4. Thermodynamics

Can you recall?

1. When a piece of ice is placed in water at room temperature, the ice melts and water cools down. Why does their temperature change?
2. When water boils, why does its temperature remains constant?
3. When an inflated balloon is suddenly burst, why is the emerging air slightly cooled?

4.1 Introduction:

In XIth Std. we have studied thermal properties of matter. In this chapter, we shall study the laws that govern the behavior of thermal energy. We shall study the processes where work is converted into heat and vice versa.

When we drive a vehicle, its engine gets warmer after some time. Similarly, when we exercise, we also feel warmth in our body. Similar physics is involved in both the cases. The engine of a vehicle as well as our muscles do some work and both produce some heat. It is, therefore, natural to think that if the work done by an engine or our muscles produces some heat then heat should also be able to 'do' some work. Thermodynamics is mostly the study of conversion of work (or any form of energy) into heat and the other way round.

When a hot object is in contact with a cold object, we notice that both objects reach the same temperature after some time. The hot object gets cooler and the cold object becomes warmer. That means something is exchanged between the two objects. *This 'something' is heat. According to modern theory, heat is a form of energy*.

In the year 1798 it was observed by Benjamin Thomson, a British scientist, that tremendous heat is produced when brass canons were bored. The heat thus produced was large enough to boil water. A very important observation was that the amount of heat produced was related to the work done in turning the drill that was used to bore the canon. *It was also noticed that more heat was produced when the drill bored for a longer time*. It did not depend on the sharpness of the drills used. A sharper drill would have removed more heat according to the older theory of heat, which assumed heat to be some form of a fluid. This observation could be explained only if heat was a form of energy and not any fluid. It is natural to conclude from these observations that energy can be converted from one form to another form. In this particular case, a very important law of physics can be proposed that, *'the work done by a system is converted into heat'*. (The drills used to bore the canons 'do' the work and the canons get heated up).

This was, probably, one of the pioneer experiments in thermodynamics. *Thermodynamics is the branch of physics that deals with the concepts of heat and temperature and the inter-conversion of heat and other forms of energy*.

It is the field of study that allows us to understand nature of many of the fundamental interactions in the universe. It can explain phenomena as simple as water boiling in a vessel, and also something as complex as the creation of a new star. Thermodynamics is an important branch of physics having many practical applications.

In this chapter we will try to understand a thermodynamic system, thermodynamic variables, thermodynamic processes and the laws that govern these processes. We will also study the most important and useful applications of thermodynamics, the heat engines and their efficiency.

4.2 Thermal Equilibrium:

The thermal properties of materials discussed in XI^th^ Std. are useful to understand the behaviour of a material when it is heated or cooled. When you put a piece of ice in water at room temperature, the ice melts. This is because the water at room temperature (higher than the ice temperature) transfers its heat to ice and helps ice melt. Similarly, when hot water is mixed with cold water, it transfers its heat to the cold water. The hot water cools down. In both these examples, we notice that the two components reach a stage where there is no more transfer of heat. In such cases, we assume that *heat is something that is transferred from a substance at a higher temperature to that at a lower temperature*. This transfer continues till the level of heat content in both the substances is the same. Then we say that a *thermal equilibrium* is reached between the two substances. We can say that *when two objects are at the same temperature, they are in thermal equilibrium*. This concept of thermal equilibrium is used in the Zeroth Law of thermodynamics. It is called the Zeroth Law because it was proposed after the First and the Second laws of thermodynamics were formulated.

Remember this

Thermal equilibrium: Two systems in thermal contact with each other are in thermal equilibrium if they do not transfer heat between each other.

Can you tell?

Why different objects kept on a table at room temperature do not exchange heat with the table?

4.3 Zeroth Law of Thermodynamics:

The Zeroth law is very important as it helps us to define the concept of a temperature scale. The formal statement of the Zeroth law of thermodynamics is as follows:

"If two systems are each in thermal equilibrium with a third system, they are also in thermal equilibrium with each other".

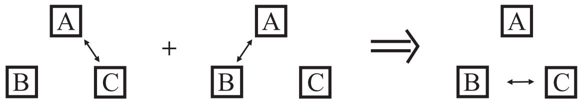


Fig. 4.1: Schematic representation of Zeroth law of thermodynamics.

Figure 4.1 shows a schematic representation of the Zeroth law of thermodynamics. The double arrow represents thermal equilibrium between systems. If system A and C are in thermal equilibrium, and systems A and B are in thermal equilibrium, then systems B and C must be in thermal equilibrium. Then systems A, B and C are at the same temperature.

For example, when we use a thermometer to measure temperature of an object, we use the same principle. When the thermometer and the object are in thermal equilibrium, the thermometer indicates the temperature of the object. The zeroth law, therefore, enables us to use a thermometer to compare the temperatures of different objects. This is schematically shown in the Fig 4.2. It also implies that temperature is a measurable quantity. The science of measuring temperatures is called *Thermometry* which involves different temperature scales and methods of measuring temperature. This is already discussed in XI^th^ Std.

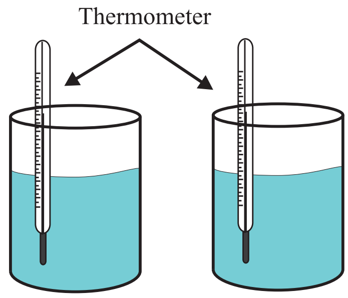


Fig. 4.2: Concept of temperature measurement.

Remember this

The Zeroth Law of Thermodynamics states that systems in thermal equilibrium are at the same temperature.

Can you tell?

Why is it necessary to make a physical contact between a thermocouple and the object for measuring its temperature?

4.4 Heat, Internal Energy and Work:

Earlier in this chapter, we saw that when two substances, initially at different temperatures, are brought in contact with each other, the substance at higher temperature loses its heat and the substance at lower temperature gains it. We did not discuss the reasons why any substances can 'have' that heat and what exactly is the nature of the heat content of that substance. The examples we discussed in the previous section and in chapter 7 (XIth Std.), help us understand the transfer of heat from one body to the other. But they do not help us in explaining why the action of rubbing our palms together generates warmth, or why an engine gets warmer when it is running. These and similar phenomena can be explained on the basis of the concept of the internal energy of a system, the conversion of work and heat into each other and the laws governing these inter conversions.

4.4.1 Internal Energy:

We know that every system (large or small) consists of a large number of molecules. *Internal energy is defined as the energy associated with the random, disordered motion of the molecules of a system*. It is different than the macroscopic ordered energy of a moving object. For example, a glass of water kept on a table has no kinetic energy because it is not moving. Its potential energy can also be taken as zero. But we know, from the kinetic theory, that the water molecules in the glass at the given temperature move at a random speed. Thus, we can say that, the internal energy of a substance is the total energy of all its atoms/molecules.

For an ideal monatomic gas such as argon, the internal energy is just the translational kinetic energy of the atoms having a linear motion. (Discussed in Chapter 3). For a polyatomic gas such as carbon di-oxide, we consider the rotational and vibrational kinetic energy of the molecules in addition to their translational kinetic energy. In case of liquids and solids, we need to consider the potential energy of the molecules due to the intermolecular attractive forces amongst them. Remember this is again at the molecular level (microscopic scale) only. This internal energy of a system is denoted by U .

Example 4.1: Calculate the internal energy of argon and oxygen.

Solution: Arogon is a monatomic gas. Internal energy of a gas depends only on its temperature. Hence, its internal energy is given by 3/2 kT. Oxygen is a dia-atomic gas its internal energy is 5/2 kT.

4.4.2 Thermodynamic system and Thermodynamic Process:

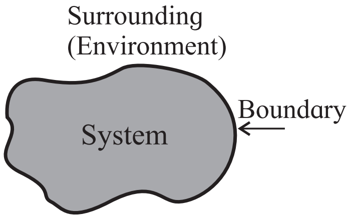


Figure 4.3 (a): a system, its boundary and environment.

Let us understand what is meant by a thermodynamic system and a thermodynamic process first.

A thermodynamic system is a collection or a group of objects that can form a unit which may have ability to exchange energy with its surroundings. Anything that is not a part of the system is its surrounding or its environment. For example, water kept in a vessel is a system, the vessel is its boundary and the atmosphere around it is its surrounding. Figure 4.3 (a) shows this schematically.

Thermodynamic systems can be classified on the basis of the possible transfer of heat and matter to environment. Based on this, they are classified as open, closed or isolated systems.

An open system is a system that freely allows exchange of energy and matter with its environment. For example, water boiling in a kettle is an open system. Heat escapes into the air. This is the exchange of energy with the surroundings. At the same time, steam also escapes into the air. This is exchange of matter with the surroundings.

A closed system, on the other hand, does not allow the exchange of matter but allows energy to be transferred. For example, water boiling in a boiler is a closed system. It allows heat (energy) to be transferred from the source of heat (a burner) to the water (system) inside. Similarly, heat is also transferred to the surroundings. Steam (matter) is not allowed to escape as long as the valve is kept closed.

An isolated system is completely sealed (isolated from its environment). Matter as well as heat cannot be exchanged with its environment. A thermos flask is a very familiar example of an isolated system.

Figure 4.3 (b) shows an open system, a closed system, and an isolated system schematically.

