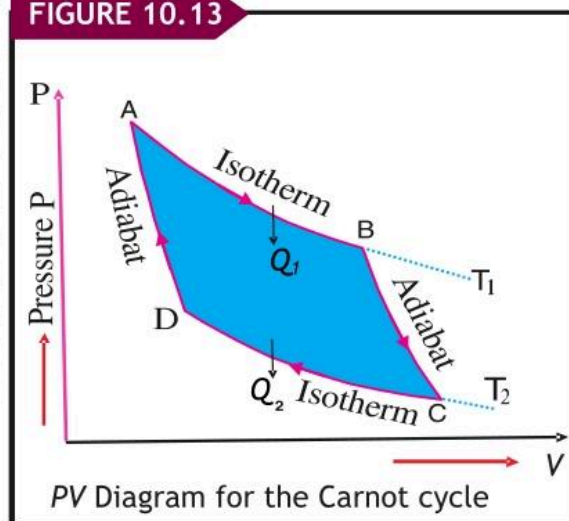
FOR YOUR INFORMATION



French Engineer Sadi Carnot .
Carnot is pronounced as Karno.

possess dissipative effects. Hence the efficiency of a heat engine is reduced considerably. In order to set an ultimate limit of the efficiency of a heat engine. A French military engineer Sadi Carnot, in 1824 considered a hypothetical, idealized heat engine which is free from all sorts of heat losses and friction, called “Carnot heat engine”. The efficiency of an actual heat engine is always less than that of Carnot heat engine.

FIGURE 10.13



A Carnot heat engine consists of:

- A gas cylinder with perfectly insulating walls and perfectly conducting base.
- A perfectly insulated, weightless and frictionless piston in cylinder.

10.11.1 Carnot Cycle

A cycle of heat engine is completed when the properties of a system have returned to the original state. The operating cycle of the most efficient engine (Carnot engine) is called “Carnot cycle”. It consists of four processes, two isothermal and two adiabatic processes.

1. Isothermal expansion: Consider a Carnot heat engine. Let the working substance (system) be at pressure P_1 , volume V_1 and temperature T_1 . Let the gas cylinder be placed on a high temperature reservoir at temperature T_1 and some amount of heat energy $+Q_1$ is absorbed by the gas keeping temperature of the gas constant. The volume increases but pressure decreases.

The state of the gas P_1, V_1, T_1 , changes to P_2, V_2, T_1 , with the absorption of heat $+Q_1$. For a gaseous system, the process is that of isothermal expansion and is represented by the isotherm A - B in Figure 10.13.

2. Adiabatic expansion: The gas cylinder is now being placed on an insulating stand. Then no heat enters the system or leaves the gas (system). Suppose the gas is allowed to expand till the volume increases from V_2 to V_3 . Thus temperature falls from T_1 to T_2 and pressure decreases from P_2 to P_3 . The process is an adiabatic expansion along the adiabat B-C as shown in Figure 10.13.

3. Isothermal compression: The gas cylinder (Carnot heat engine) is then placed on a low temperature reservoir at temperature T_2 . Now the gas is allowed to expand by increasing load on the piston, the heat energy $-Q_2$ is rejected by the gas. The volume decreases from V_3 to V_4 and pressure increases from P_3 to P_4 at constant temperature T_2 . This process is represented by the reversible isotherm C - D in Figure 10.13.

4. Adiabatic compression: The gas cylinder is once again placed on an insulating stand, so that no heat enter the system or leave the gas (system). The gas is compressed adiabatically to its initial state. The gas cylinder returns to its initial state i.e., P_1, V_1, T_1 . For a gaseous system, the process is represented by the adiabat D - A in Figure 10.13. This completes the cycle.

During one cycle, Carnot heat engine performs a net amount of work ΔW , which is the difference between the work done on the engine during the two expansions and the two compressions. The net amount of heat absorbed by the engine in one cycle is $Q_1 - Q_2$, where Q_1 is the heat absorbed during the isothermal expansion and Q_2 is the heat rejected during the isothermal compression.