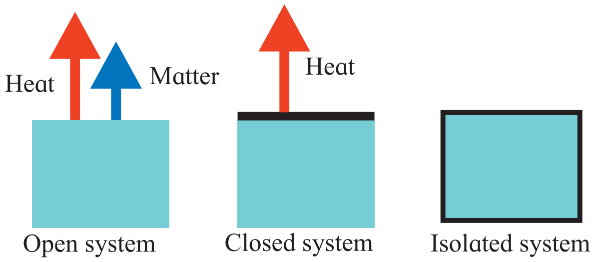


Figure 4.3 (b): Thermodynamic systems; open system, closed system, and isolated system.

A thermodynamic process is a process in which the thermodynamic state of a system is changed. For example, water contained in a vessel with a lid on it is an open system. When the pot is heated externally, water starts boiling after some time and steam is produced which exerts pressure on the walls of the vessel. In this case, the state of the water in the container is changed. This is because, the temperature (T), the volume (V), and the pressure (P) of the water inside the vessel change when it starts boiling. Thus, we can describe the state of a system by using temperature, pressure and volume as its variables. We will discuss these in some details at a later stage in section 4.5.1.

4.4.3 Heat:

Let us now try to understand heat and its relation with the internal energy of a system. Consider a glass filled with water on a table. The glass, along with the water in it forms a system. Let the temperature of this system be T_S. The table on which the glass is kept and the other relevant parts of the room will then be its surrounding or the environment. Let the temperature of the environment be T_E. We notice that if T_S and T_E are not the same, then T_S will change until both the temperatures are equal and a thermal equilibrium will be reached between the 'system' and the 'environment'. T_S will also change to some extent, but the end result is that the 'system' and the 'environment' reach thermal equilibrium. If the environment is very large, the change in T_E may not be measurable, but certainly not zero.

Such a change in temperature is caused by the transfer of internal energy between the system and its environment. In this case, the transfer of energy is between the glass of water and its surrounding.

Remember this

When transfer of energy takes place between a system and its environment, we observe the following conventions.

1. When the energy is transferred to a system from its environment, it is positive. We say that the system gains (or absorbs) energy.
2. When the energy is transferred from the system to its environment, it is negative. We say that the system loses (or releases) energy.

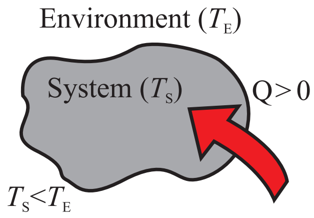


Fig. 4.4 (a): Energy flows into the system.

Consider Fig. 4.4 which shows energy transfer between a system and its environment. Let T_S and T_E be the temperatures of the system and its environment respectively. Let Q be the energy transferred between the system and its environment. As shown in Fig. 4.4 (a), $T_S<T_E$, the system gains energy, and Q is positive.

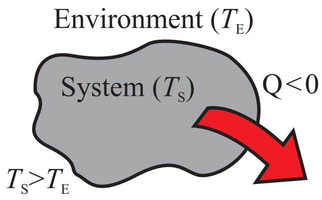


Fig. 4.4 (b): Energy flows from the system.

In Fig. 4.4 (b), $T_S > T_E$ the system loses energy, and Q is negative. In Fig.4.4 (c), $T_S = T_E$, the system and the environment are in thermal equilibrium and there is no transfer of energy ($Q = 0$).

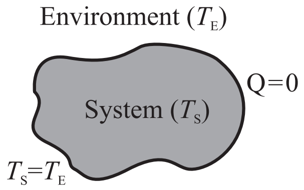


Fig. 4.4 (c): No transfer energy.

Using these observations, we can now define heat as the energy that is transferred (between the system and its environment) due to a temperature difference that exists between the two. It is denoted by Q.

4.4.4 Change in Internal Energy of a System:

In the previous discussion we have seen that the internal energy of a system can be changed (it can be gained or released) due to exchange with its environment. Now we will try to understand how this transfer of energy between a system and its environment is possible. Consider the following experiment. Figure 4.5 (a) shows a cylinder filled with some gas in it. This cylinder is provided with a movable, massless, and frictionless piston at one end as shown. The gas inside the cylinder is our system and the rest is its environment. Let the temperature of the gas be T_S and that of the environment be T_E.

Internal energy of the system (the gas) can be changed in two different ways or by both.

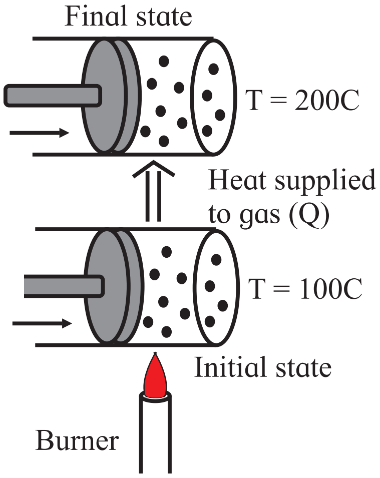


Fig. 4.5: (a) Change in internal energy of a system can be brought about by heating the system.

i) The cylinder can be brought in contact with a source of heat such as a burner as shown in Fig. 4.5.(a). As discussed previously, the temperature difference between the source of heat (environment) and the system will cause a flow of energy (heat) towards the gas in the cylinder. This is because $T_E > T_S$. Thus, there will be an increase in the internal energy of the gas. Such exchange of energy is possible in another way also. If the surrounding is at temperature lower than the gas, $T_S > T_E$, the gas will lose energy to its environment and cool down.

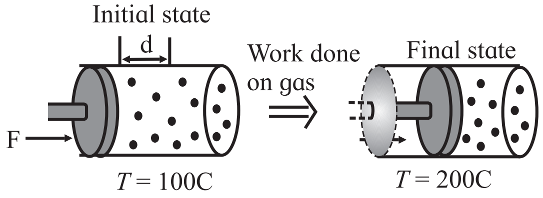


Fig. 4.5: (b) Change in internal energy of a system can be brought about by doing some work on it.

ii) The other way to increase the internal energy of the gas is to quickly push the piston inside the cylinder, so that the gas is compressed, as shown in Fig. 4.5.(b). In this case, we know that the piston does some work on the gas in moving it through some distance. The gas gains energy and its temperature is increased. On the other hand, if the gas pushes the piston out, so that the gas is expanded, some work is done by the gas. It loses some of its energy and the gas cools down.

Use your brain power

Why is there a change in the energy of a gas when its volume changes?

Thus, we see that the internal energy of a system can be changed in two different ways, 1) by heating it or 2) by doing work on it. The experiment we discussed just now can be carried out in a very meticulous way so that we achieve the same change in temperature of the gas by both the methods.

Conclusion of this experiment leads us to a very important principle of thermodynamics. It is related to the work done on the system (or, by the system) and the change in the internal energy of the system. Both are related through the energy that is transferred to (or, by) the system and the heat that is involved in the process. This leads us to the First Law of Thermodynamics.

Can you recall?

During the middle of nineteenth century, James Joule showed that mechanical work done and the heat produced while doing that work are equivalent. This equivalence is the mechanical equivalent of heat. The relation between the mechanical work W and the corresponding heat produced H is $W = J \times H$. The constant J is the mechanical equivalent of heat.

4.5 First Law of Thermodynamics: (Work and Heat are related)

The first law of thermodynamics gives the mathematical relation between heat and work.

4.5.1 First Law of Thermodynamics

Consider a very common thermodynamic system which consists of some quantity of an ideal gas enclosed in a cylinder with a movable, massless, and frictionless piston. Figure 4.6 shows such arrangement. In this, the gas inside the cylinder is the system and the cylinder along with the piston is its environment.

At this stage, we will tentatively base our discussion on the basis of the kinetic theory, that is, the microscopic description of a system. It is important to keep in mind that a thermodynamic system can be completely described on the basis of the macroscopic model. (We will discuss it briefly at a later stage).

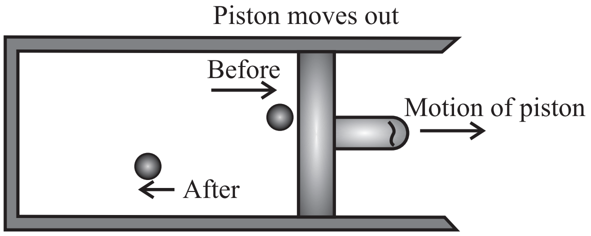


Fig. 4.6 (a): Positive work done by a system.

First, consider the work done by the system (the gas) in increasing the volume of the cylinder. During expansion, (Fig.4.6 (a)) the gas molecules which strike the piston lose their momentum to it, and exert a pressure on it. As a result, the piston moves through a finite distance. *The gas does a positive work on the piston*. When the piston is pushed in so that the volume of the gas decreases, (Fig.4.6 (b)) the gas molecules striking it gain momentum from the piston. *The gas does a negative work on the piston*.

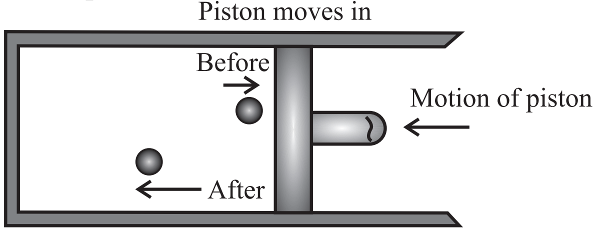
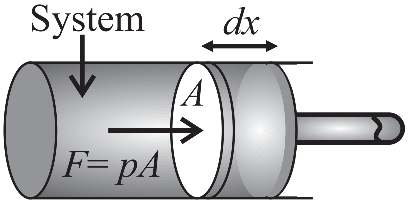


Fig. 4.6 (b): Negative work done by a system.