The area ABCDA enclosed by the cyclic path represents the net work done by the engine in one cycle. Thermal efficiency η is given by :

$$\text{Efficiency} = \frac{\text{Out put}}{\text{Input}} = \frac{\text{Work Obtained}}{\text{Heat Supplied}}$$

$$\eta = \frac{\Delta W}{Q_1} \quad (10.12)$$

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

$$\eta = 1 - \frac{Q_2}{Q_1} \quad (10.13)$$

We know that the absolute temperature of an ideal gas is directly proportional to the average kinetic energy of its molecules.

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \quad (10.14)$$

The thermal efficiency of a Carnot engine can be also written as

$$\eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1} \quad (10.15)$$

Thus the efficiency of Carnot engine depends on the temperatures of high and low temperature reservoirs, and it is independent of nature of working substance. If we take temperature of low temperature reservoir as 0 K then

from Eq (10.15) we have $\eta = 1 - \frac{0}{T_1} = 1$ or 100%

It means that the work done by a Carnot heat engine is equal to Q_1 i.e. all heat energy absorbed by the heat engine is converted into work. This is against the Kelvin's statement of the second law of thermodynamics. Hence it is not possible to achieve temperature of absolute zero.

The efficiency of an ideal heat engine by a theoretical limit. It is always less than 1 or 100%. The real heat engine cannot attain Carnot efficiency due to presence of friction and heat losses by conduction and radiation.

Carnot deduced from his studies that no engine could have 100 % efficiency. He showed that the efficiency of the best heat engine that could be made was a function of the two temperatures at which heat was supplied and rejected in the cycle and was independent of the nature of the working substance. This statement is called Carnot theorem.

No real heat engine operating between two heat reservoirs can be more efficient than a Carnot engine, operating between the same two reservoirs.

For Your Information

The first successful petrol engine was invented by Nikolaus Otto in the year 1876 and the Diesel engine was invented by Rudolph Diesel in 1892.

Example 10.5

CARNOT HEAT ENGINE

A Carnot heat engine has a maximum efficiency of 55 %. It takes certain amount of heat from a source, converts a part of it into work and rejects the remaining heat towards the heat sink. If the temperature of the heat source is 600 K then, find the temperature of the heat sink.

GIVEN

Temperature of the heat source $T_1 = 600\text{K}$
Maximum efficiency of Carnot heat engine $\eta = 55\% = 0.55$

REQUIRED

Temperature of the heat sink $T_2 = ?$

SOLUTION

Using the equation

$$\eta = 1 - \frac{T_2}{T_1} \qquad \frac{T_2}{600 \text{ K}} = 1 - 0.55$$

$$T_2 = 600 \text{ K} \times 0.45 = 324 \text{ K}$$

$$= 324 \text{ K}$$

Answer**10.12 REFRIGERATOR**

The device which will either cool or maintain a body temperature below that of the surroundings is called refrigerating machine.

Hence, heat must be made to flow from a body at low temperature to the surroundings at high temperature. We see that in nature that heat spontaneously flows from a high temperature body to a low temperature body.

The reverse process to complete the thermodynamics cycle, in which heat Q will flow back from the low temperature body to the high temperature body, is not possible. When refrigerator is used for cooling in summer, it is called refrigerator and when it is used for heating in winter it is called a heat pump.

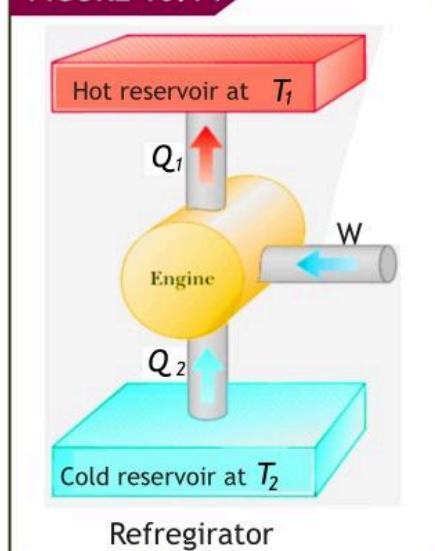
The device in which the working substance performs cycle in a direction opposite to that of a heat engine is called refrigerator.