Consider Fig. 4.7 which shows a system enclosed in a cylinder with a movable, massless, and frictionless piston so that its volume can change. Let the cross sectional area of the cylinder (and the piston) be A, and the constant pressure exerted by the system on the piston be p. The total force exerted by the system on the piston will be $F = pA$. If the piston moves through an infinitesimal (very small) distance dx, the work done by this force is,



Force that system exerts on piston

Fig.4.7: A system enclosed in a cylinder.

$$dW = pdV$$

But $Adx = dV$, the infinitesimal change in the volume of the cylinder. Hence, the work done by the system in bringing out this infinitesimal change in the volume can be written as,

$$dW = pdV \qquad \text{--- (4.1)}$$

If the initial volume of the cylinder is V_i and its volume after some finite change is V_f, then the total work done in changing the volume of the cylinder is,

$$W = \int_{V_i}^{V_f} pdV = p\left(V_f - V_i\right) \qquad \text{--- (4.2)}$$

The change in volume in this case is small.

Example 4.2 : A gas enclosed in a cylinder is expanded to double its initial volume at a constant pressure of one atmosphere. How much work is done in this process?.

Solution : Given: Pressure of one atmosphere $p = 1.01 \times 10^5$ Pa, change in volume $(V_f - V_i) = 0.5$.

$W = p\,(V_f - V_i) = 1.01 \times 10^5\ (+\,0.5)$
$\quad = 0.505 \times 10^5 = 5.05 \times 10^5\,J$

Is this work done on the gas or by the gas? How do you know this?

Now we know that the internal energy of a system can be changed either by providing some heat to it (or, by removing heat from it) or, by doing some work on it (or extracting work from it). Equation (4.2) gives the amount of work done in changing the volume of a system.

When the amount of heat Q is added to the system and the system does not do any work during the process, its internal energy increases by the amount, $\Delta U = Q$. On the other hand, when the system does some work to increase its volume, and no heat is added to it while expanding, the system loses energy to its surrounding and its internal energy decreases. This means that when W is positive, ΔU is negative and, vice versa. Therefore, we can write, $\Delta U = -W$.

In practice, the internal energy can change by both the ways. Therefore, we consider the effect of both together and write the total change in the internal energy as,

$$\Delta U = Q - W \qquad \text{--- (4.3)}$$

This is the mathematical statement of the first law of thermodynamics. This equation tells that the change in the internal energy of a system is the difference between the heat supplied to the system and the work done by the system on its surroundings.

We can rearrange the Eq. (4.3) and write,

$$Q = \Delta U + W \qquad \text{--- (4.4)}$$

This is also the first law of thermodynamics. Both forms of the law are used while studying a system. Equation (4.4) means that when the amount of heat Q is added to a system, its internal energy is increased by an amount ΔU and the remaining is lost in the form of work done W on the surrounding.

Can you tell?

Can you explain the thermodynamics involved in cooking food using a pressure cooker?

Example 4.3 : 1.0 kg of liquid water is boiled at 100 °C and all of it is converted to steam. If the change of state takes place at the atmospheric pressure (1.01×10^5 Pa), calculate (a) the energy transferred to the system, (b) the work done by the system during this change, and (c) the change in the internal energy of the system. Given, the volume of water changes from 1.0×10^{-3} m^3 in liquid form to 1.671 m^3 when in the form of steam. L = 2256kJ/kg.

Solution : (a) Liquid water changes to steam by absorbing the heat of vaporization. In case of water, this is $Q = L \cdot m$

$$\therefore Q = \left(2256 \frac{\text{kJ}}{\text{kg}}\right) \cdot (1.0\text{kg}) = 2256\,\text{kJ}$$

(b) The work done can be calculated by using Eq. (4.1). Here, the pressure is 1.01×10^5 Pa and the change in volume is $dV = (1.671\ \text{m}^3 - 1.0\text{x}10^{-3}\ \text{m}^3)$

The work done is,

$W = pdV = (1.01 \times 10^5\text{Pa}) \times (1.671\ \text{m}^3 - 1.0\text{x}10^{-3}\ \text{m}^3)$

$= 1.69\text{x}10^5\ \text{J} = 169\text{kJ}$

(c) Change in the internal energy of the system can be calculated by using Eq. (4.3).

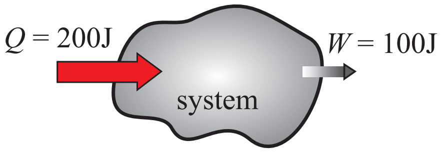
$\Delta U = Q - W$

$= 2256\ \text{kJ} - 169\ \text{kJ} = 2087\ \text{kJ}$

This energy is positive which means that there is an increase in the internal energy of water when it boils. This energy is used to separate water molecules from each other which are closer in liquid water than in water in vapour form.

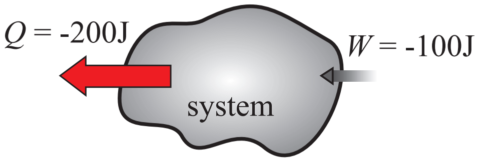
Can you explain how the work done by the system is utilized?

The quantities W and Q can be positive, negative or zero, therefore, ΔU can be positive, negative, or zero. Figure 4.8 shows these three cases. Figure 4.8. (a) shows the case when more heat is added to the system than the work done by it. The internal energy of the system increases, ($\Delta U > 0$). Figure 4.8. (b) shows the case when more work is done by the system than the heat added to it. In this case, the internal energy of the system decreases, ($\Delta U < 0$). Figure 4.8.(c) shows the case when heat added to the system and the work done by it are the same. The internal energy of the system remains unchanged, ($\Delta U = 0$).



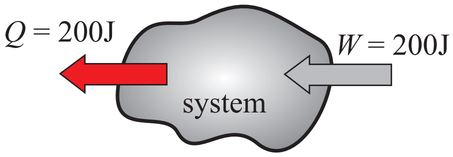
$\Delta U = Q - W = +100$J

Fig. 4.8 (a) : Increase in internal energy ($\Delta U > 0$).



$\Delta U = Q - W = -100$J

Fig. 4.8 (b): Decrease in internal energy ($\Delta U < 0$)



$\Delta U = Q - W = 0$

Fig. 4.8 (c): No change in internal energy ($\Delta U = 0$)

The law of conservation of energy we studied in XI$^{\text{th}}$ Std. was applicable to an isolated system, i.e., to a system in which there is no exchange of energy. The first law of thermodynamics, Eq. (4.3) and Eq. (4.4) is an extension of the law of conservation of energy to systems which are not isolated, i.e., systems that can exchange energy. This exchange can be in the form of work W, or heat Q. The first law of thermodynamics is thus a generalization of the law of conservation of energy.

We started this discussion on the basis of the microscopic view (kinetic theory) of internal energy. In practice, this is not useful because it does not help us in calculating the internal energy of a system. In physics, we need some measurable quantities so that the internal energy of a system can be measured, though indirectly. Equation(4.3), $\Delta U = Q - W$, provides this method. The internal energy appears as the difference between the heat Q supplied to (or released by) the system and the work W done by (or done on) the system. Both are measurable quantities. In physics, we generally discuss volume expansion of a gas when heat is added to it. In this case, the heat added and the resulting expansion of the gas can be measured. The expansion of a gas to do work in moving a piston in an internal combustion engine can also be measured.

Example 4.4: 104 kJ of work is done on certain volume of a gas. If the gas releases 125 kJ of heat, calculate the change in internal energy (in kJ) of the gas.

Solution: We know from the first law of thermodynamics that $\Delta U = Q - W$

Given, W = 104 kJ. This work is done on the gas, hence we write $W = -104$ kJ.

Similarly, the heat is released by the gas and we write Q = - 125 kJ.

Therefore, from the first law of thermodynamics, we have,

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

$$\therefore \Delta U = (125 - 104) = 21 \text{ kJ}$$

Remember this

The first law of thermodynamics gives the relationship between the heat transfer, the work done, and the change in the internal energy of a system.

4.6 Thermodynamic state variables

Earlier, we have discussed thermal equilibrium and understood the concept of temperature and the Zeroth law of thermodynamics. Thermodynamics is not the study of changes in temperature of a system only. As we have seen earlier, when temperature of a system changes (it gains or releases energy), its other properties can also change. Let us understand these properties. We will define the term property of a thermodynamic system first.

Property of a system or a system variable:

It is any measurable or observable characteristic or property of a system when the system remains in equilibrium. A property is also called a state variable of the system. We will use the term variable to describe characteristic of a system. For example, pressure, volume, temperature, density and mass of a system are some of the variables that are used to describe a system. These are measurable properties and are called macroscopic variables of a system.

Intensive and Extensive variables:

Intensive variables do not depend on the size of the system. Extensive variables depend on the size of the system. Consider a system in equilibrium. Let this system be divided into two equal compartments, each with half the original volume. We notice that the pressure p, the temperature T, and the density ρ are the same in both compartments. These are intensive variables. The total mass M, and the internal energy U of the system are equally divided in the two compartments and are extensive variables of the system.

4.6.1 Thermodynamic Equilibrium:

A system is in thermodynamic equilibrium if the following three conditions of equilibrium are satisfied simultaneously. These are, 1) Mechanical equilibrium, 2) Chemical equilibrium, and 3) Thermal equilibrium.

1) Mechanical equilibrium: When there are no unbalanced forces within the system and between the system and its surrounding, the system is said to be in mechanical equilibrium. The system is also said to be in mechanical equilibrium when the pressure throughout the system and between the system and its surrounding is the same. Whenever some unbalanced forces exist within the system, they will get neutralized with time to attain the condition of equilibrium. A system is in mechanical equilibrium when the pressure in it is the sane throughout and does not change with time.

2) Chemical equilibrium: A system is said to be in chemical equilibrium when there are no chemical reactions going on within the system, or there is no transfer of matter from one part of the system to the other due to diffusion. A system is in chemical equilibrium when its chemical composition is the sane throughout and does not change with time.

3) Thermal equilibrium: When the temperature of a system is uniform throughout and does not change with time, the system is said to be in thermal equilibrium. We have discussed thermal equilibrium at length earlier.

Activity

Identify different thermodynamic systems and study their equilibrium. Classify them in to one of the categories we just discussed.

4.6.2 Thermodynamic State Variables and Equation of State

Every equilibrium state of a thermodynamic system is completely described by specific values of some macroscopic variables, also called state variables. For example, an equilibrium state of a gas is completely described by the values of its pressure p, volume V, temperature T, and mass m. Consider a mixture of gases or vapours as in case of the fuel in an automobile engine. Its state can be described by the state variables but we also need its composition to describe its state.

Fig. 4.9: Non equilibrium state.

A thermodynamic system is not always in equilibrium. Figure 4.9 shows such case. For example, when an inflated ball is punctured, the air inside it suddenly expands to the atmosphere. This is not an equilibrium state. During the rapid expansion, pressure of the air may not be uniform throughout. Similarly, the fuel (a mixture of petrol vapour) in the cylinder of an automobile engine undergoing an explosive chemical reaction when ignited by a spark is not an equilibrium state. This is because its temperature and pressure are not uniform. *Such system which is not in equilibrium cannot be described in terms of the state variables*. Eventually, the air in first case, and the fuel in the second case reach a uniform temperature and pressure and attain thermal and mechanical equilibrium with its surroundings. Thus it attains thermodynamic equilibrium.

In simple words, thermodynamic state variables describe the equilibrium states of a system. The various state variables are not always independent. They can be mathematically related. *The mathematical relation between the state variables is called the equation of state*. For example, for an ideal gas, the equation of state is the ideal gas equation,

$$pV = nRT \qquad \text{--- (4.5)}$$

Where, p, V and T are the pressure, the volume and the temperature of the gas, n is the number of moles of the gas and R is the gas constant. For a fixed amount of the gas, i.e., for given n, there are thus, only two independent variables. It could be p and V, or p and T, or V and T.

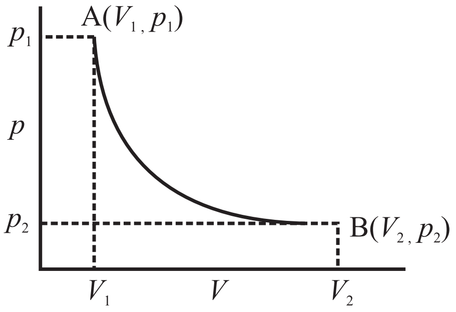


Fig. 4.10: A typical *p-V* diagram.

The graphical representation of equation of state of a system (of a gas) is called the p - V diagram, or the p - V curve (the pressure – volume curve), or the indicator diagram of the system. Figure 4.10 shows a typical p-V diagram for an ideal gas at some constant temperature. The pressure-volume curve for a constant temperature is called an isotherm. Real gases may have more complicated equations of state and therefore, a complicated *p-V* diagram. (The Van-der–Wall's equation with various corrections for example, is complicated for a real gas and is equally interesting). The equation of state of a system (usually a gas confined to a cylinder with a movable, frictionless and massless piston) and its *p - V* diagram are very useful in studying its behavior. In the following sections, we will discuss some systems and their behavior using *p - V* diagrams.

4.6.3 The *p - V* diagram:

Consider Eq. (4.2), i.e.,

$$W = \int_{V_i}^{V_f} \mathrm{d}W = \int_{V_i}^{V_f} P\mathrm{d}V$$

The integral in this equation can be evaluated if we know the relation between the pressure p and the volume V, or the path between the limits of integration. Equation. (4.2) can be represented graphically.

A gas confined to a cylinder with a movable, frictionless, and massless piston can be, 1) expanded with varying pressure (Figure 4.11 a), or 2) it can be compressed with varying pressure Fig. 4.11 (b), or 3) it can expand at constant pressure Fig. 4.11 (c).

The area under the curve in the *p-V* diagram, is the graphical representation of the value of the integral in Eq. (4.2). *Since this integral represents the work done in changing the volume of the gas, the area under the p-V curve also represents the work done in this process.*

Use your brain power

Verify that the area under the *p-V* curve has dimensions of work

Figure 4.11 (a) shows expansion of the gas. Its volume changes due to outward displacement of the piston and the pressure of the gas decreases. The work done by the gas in this case is positive because the volume of the gas has increased.

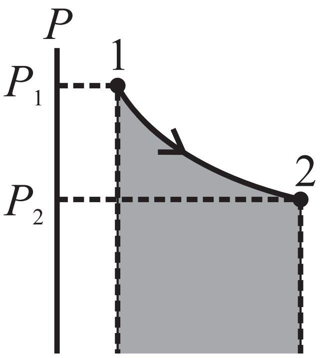


Fig. 4.11 (a): Positive work with varying pressure.

Similarly, Fig. 4.11 (b) shows compression due to inward displacement of the piston. The pressure of the gas is increased and the work done by the gas is now negative.

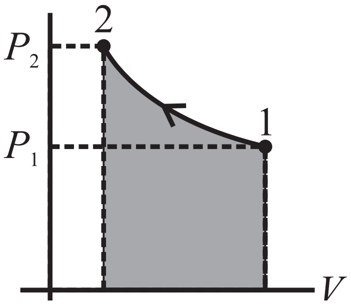
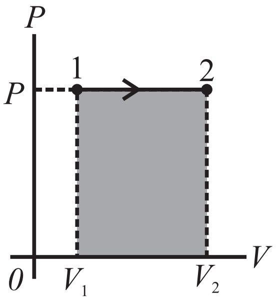


Fig. 4.11 (b): Negative work with varying pressure.

Figure 4.11 (c) shows the *p-V* diagram when the volume of the gas changes from V_1 to V_2 at a constant pressure. The curve is actually a line parallel to the volume axis. The work done during volume change at constant pressure is $W = P(V_2 - V_1)$, (Only in this case the integration is $P(\mathrm{d}V)$)



Work = Area
$= P(v_2 - v_1) > 0$

Fig. 4.11 (c): Positive work at constant pressure.

When the volume is constant in any thermodynamic process, the work done is zero because there is no displacement. These changes are very slow. We will discuss such processes in some details in a later section.

4.7 Thermodynamic Process:

A thermodynamic process is a procedure by which the initial state of a system changes to its final state. During such a change, there may be a transfer of heat into the system from its environment, (positive heat), for example when water boils heat is transferred to water. Heat may be released from the system to its environment (negative heat). Similarly, some work can be done by the system (positive work), or some work can be done on the system (negative work). When the piston in a cylinder is pushed in, some work is done on the system. We know that these changes should occur infinitesimally slowly so that the system is always in thermodynamic equilibrium. Such processes in which changes in the state variables of a system occur infinitesimally slowly are called *quasi static systems*.

When a thermodynamic system changes from its initial state to its final state, it passes through a series of intermediate states. This series of intermediate states when plotted on a p - V diagram is called a path. The p - V curve or the p - V diagram, shown in Fig. 4.11 is such a path. It tells us the way a system has gone through a change.

4.7.1 Work Done During a Thermodynamic Process:

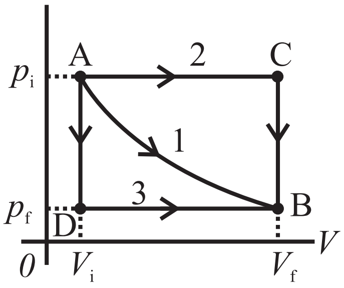


Fig. 4.12 (a): Different ways to change a system.

Let us understand the relation between a path and the work done along a path. Consider Fig. 4.12 (a) which describes different ways in which we can change the state of a system. The system is initially at state A on the p-V diagram. Its pressure is p_i and volume is V_i. We say that the state is indicated by the coordinates (V_i, p_i). The final state of the system is shown by the point B with its coordinates given by (V_f , p_f). The curve 1 (path 1) shown in the Fig. 4.12 (a) is one of the many ways (paths) in which we can change the system from state A to the state B. When the system changes itself from A to B along the path 1, both its pressure and volume change. The pressure decreases while the volume increases. The work done by the system is positive (because the volume increases). It is given by the area under the curve 1 as shown in the Fig. 4.12 (b).

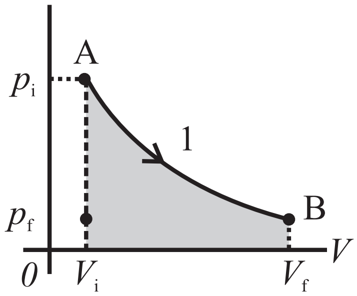


Fig. 4.12 (b): Pressure and volume both change.

Second way to change the state from A to state B is path 2 as shown in Fig. 4.12 (c). In this case, the volume increases to V_f from the point A up to the point C at the constant pressure p_i. The pressure then decrease to p_f as shown. The volume remains constant during this change. The system is now in the state B with its coordinates given by (V_f, p_f).