The working substance used in it is called refrigerant.

In principle, a refrigerator is a device through whose agency a system or refrigerant is taken through a cycle in such a way that some amount of heat Q_2 is removed from a low temperature source at temperature T_2 as shown in Figure 10.14. A work W is performed by the compressor of the refrigerator on the working substance (refrigerant). The quantity of heat Q_1 .

$$Q_1 = W + Q_2 \qquad (10.15)$$

is rejected to the high temperature source

FIGURE 10.14

(atmosphere) at temperature T_1 by the radiator fixed at the back side of the refrigerator. The purpose of a refrigerator is to extract as much heat Q_2 as possible from the cold reservoir with the expenditure of as little work as possible.

10.12.1 Coefficient of performance or energy ratio of refrigerator

The performance of a heat engine is described by its thermal efficiency. Coefficient of performance is defined as the ratio of the amount of heat removed from the heat sink to the work required to do so.

Coefficient of performance for cooling or cooling energy ratio is

$$E_{\text{Cooling}} = \frac{Q_2}{W}$$

From Eq 10.15 we have $W = Q_1 - Q_2$

$$\text{Thus } E_{\text{Cooling}} = \frac{Q_2}{Q_1 - Q_2} \quad (10.16)$$

$$\text{Thus } E_{\text{Cooling}} = \frac{T_2}{T_1 - T_2} \quad \therefore \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

Coefficient of performance for heating or heating energy ratio is

$$E_{\text{Heating}} = \frac{Q_1}{W}$$

$$\text{Thus } E_{\text{Heating}} = \frac{Q_1}{Q_2 - Q_1} \quad \therefore W = Q_2 - Q_1$$

$$E_{\text{Heating}} = \frac{T_1}{T_2 - T_1}$$

No cyclic device has ever been built that will extract heat Q_2 from a cold reservoir and reject it entirely to a hotter reservoir without the expenditure of work. This statement is referred to as the Clausius statement of the second law of thermodynamics.

Example 10.6

REFRIGERATOR

A refrigerator has a coefficient of performance 8. If the temperature in the freezer is -23°C . What is the temperature at which it rejects heat?

GIVEN

The coefficient of performance, $E = 8$

Temperature of the heat sink, $T_2 = -23^\circ\text{C} = 250\text{K}$

REQUIRED

Temperature of the heat source, $T_1 = ?$

SOLUTION

Using the equation

$$E = \frac{T_2}{T_1 - T_2} \quad \Rightarrow \quad 8 = \frac{250 \text{ K}}{T_1 - 250 \text{ K}}$$

$$T_1 = 281.25 \text{ K} = 281.25 - 273 = 8.2 \text{ }^\circ\text{C}$$

Point to Ponder

Why is the freezer in the upper part of the refrigerator?

Why do we not keep bananas in the refrigerator?

Why does the refrigerator switch itself OFF intermittently with some noise?

10.13 ENTROPY

The concept of entropy was introduced into the study of thermodynamics by Rudolph Clausius in 1856 to give a quantitative basis for the second law. It provides another variable to describe the state of a system to go along with pressure, volume, temperature and internal energy. If a system undergoes a reversible process during which it absorbs a quantity of heat ΔQ at absolute temperature T , then the increase in the state variable called entropy S of the

system is given by $\Delta S = \frac{\Delta Q}{T}$ (10.17)

Like potential energy or internal energy, it is the change in entropy of the system which is important.

Change in entropy is positive when heat is added and negative when heat is removed from the system. Suppose, an amount of heat Q flows from a reservoir at temperature T_1 through a conduction rod to a reservoir at temperature T_2 when $T_1 > T_2$. The change in entropy of the reservoir, at temperature T_1 , which loses heat, decreases by Q/T_1 and of the reservoir at temperature T_2 , which gains heat, increase by Q/T_2 . As $T_1 > T_2$ so Q/T_2 will be greater than Q/T_1 i.e. $Q/T_2 > Q/T_1$.