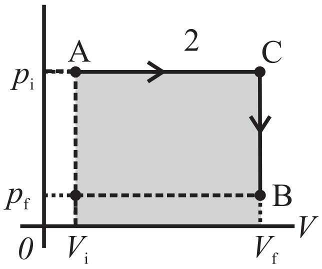


Fig. 4.12 (c): First the volume changes at constant pressure and then pressure changes at constant volume.

The work done in this process is represented by the shaded area under the curve 2 as in Fig. 4.12 (c).

Third way to change the state from A to state B is path 3 as shown in Fig. 4.12 (d). In this case, the pressure decreases from p_i to p_f but the volume remains the same. Next, the volume changes to V_f at constant pressure p_f. The work done in this process is represented by the shaded area under the curve 3 as in Fig. 4.12 (d). *It is easily noticed that in the three cases we discussed, the amount of work done is not the same.*

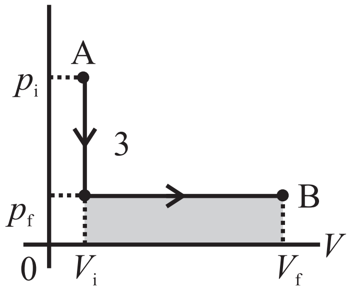


Fig. 4.12 (d): First the pressure drops at constant volume and then volume increases at constant pressure.

Remember that these are only three paths amongst many along which the system can change its state. It is interesting to note that in all these cases, though work done during the change of state is different, the initial and the final state of the system is the same.

We conclude that *the work done by a system depends not only on the initial and the final states, but also on the intermediate states, i.e., on the paths along which the change takes place.*

4.7.2 Heat Added During a Thermodynamic Process:

Thermodynamic state of a system can be changed by adding heat also. Consider a thermodynamic system consisting of an ideal gas confined to a cylinder with a movable, frictionless, and massless piston. Suppose we want to change the initial volume V_i of the gas to the final volume V_f at a constant temperature.

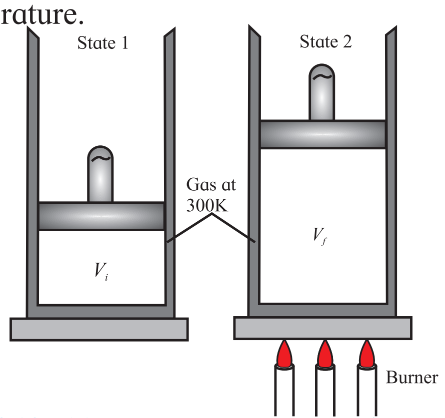


Fig. 4.13 (a): Isothermal expansion of gas, Burner supplies heat, system does work on piston (W>0, Q>0).

There are two different ways in which this change in volume can be made. Figure 4.13 (a) shows the first method. In this case, the gas is heated slowly, in a controlled manner so that it expands at a constant temperature. It reaches the final volume V_f isothermally. The system absorbs a finite amount of heat during this process.

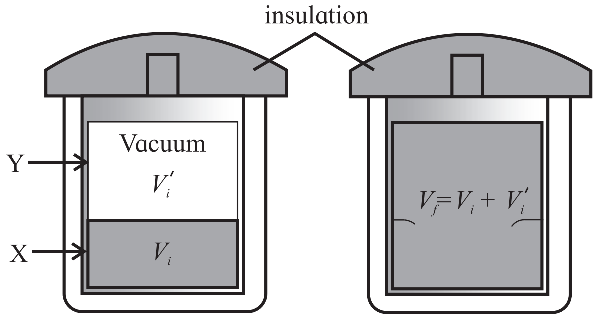


Fig. 4.13 (b): Sudden uncontrolled expansion of gas. No heat enters, system does no work (W=0, Q=0).

In the second case, shown in Fig. 4.13 (b) gas cylinder is now surrounded by an insulating material and it is divided into two compartments by a thin, breakable partition. The compartment X has a volume V_i and the compartment Y has a volume V'_i so that $V_i + V'_i = V_f$. The compartment X of the cylinder is filled with the same amount of gas at the same temperature as that in the first case shown in the Fig. 4.13 (a). The compartment Y is empty, it contains no gas particles or any other form of matter. The initial state of the system is the same in both cases.

The partition is now suddenly broken. This causes a sudden, uncontrolled expansion of the volume of the gas. The gas occupies the volume that was empty before the partition is broken. There is no exchange of heat between the gas and its environment because the cylinder is now surrounded by an insulating material. The final volume of the system after the partition is broken is V_f. In this case, the gas has not done any work during its expansion because it has not pushed any piston or any other surface for its expansion. Such expansion is called free expansion. A common example of free expansion is abrupt puncturing of an inflated balloon or a tyre.

It is experimentally observed that when an ideal gas undergoes a free expansion, there is no change of temperature. Therefore, the final state of the gas in this case also, is the same as the first case. The intermediate states or the paths during the change of state in the first and the second case are different. But the initial and the final states are the same in both cases. Figures 4.13 (a) and (b) represent two different ways of taking a system from the initial state to the final state. This means we have two different paths connecting the same initial and the final states of a system.

In case of the method shown in Fig. 4.13 (a) there is an exchange of heat. In case of the method shown in Fig. 4.13 (b), there is no exchange of heat and also, the system does not do any work at all because there is no displacement of any piston or any other surface.

To conclude, heat transferred to a system also depends on the path.

4.7.3 Classification of Thermodynamic Processes:

As we have seen earlier, a thermodynamic state can be described by its pressure p, volume V, and temperature T. These are the state variables of a system. At present, we will restrict our description of a thermodynamic system only to its pressure, volume and temperature.

A process by which two or more of these variables can be changed is called a thermodynamic process or a thermodynamic change. As we have discussed earlier, there can be a number of different ways to change these parameters, that is, there are different thermodynamic processes. But in practice, for the sake of measurement, any one of the state variables is held constant and other two are varied. This leads us to a very useful way of classifying thermodynamic processes.

1. Reversible and Irreversible Processes:

We know that when two objects at different temperatures are brought in thermal contact they reach a thermal equilibrium. In this process, the object at higher temperature loses its heat and the object at lower temperature gains heat. (But we never observe that after some time, the two objects are back to their initial temperatures). The object that was previously hot never becomes hot again and the previously cold object never becomes cold again once they reach thermal equilibrium. That means the two objects at different temperatures reaching thermal equilibrium is an irreversible process. Such processes do not restore the initial state of the system. Puncturing an inflated balloon or a tyre, rubbing our palms together, burning a candle are some familiar examples of irreversible thermodynamic processes.

Some processes such as melting of ice, freezing of water, boiling of water, condensation of steam can be reversed. That means the initial sates of the system can be restored. These are some familiar thermodynamic processes that are reversible.

A thermodynamic process (change) can be a reversible process (change) or it can be an irreversible process (change).

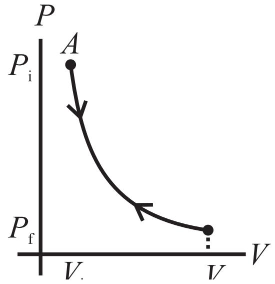


Fig. 4.14 (a): p-V diagram of Reversible process.

Earlier, we have seen that a thermodynamic process can be represented by a p - V diagram. A reversible process is a change that can be retraced in reverse (opposite) direction. The path of a reversible thermodynamic process is the same in the forward and the reverse direction. Figure 4.14 (a) shows the path of a reversible thermodynamic process. This path shows a reversible expansion of a gas followed by its reversible compression. Such changes are very slow and there is no loss of any energy in the process and the system is back to its initial state after it is taken along the reverse path. Reversible processes are ideal processes. *A real thermodynamic process will always encounter some loss due to friction or some other dissipative forces.*

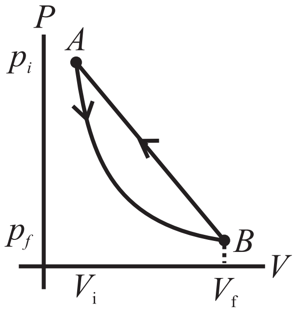


Fig. 4.13 (b): p-V diagram of Irreversible process.

An irreversible process is a change that cannot be retraced in reverse (opposite) direction. The path of an irreversible thermodynamic process is not the same in the forward and the reverse direction. Figure 4.14 (b) shows the path of an irreversible thermodynamic process. There is a permanent loss of energy from the system due to friction or other dissipative forces in an irreversible process. The change of state depends on the path taken to change the state during an irreversible process. An irreversible process shows a hysteresis. Most real life thermodynamic processes that we deal with are irreversible.

Try this

Rub your palms in one direction only (say away from your wrist) till you feel warmth. Rub them in the opposite way. Do you feel warm again or you feel cold? Discuss your experience.

Cause of Irreversibility:

There are two main reasons of the irreversibility of a thermodynamic process.

1. Many processes such as a free expansion or an explosive chemical reaction take the system to non-equilibrium states.
2. Most processes involve friction, viscosity or some other dissipative forces. For example, an object sliding on a surface stops after moving through some distance due to friction and loses its mechanical energy in the form of heat to the surface and it gets heated itself. The dissipative forces are always present everywhere and can be minimized at best, but cannot be fully eliminated.

Remember this

All spontaneous natural processes are irreversible. For example, heat always flows from a higher temperature to a lower temperature on its own. We can say that an irreversible process gives us the preferred direction of a thermodynamic process. *An irreversible process can be said to be unidirectional process.*

Assumptions for discussion of thermodynamic processes:

We will be discussing various types of thermodynamic systems in the following sections. Here are the assumptions we make for this discussion.

i) Majority of the thermodynamic processes we will be discussing in the following sections are reversible. That is, they are quasistatic in nature. They are extremely slow and the system undergoes infinitesimal change at every stage except the adiabatic processes. The system is, therefore, in thermodynamic equilibrium during all the change.

ii) The 'system' involved in all the processes is an ideal gas enclosed in a cylinder having a movable, frictionless, and massless piston. Depending on the requirements of the process, the walls of the cylinder can be good thermal conductors (for an isothermal process) or can be thermally insulating (for an adiabatic process).

iii) The ideal gas equation is applicable to the system.

2. Isothermal process:

A process in which change in pressure and volume takes place at a constant temperature is called an isothermal process or isothermal change. For such a system $\Delta T = 0$. *Isothermal process is a constant temperature process*. This is possible when a system is in good thermal contact with its environment, and the transfer of heat from, or to the system, is extremely slow so that thermal equilibrium is maintained throughout the change.

For example, melting of ice, which takes place at constant temperature, is an isothermal process.

Remember this

1. For an isothermal process, none of the quantities Q and W is zero.
2. For an isothermal change, total amount of heat of the system does not remain constant.

Thermodynamics of Isothermal Process:

The temperature of a system remains constant in an isothermal change and Boyle's law can be applied to study these changes. Therefore, the equation of state for an isothermal change is given by,

$$pV = \text{constant} \qquad \text{--- (4.6)}$$

If p_i, V_i and p_f, V_f are the variables of a system in its initial and the final states respectively, then for an isothermal change,

$p_i V_i = p_f V_f =$ constant.

Consider the isothermal expansion of an ideal gas. Let its initial volume be V_i and the final volume be V_f. The work done in an infinitesimally small isothermal expansion is given by Eq. (4.1), $dW = pdV$. The total work done in bringing out the expansion from the initial volume V_i to the final volume V_f is given by,

$$W = \int_{V_i}^{V_f} pdV$$

But we know that for an ideal gas, $pV = nRT$. Using this in the previous equation we get,

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

$$\therefore W = nRT ln \frac{V_f}{V_i} \qquad \text{--- (4.7)}$$

For an ideal gas, its internal energy depends on its temperature. Therefore, during an isothermal process, the internal energy of an ideal gas remains constant ($\Delta U = 0$) because its temperature is constant ($\Delta T = 0$).

The first law of thermodynamics (Eq. 4.4) when applied to an isothermal process would now read as,

$$Q = W \qquad \text{--- (4.8)}$$

$$\therefore Q = W = nRT ln \frac{V_f}{V_i} \qquad \text{--- (4.9)}$$

Thus, the heat transferred to the gas is completely converted into the work done, i.e., for expansion of the gas. From Eq. (4.8) it is obvious that when the gas absorbs heat, it does positive work and its volume expands. When the gas is compressed, it releases heat and it does negative work.

Any change of phase occurs at a constant temperature, and therefore, it is an isothermal process. Figure 4.15 shows the p - V diagram of an isothermal process. It is called as an *isotherm*.

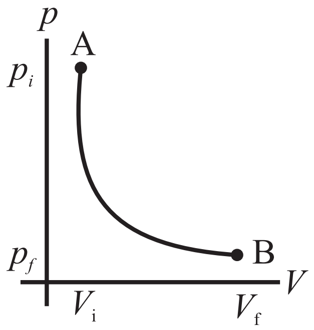


Fig. 4.15: p-V diagram of an isothermal process.

Example 4.5:

0.5 mole of gas at temp 300 K expands isothermally from an initial volume of 2.0L to final volume of 6.0L. (a) What is the work done by the gas ? ($R = 8.319$ J mol^{-1} K^{-1}), (b) How much heat is supplied to the gas?

Solution: (a) The work done in isothermal expansion is $W = nRT\ln\left(\frac{V_f}{V_i}\right)$

Where n = 0.5, $V_f = 6L$, $V_i = 2L$

$$W = 0.5 \text{ mol} \times \frac{8.319}{\text{mol}\cdot\text{K}} \times 300K.\ln\left(\frac{6L}{2L}\right)$$

$$= 1.369 \text{ kJ}.$$

(b) From the first law of thermodynamics, the heat supplied in an isothermal process is spent to do work on a system. Therefore, Q = W = 1.369 kJ.

Can you explain the significance of positive sign of the work done and the heat?

Remember this

Always remember for an isothermal process:

1. Equation of state: pV = constant
2. $\Delta T = 0$. Constant temperature process, perfect thermal equilibrium with environment.
3. $\Delta U = 0$. No change in internal energy, energy is exchanged with the environment.
4. $Q = W$. Energy exchanged is used to do work.
5. $W = p\,\Delta V$
6. An isothermal change is a very slow change. The system exchanges heat with its environment and is in thermal equilibrium with it throughout the change.

Use your brain power

Show that the isothermal work may also be expressed as $W = nRT\ln\left(\frac{P_i}{P_f}\right)$.

3. Isobaric process:

It is a constant pressure process. Boiling water at constant pressure, normally at atmospheric pressure, is an isobaric process. Figure (4.16) shows the *p-V* diagram of an isobaric process. It is called as an *isobar*. The different curves shown on the maps provided by the meteorology department are isobars. They indicate the locations having same pressure in a region. *For an isobaric process, none of the quantities* ΔU, Q *and* W *is zero*.

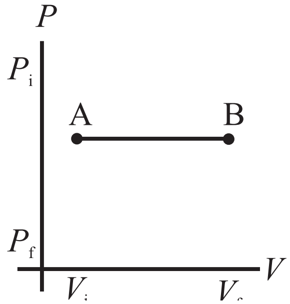


Fig. 4.16 : *p - V* diagram of an isobaric process.

Thermodynamics of Isobaric process:

The pressure of a system remains constant in this process i.e. $\Delta p = 0$. Consider an ideal gas undergoing volume expansion at constant pressure. If V_i and T_i are its volume and temperature in the initial state of a system and V_f and T_f are its final volume and temperature respectively, the work done in the expansion is given by

$$W = PdV = P\left(V_f - V_i\right) = nR\left(T_f - T_i\right) \quad \text{--- (4.10)}$$

Also, the change in the internal energy of a system is given by,

$$\Delta U = nC_V\Delta T = nC_V\left(T_f - T_i\right) \quad \text{--- (4.11)}$$

Where, C_V is the specific heat at constant volume and $\Delta T = (T_f - T_i)$ is the change in its temperature during the isobaric process.

According to the first law of thermodynamics, the heat exchanged is given by, $Q = \Delta U + W$

Using the previous two equations we get,

$$Q = nC_V\left(T_f - T_i\right) + nR\left(T_f - T_i\right)$$

$$Q = \left(nC_V + nR\right)\left(T_f - T_i\right)$$

$$Q = nC_P\left(T_f - T_i\right) \quad \text{--- (4.12)}$$

Where, C_p is the specific heat at constant pressure $\therefore C_p = C_V + R$.

Equation (4.12) tells that *the temperature of a system changes in an isobaric process therefore, its internal energy also changes* (Eq. 4.11). The heat exchanged (Eq. 4.12) is partly used for increasing the temperature and partly to do some work. The change in the temperature of the system depends on the specific heat at constant pressure C_p.

Example 4.6:

One mole of an ideal gas is initially kept in a cylinder with a movable frictionless and massless piston at pressure of 1.01MPa, and temperature 27°C. It is then expanded till its volume is doubled. How much work is done if the expansion is isobaric? (R = 8.314 SI Units)

Solution: Work done in isobaric process given by $W = P\Delta V = (V_f - V_i)$.

$V_f = 2V_i \therefore \mathrm{W} = pV_i$.

V_i can be found by using the ideal gas equation for initial state.

$P_i V_i = nRT_i$ for n = 1 mol,

$$V_i = \frac{RT_i}{P_i} = 8.314 \times \frac{300}{1 \times 10^6} = 2.494 \times 10^{-3}\,\mathrm{m}^3$$

$$\therefore W = 10^6 \times 2.494 \times 10^{-3}$$

$$W = 2.494\ \mathrm{kJ}$$

Remember this

Always remember for an isobaric process:

1. $\Delta p = 0$. Constant pressure process.
2. Temperature of the system changes, $\Delta T \neq 0$.
3. $Q = \Delta U + W$. Energy exchanged is used to do work and also to change internal energy, i.e., to increase its temperature.
4. $W = p\Delta V$. Volume changes when work is done.

4. Isochoric process:

It is a constant volume process. A system does no work on its environment during an isochoric change. Figure 4.17 shows the *p-V* diagram of an isochoric process. For an isochoric process, $\Delta V = 0$, and we have, from the first law of thermodynamics, $\Delta U = Q$. This means that for an isochoric change, all the energy added in the form of heat remains in the system itself and causes an increase in its internal energy. Heating a gas in a constant volume container or diffusion of a gas in a closed chamber are some examples of isochoric process.

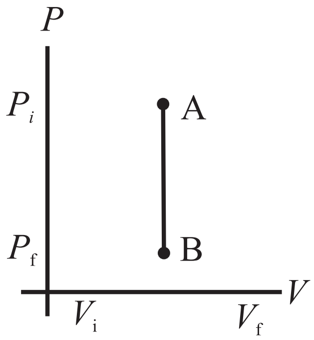


Fig. 4.17: p-V diagram of isochoric process.