Hence, net change in entropy = $\frac{Q}{T_2} - \frac{Q}{T_1}$ is positive.

It follows that in all natural processes where heat flows from one system to another; there is always a net increase in entropy. Another statement of 2nd law of

thermodynamics.

If a system undergoes a natural process, it will go in the direction that causes the entropy of the system plus the environment to increase.

It is observed that a natural process tends to proceed towards a state of greater disorder. Thus, there is a relation between entropy and molecular disorder. For example an irreversible heat flows from a hot to a cold substance of a system increases disorder because the molecules are initially sorted out in hotter and cooler regions. This order is lost when the system comes to thermal equilibrium. Addition of heat to a system increases its disorder because of increase average molecular speeds and therefore, the randomness of molecular motion. Similarly, free expansion of gas increases its disorder because the molecules have greater randomness of position after expansion than before. Thus in both examples, entropy is said to be increased.

We can conclude that only those processes are probable for which entropy of the system increases or remain constant. The process; whereas for all irreversible processes, entropy of the system increases.

Entropy of a system is also defined as a measure of disorder of a system.

In order to understand this definition, we consider the following examples.

Consider a box containing equal number of red and green balls. Red balls are arranged on one side and green balls on the other side of the box. If we shake the box, the balls will mix. The state of the balls has changed from an initially ordered state to a finally disordered state. The entropy has increased in this process. Like wise it can be proved that disorder increases in any natural process. We have seen that the entropy of a system during any natural process increases. Thus we can say that entropy is a measure of disorder of a system.

It is also observed that in all natural processes, energy tends to pass from a more useful form to a less useful form. This is called “degradation of energy.”

The continual increase in the entropy and the state of disorder of the universe affects the availability of energy to do useful work. Energy is continually degrading for doing useful work. Ultimately, the entropy of the Universe should reach a maximum. At this point, the Universe will be in a state of uniform temperature and density. All physical, chemical and biological processes will have ceased because a state of perfect disorder implies no energy available for doing work. This state of affairs is referred as heat death of the universe.

Example 10.7**CHANGE IN ENTROPY OF WATER**

What is the change in entropy of 30 g of water at 0°C as it is changed into ice at 0°C ? Take the latent heat of fusion of ice = 336000 J kg^{-1} .

GIVEN

Mass of water $m = 30\text{ g} = 0.03\text{ kg}$

Constant temperature at fusion point $T = 0^\circ\text{C} = 273\text{ K}$

Latent heat of fusion of ice $H_f = 336000\text{ J kg}^{-1}$

REQUIRED

Change in entropy: $\Delta S = ?$

SOLUTION

Heat removed from water = $\Delta Q = m H_f = 0.03 \times 336000\text{ J} = 10080\text{ J}$

$$\text{Change in entropy: } \Delta S = \frac{\Delta Q}{T} = \frac{10080\text{ J}}{273\text{ K}} = 36.92\text{ J K}^{-1}$$

36.92 J K⁻¹

Answer

Assignment 3:**MELTING A PIECE OF LEAD**

(a) Find the change in entropy of $3.00 \times 10^2\text{ g}$ of lead when it melts at 327°C . Lead has a latent heat of fusion of $2.45 \times 10^4\text{ J/kg}$. (b) Suppose the same amount of energy is used to melt part of a piece of silver, which is already at its melting point of 961°C . Find the change in the entropy of the silver.

(12.3 J/K, 5.96 J/K)

KEY POINTS

- ❖ **Thermodynamics:** The branch of physics which deals with the laws of transformation of heat into other forms of energy and vice versa is called thermodynamics.
- ❖ **Internal energy:** The sum of the kinetic and potential energies associated with the random motion of the atoms of the substance is called the internal energy of the substance.
- ❖ **First law of thermodynamics:** This law states that if an amount of heat energy ΔQ is supplied to a system a part of it may increase in internal energy by an amount ΔU while the remaining part may be used up as the external work ΔW by the system. $\Delta Q = \Delta U + \Delta W$
- ❖ **Molar specific Heat:** The quantity of heat required to raise the temperature of one mole of the substance (gas) by 1°C or 1 K is called molar specific heat or molar specific heat capacity of that substance.