Thermodynamics of Isochoric process:

For an isochoric process, we have, $\Delta V = 0$. The system does not do any work and all the energy supplied to the system is converted into its internal energy. The first law of thermodynamics for isochoric process is

$$Q = \Delta U \qquad \text{--- (4.13)}$$

The change in internal energy is given by

$$\Delta U = nC_V\,\Delta T$$

The work done is given by

$W = p\Delta V = 0$ (because $\Delta V = 0$).

The heat exchanged is given by the first law of thermodynamics,

$$Q = \Delta U + W = \Delta U = nC_V\,\Delta T \qquad \text{--- (4.14)}$$

Remember this

Always remember for an isochoric process:

1. $\Delta V = 0$. Constant volume process.
2. $W = 0$. No work is done because volume remains constant, $\Delta V = 0$.
3. $Q = \Delta U$. Energy exchanged is used to change internal energy.
4. $\Delta T \neq 0$. Temperature of the system changes.

5. Adiabatic process:

It is a process during which there is no transfer of heat from or to the system. Figure 4.18 shows the P-V diagram of an adiabatic process. For an adiabatic change, $Q = 0$. Heat transfer to or from the system is prevented by either perfectly insulating the system from its environment, or by carrying out the change rapidly so that there is no time for any exchange of heat. Puncturing an inflated balloon or a tyre are some familiar examples of adiabatic changes. For an adiabatic change,

$$\Delta U = - W \qquad \text{--- (4.15)}$$

When a system expands adiabatically, W is positive (work is done by the system) and ΔU is negative, the internal energy of the system decreases. When a system is compressed adiabatically, W is negative (work is done on the system), and ΔU is positive. *The internal energy of the system increases in an adiabatic process.* It is observed that for many systems, temperature increases when internal energy increases and decreases when the internal energy is decreased.

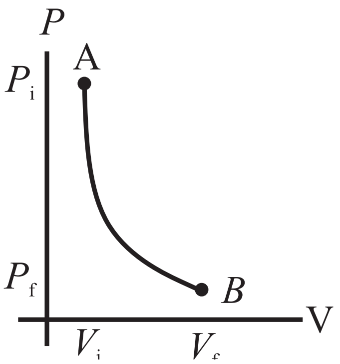


Fig. 4.18: p-V diagram of adiabatic process.

Thermodynamics of Adiabatic process:

For an adiabatic process we have,

$$PV^{\gamma} = \text{constant} = C \qquad \text{--- (4.16)}$$

where, γ is the ratio of the specific heat at constant pressure to the specific heat at constant volume, i.e., $\gamma = \frac{C_p}{C_V}$

γ is also called *adiabatic ratio*. For moderate temperature changes, the value of γ is $\frac{5}{3}$ for monoatomic gases, $\frac{7}{5}$ for diatomic gases and $\frac{8}{6} = \frac{4}{3}$ for triatomic gases. The values have been calculated in Chapter 3, Equations (3.30), (3.33) and (3.39) can be extended to obtain these values.

An adiabatic system is thermally isolated from its environment, therefore, it cannot exchange heat with it. Therefore, when a system undergoes an adiabatic change, its temperature and internal energy both change. The change in internal energy is,

$$\Delta U = C_v\,(\Delta T) \qquad \text{--- (4.17)}$$

The work done is,

$$W = \int_{V_i}^{V_f} P\mathrm{d}V$$

Using Eq. (4.16) we have,

$$W = C\int_{V_i}^{V_f} \frac{\mathrm{d}V}{V^{\gamma}}$$

$$W = C \times \left[\frac{V^{(-\gamma+1)}}{1-\gamma}\right]_{V_i}^{V_f},$$

where V changes from V_i to V_f.

$$W = \frac{C}{(1-\gamma)} \times \left[\frac{1}{V_f^{(\gamma-1)}} - \frac{1}{V_i^{(\gamma-1)}}\right] \qquad \text{--- (4.18)}$$

From (Eq. 4.16) we have,

$$pV^{\gamma} = C$$

or,

$$p_i V_i^{\gamma} = p_f V_f^{\gamma}$$

Therefore, we can write (Eq. 4.18) as,

$$W = \frac{1}{(1-\gamma)} \times \left[\frac{p_f V_f^{\gamma}}{V_f^{(\gamma-1)}} - \frac{p_i V_i^{\gamma}}{V_i^{(\gamma-1)}}\right]$$

$$W = \frac{1}{(1-\gamma)} \times \left(p_f V_f - p_i V_i\right) \qquad \text{--- (4.19)}$$

$$W = \frac{\left(p_f V_f - p_i V_i\right)}{(1-\gamma)} \qquad \text{--- (4.20)}$$

Equation (4.20) implies that when work is done by the gas, i.e., when the gas expands, $W > 0$, and $T_i > T_f$. This mean that the gas will cool down. Similarly, if the work is done on the gas, i.e., if the gas is compressed $W < 0$, and $T_i < T_f$. This means that the gas will warm up.

Remember this

Always remember for an adiabatic process:

1. Equation of state: pV^{γ} = constant.
2. $Q = 0$. No exchange of heat with the surroundings. The system is perfectly insulated from its environment, or the change is very rapid.
3. $\Delta U = -W$. All the work is utilized to change the internal energy of the system.
4. $\Delta T \neq 0$. Temperature of the system changes.
5. Adiabatic expansion causes cooling and adiabatic compression causes heating up of the system.
6. $W = \dfrac{nR\left(T_i - T_f\right)}{\left(1-\gamma\right)} = \dfrac{\left(p_f V_f - p_i V_i\right)}{\left(1-\gamma\right)}$
7. Most of the times, an adiabatic change is a sudden change. During a sudden change, the system does not find any time to exchange heat with its environment.

Example 4.7: An ideal gas of volume 1.0L is adiabatically compressed to (1/15)th of its initial volume. Its initial pressure and temperature is 1.01 ×10^5 Pa and 27°C respectively. Given C_V for ideal gas = 20.8J/mol.K and γ = 1.4. Calculate (a) final pressure, (b) work done, and (c) final temperature. (d) How would your answers change, if the process were isothermal ?

Solution: (a) To calculate the final pressure p_f. This can be calculated by using

$$P_f = P_i\left(\frac{V_i}{V_f}\right)^{\gamma}$$

$$= (1.01\times10^5\,\text{Pa})\,(15)^{1.4}$$

$$= 44.8\times10^5\,\text{Pa (about 45 atm)}\,.$$

(b) To calculate the work done,

$$W = \frac{\left(P_f V_f - P_i V_i\right)}{\left(1-\gamma\right)}$$

$$W = \frac{1}{\gamma-1}\left(P_i V_i - P_f P_f\right)$$

$$= \frac{1}{1.4-1}\left[\begin{matrix}\left[(1.01\times10^5)(1.0\times10^{-3})\right]\\ -\left[(44.8\times10^5)\left(\dfrac{1.0\times10^{-3}\,\text{m}^3}{15}\right)\right]\end{matrix}\right]$$

$$= -\,494\ \text{J}$$

(c) To calculate final temperature T_f consider,

$$T_f = T_i\left(\frac{V_i}{V_f}\right)^{\gamma-1} = (300\,\text{K})\,(15)^{0.40}$$

$$= 886\text{K} = 613°\text{C}$$

The pressure involved in this process is about 45 atm. This is an adiabatic compression. The temperature of the gas is increased without any transfer of heat. Similar heating is used in automobile (diesel) engines. The fuel used in the engine is heated rapidly to such a high temperature that it ignites without any spark plug.

(d)

(i) Pressure in isothermal process is given by

$P_i V_i = P_f V_f$

$$P_f = \frac{P_i V_i}{V_f} = 15\ \text{atm}$$

(ii) There will be no change in the temperature because it is an isothermal process.

(iii) Work done in isothermal process is given by

$$W = nRT\ln\left(\frac{V_f}{V_i}\right),\ n = 0.405$$

$$= 0.0405\times831\times300\,(-0.270)$$

$$= -2726\ \text{J}$$

n = 0.0405 mol. n, the number of moles, can be calculated by using $PV = nRT$.

The work done during adiabatic process is very much less than the work done during isothermal process. Can you explain this? What happens to this work which is apparently 'lost' ?

Use your brain power

1. Why is the p-V curve for adiabatic process steeper than that for isothermal process? 2. Explain formation of clouds at high altitude.

Can you tell?

When the temperature of a system is increased or decreased in an adiabatic heating or cooling, is there any transfer of heat to the system or from the system?

6. Cyclic Process:

A thermodynamic process that returns a system to its initial state is a cyclic process. In this process, the initial and the final state is the same. Figure 4.19 shows the *p*-*V* diagram of a cyclic process. For a cyclic process, the total change in the internal energy of a system is zero. ($\Delta U = 0$). According to the first law of thermodynamics, we have, for a cyclic process,

$$Q = W \qquad \text{--- (4.21)}$$

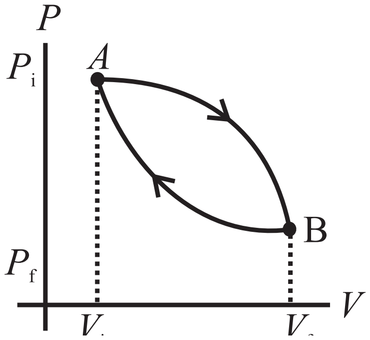


Fig. 4.19: p-V diagram of cyclic process.

Remember this

Working of all heat engines is a cyclic process.

Example 4.8: Cyclic process:

The total work done in the cyclic process shown in the Fig. 4.19 is -1000 J. (a) What does the negative sign mean? (b) What is the change in internal energy and the heat transferred during this process. (c) What will happen when the direction of the cycle is changed?