- ❖ **Reversible Process:** A process is said to be reversible if it can be retraced exactly in reverse order without producing any change in the surroundings.
- ❖ **Irreversible Process:** A process which cannot be retraced in the backward direction by reversing the controlling factors is said to be irreversible.
- ❖ **Heat engine:** A heat engine is a device for converting heat energy into mechanical work.
- ❖ **Reversible heat engine:** The engine in which the process can be retraced at any stage of its operation by reversing the boundary conditions is called a reversible heat engine.
- ❖ **Heat Source:** A body of infinite heat capacity which is capable of absorbing or rejecting an unlimited quantity of heat without any change in its temperature is called heat source or heat reservoir.
- ❖ **Principle of increase of entropy:** Any process taking place within a thermally isolated system, the entropy of the system either increases or remains constant.
- ❖ **Degradation of energy:** The conversion of heat energy from high ordered state to a less ordered state is called degradation of energy.

EXERCISE

MULTIPLE CHOICE QUESTIONS

Choose the best possible answer

- 1 Assume we can change the equilibrium state of a system via two different processes. Assume that the initial and the final state are the same. Which of the quantities ΔU , ΔQ , ΔW , and ΔT must be the same for the two processes?
a. only ΔQ and ΔW b. only ΔU and ΔT
c. only ΔQ and ΔT d. only ΔU and ΔW
- 1 In any process the maximum amount of mechanical energy that can be converted to heat
a. Depends upon the amount of friction
b. Depends upon the intake and exhaust temperature
c. Depends upon whether kinetic or potential energy is involved
d. Is 100 %

- 3 In an isothermal change, internal energy
a. Decreases b. Increases
c. Becomes zero d. Remains constant
- 4 A thermos bottle containing hot coffee is vigorously shaken. Consider coffee as the system, then its temperature
a. Increases b. Decreases below than 0°C
c. Remains the same d. Decreases
- 5 Maximum work can be obtained in the process called
a. Cyclic b. Isothermal
c. Adiabatic d. Isochoric
- 6 A heat engine takes in 800 J of heat at 1000 K and exhausts 600 J of heat at 400 K. What is the actual efficiency of this engine?
a. 25% b. 40%
c. 50% d. 75%
- 7 If the temperature of the heat source is increased, the efficiency of a Carnot's engine
a. Increases b. Decreases
c. Remains constant d. First increases and then becomes constant
- 8 Triple point of water is
a. 273.16°F b. 372.16 K
c. 273.16°C d. 273.16 K
- 9 A real gas can be approximated to an ideal gas at
a. Low density b. High pressure
c. High density d. Low temperature
- 10 If the volume of the gas is to be increased by 4 times, then
a. Temperature and pressure must be double
b. At constant P the temperature must be increased by four times
c. At constant T the pressure must be increased by four times
d. It cannot be increased
- 11 In which of the systems listed below is the entropy decreasing?
a. A gas is cooled. b. A plate is shattered.
c. An egg is scrambled. d. A drop of dye diffuses in a cup of water.
- 12 If the temperature of source and sink of a Carnot engine having efficiency η are each decreased by 100K, then the efficiency η
a. remain constant b. become 1.
c. increases. d. decreases

CONCEPTUAL QUESTIONS

Give the short answer to the following questions.

- 1 Why is the earth not in thermal equilibrium with the sun?
- 2 When a block with a hole in it is heated, why does not the material around the hole expand into the hole and make it small?
- 3 A thermometer is placed in direct sunlight. Will it read the temperature of the air, or of the sun, or of some thing else?
- 4 The pressure in a gas cylinder containing hydrogen will leak more quickly than if it is containing oxygen. Why?
- 5 What happens to the temperature of a room in which an air conditioner is left running on a table in the middle of the room?
- 6 Why does the pressure of the air in automobile tyre increases if the automobile is driven for a while?
- 7 On removing the valve, the air escaping from a cycle tube cool. Why?
- 8 Write the limitations of first law of thermodynamics.
- 9 Is it possible, according to the second law of thermodynamics, to construct an heat engine that is free from thermal pollution?
- 10 Can specific heat of a gas be zero or infinity? Can specific heat be negative?
- 11 An inventor claims to have developed an heat engine, working between 27°C and 227°C having an efficiency of 45 %. Is the claim valid? Why?

COMPREHENSIVE QUESTIONS

Give extended response to the following question

- 1 Explain, briefly, the following terms used in thermodynamics: System, Surroundings, Boundary and State variables.
- 2 Distinguish among the three forms of energy: work; heat and internal energy.
- 3 State and explain the first law of thermodynamics.

- 4 Define the molar heat capacities C_p and C_v for a gas. Show that, for a mole of an ideal gas, $C_p - C_v = R$
- 5 Explain with examples reversible and irreversible processes.
- 6 What is meant by a heat engine? What is its main purpose? How is its efficiency defined?
- 7 State the second law of thermodynamics in its alternative forms. Discuss the assertions of the first and second laws about heat and work energies.
- 8 What were the basic questions that led Carnot to invent Carnot engine?
- 9 State Carnot Theorem about the characteristics of a Carnot engine.
- 10 What do you mean by a refrigerator? How does it function? Derive an expression for the Coefficient of performance of a refrigerator.
- 11 Explain the concept of entropy. Mention its major properties. How is the second law of thermodynamics expressed in terms of entropy?

NUMERICAL QUESTIONS

- 1 Water at 20°C falls from a height of 854 meters. If the whole energy is used in increasing the temperature, find out the final temperature. Specific heat of water is $4200 \text{ J K}^{-1} \text{ kg}^{-1}$ (22 °C)
- 2 25200 J of heat is supplied to the system while the system does 6000 J of work. Calculate the change in internal energy of the system. (19200 J)
- 3 A sample of ideal gas is uniformly heated at constant pressure. If the amount of 180 J of heat is supplied to the gas, calculate the Change in internal energy of the gas and Work done by the gas. Take $\gamma = 1.41$ (127.66 J, 52.34 J)
- 4 Find the efficiency of a Carnot's heat engine working between the steam and ice points? (26.8 %)
- 5 A Carnot heat engine absorbs 2000 J of heat from the source of heat engine at 227°C and rejects 1200 J of heat during each cycle to sink. Calculate efficiency of engine temperature of sink and amount of work done during each cycle. (40 %, 27°C , 800 J)

- 6 What is the least amount of work that must be performed to freeze one gram of water at 0°C by means of a refrigerator? Take the temperature of the surrounding as 37°C . How much heat is passed on to the surrounding during this process? (45.54 J, 381.54 J)
- 7 Calculate the change in entropy when 10 kg of water is heated from 90°C to 100°C ? (Specific heat of water is $4180\text{ J mole}^{-1}\text{ K}^{-1}$). (1135.8 J K $^{-1}$)
- 8 A system absorbs 1176 J of heat and at the same time does 352.8 J of external work. Find the change in internal energy of the system? Find the change in internal energy in the system when it absorbs 1050 J of heat while 84 J of work is done? What will be the change in internal energy of the gas if 210J of heat is removed at constant volume? (823.2J, 966J)
- 9 An ideal gas at 20.0°C and a pressure of $1.50 \times 10^5\text{ Pa}$ is in a container having a volume of 1.00 L. (a) Determine the number of moles of gas in the container. (b) The gas pushes against a piston, expanding to twice its original volume, while the pressure falls to atmospheric pressure. Find the final temperature. ($6.16 \times 10^{-2}\text{ mol}$, 395 K)
- 10 A block of ice at 273 K is put in thermal contact with a container of steam at 373 K, converting 25.0 g of ice to water at 273 K while condensing some of the steam to water at 373 K. (a) Find the change in entropy of the ice. (b) Find the change in entropy of the steam. (c) Find the change in entropy of the Universe. (30.5 J/K, - 22.3 J/K, + 8.2 J/K)