Solution: (a) Work done in the process from A to B along path 1 is given by the area under this curve. In this process, volume is increasing therefore the work done is positive.

Work done in the process from B to A along path 2 is given by the area under this curve. In this process volume is decreasing therefore the work done is negative.

The total work done during the complete cycle, from A to B along path 1 and form B to A along path 2 is the area enclosed by the closed loop. This is the difference between the area under the curve 2 and that under the curve 1. Since the area under curve 2 is negative and larger than the area under the curve 1, the area of the loop is also negative. That means the work is done by the system is negative.

(b) This is a cyclic process which means the initial and the final state of the system is the same. For a cyclic process $\Delta U = 0$, so $Q = W = -1000$ J. That is, 1000 joules of heat must be rejected by the system.

(c) If the direction of the cycle is changed the work done will be positive. The system will do work. From this example we conclude that: The total work done in a cyclic process is *positive* if the process is goes around the cycle in a *clockwise direction*. The total work done in a cyclic process is *negative* if the process goes around the cycle in a *counterclockwise direction*.

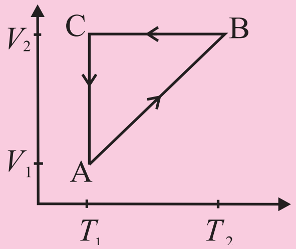
Can you tell?

1. How would you interpret the Eq. 4.21 for a cyclic process?
2. An engine works at 5000 RPM, and it performs 1000 J of work in one cycle. If the engine runs for 10 min, how much total work is done by the engine?

7. Free Expansion:

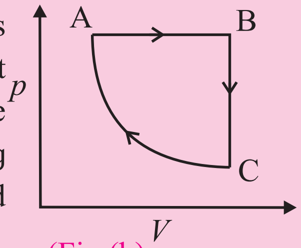
These expansions are adiabatic expansions and there is no exchange of heat between a system and its environment. Also, there is no work done on the system or by the system. $Q = W = 0$, and according to the first law of thermodynamics, $\Delta U = 0$. For example, when a balloon is ruptured suddenly, or a tyre is suddenly punctured, the air inside rushes out rapidly but there is no displacement of a piston or any other surface. Free expansion is different than other thermodynamic processes we have discussed so far because it is an *uncontrolled change*. It is an instantaneous change and *the system is not in thermodynamic equilibrium. A free expansion cannot be plotted on a p-V diagram*. Only its initial and the final state can be plotted.

Example 4.9: A cyclic process ABCA is shown in V-T diagram (Fig (a)). It is performed with a constant mass of ideal gas. How will this transform to a *p-V* digram?



(Fig (a))

Solution: Straight line form A to B on the *V-T* diagram means $V \propto T$, i.e., '*p*' is constant. *V* is constant and temperature decreases. Along B - C i.e., *p* should also decrease.



(Fig (b))

Temperature is constant along CA. That means it is an isothermal process. The *p-V* curve would look as shown in the Fig (b).

4.8 Heat Engines:

As mentioned earlier, thermodynamics is related to study of different processes involving conversion of heat and work into each other. In this section, we will study the practical machines that convert some heat into work. These are heat engines.

4.8.1 Heat Engine:

Heat engines are devices that transform heat partly into work or mechanical energy. Heat engines work by using cyclic processes and involve thermodynamic changes. Automobile engines are familiar examples of heat engines.

A heat engine receives heat from a source called *reservoir* and converts some of it into work. Remember that all the heat absorbed is *not* converted into work by a heat engine. Some heat is lost in the form of exhaust.

A typical heat engine has the following elements:

(1) A working substance: It is called the *system*. It can be an ideal gas for an ideal heat engine (to be discussed later). For a practical heat engine, the working substance can be a mixture of fuel vapour and air in a gasoline (petrol) or diesel engine, or steam in a steam engine. *It is the working substance that absorbs heat and does work.*

(2) Hot and cold reservoir: The working substance interacts with the reservoirs. The *hot reservoir* is the source of heat. It is at a relatively high temperature and is capable of providing large amount of heat at constant higher temperature, T_H. It is also called as the *source*. The *cold reservoir* absorbs large amount of heat from the working substance at constant lower temperature, T_C. It is also called as the *sink*.

(3) Cylinder: Generally, the working substance is enclosed in a cylinder with a moving, frictionless, and massless piston. The working substance does some work by displacing the piston in the cylinder. This displacement is transferred to the environment using some arrangement such as a crank shaft which transfers mechanical energy to the wheels of a vehicle.

Heat engines are of two basic types. They differ in the way the working substance absorbs heat. In an *external combustion engine*, the working substance is heated externally as in case of a steam engine. In case of the *internal combustion engine*, the working substance is heated internally similar to an automobile engine using gasoline or diesel.

Any heat engine works in following three basic steps.

1. The working substance absorbs heat from a hot reservoir at higher temperature.
2. Part of the heat absorbed by the working substance is converted into work.
3. The remaining heat is transferred to a cold reservoir at lower temperature.

Heat engines are classified according to the working substance used and the way these steps are actually implemented during its operation. Heat engines are diagrammatically represented by an energy flow diagram schematically shown in Fig. 4.20. Energy exchange takes place during various stages of working of a heat engine.

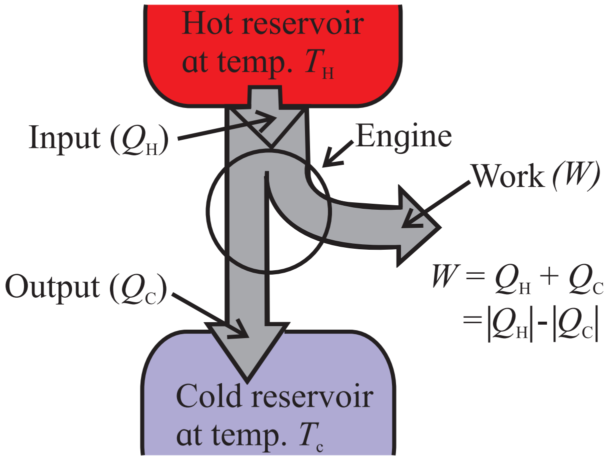


Fig. 4.20: Schematic energy flow diagram of a heat engine.

Let Q_H be the heat absorbed by the working substance at the source, and Q_C be the heat rejected by it at the sink. In a heat engine, Q_H is positive and Q_C is negative. Also, let W be the work done by the working substance.

In the Fig. 4.20, the circle represents the engine. The 'heat pipelines' shown in the diagram represent the heat absorbed, rejected, and converted into work. The width of the heat 'pipeline' indicated by Q_H, is proportional to the amount of heat absorbed at the source. Width of the branch indicated by Q_C is proportional to the magnitude $|Q_C|$ of the amount of heat rejected at the sink. Width of the branch of the pipeline indicated by W is proportional to the part of the heat converted into mechanical work.

One single execution of the steps mentioned above is one operating 'cycle' of the engine. Several such cycles are repeated when a heat engine operates. The quantities Q_H and Q_C represent the amount of heat absorbed (positive) and rejected (negative) respectivety during one cycle of operation.

Do you know?

The number of repetitions of the operating cycles of an automobile engine is indicated by its RPM or Revolutions Per Minute.

The net heat Q absorbed per operating cycle is,

$$Q = Q_H + Q_C = |Q_H| - |Q_c| \qquad \text{--- (4.22)}$$

The net work done in one operating cycle, by the working substance, is given by using the first law of thermodynamics.

$$W = Q = |Q_H| - |Q_c| \qquad \text{--- (4.23)}$$

Ideally, we would expect a heat engine to convert all the heat absorbed, Q_H, in to work. Practically, this is not possible. There is always some heat lost, i.e., $Q_C \neq 0$. The thermal efficiency η of the heat engine is defined as,

$$\eta = \frac{W}{Q_H} \qquad \text{--- (4.24)}$$

Thus, the thermal efficiency, or simply, the efficiency of a heat engine is the ratio of the work done by the working substance and the amount of heat absorbed by it. It is the ratio of the output, in the form of the work done W by the engine, and the input, in the form of the heat supplied Q_H. In simple words, *efficiency of a heat engine is the fraction of the heat absorbed that is converted into work*, Eq. (4.24).

In terms of the energy flow diagram Fig. 4.20, the 'pipeline' representing the work is as wide as possible and the pipeline representing the exhaust is as narrow as possible for the most efficient heat engine.

There is a fundamental limit on the efficiency of a heat engine set by the second law of thermodynamics, which we will discuss later.

Using Eq. (4.22) and Eq. (4.23) we can write the efficiency of a heat engine as,

$$\eta = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 - \frac{|Q_C|}{|Q_H|} \quad \text{--- (4.25)}$$

Equation (4.25) gives the thermal efficiency of a heat engine. *It is a ratio of the quantities which represent energy.* Therefore, it has no units but, we must express W, Q_H, and Q_C in the same units.

4.8.2 The Heat Engine Cycle and the *p-V* Diagram:

As discussed previously, the working of a heat engine is a well defined sequence of operations. It is a cyclic thermodynamic process. We know that a thermodynamic process can be represented by a *p-V* diagram. We will now discuss the *p-V* diagram of a heat engine. Keep in mind that this is a *p-V* diagram of a general heat engine. There are different ways of operating a heat engine. We will discuss some such heat engines in the following sections.

A heat engine uses energy absorbed in the form of heat to do work and then rejects the heat which cannot be used to do work. Heat is absorbed in one part of the cycle, work is done in another part, and the unused heat is rejected in yet other part of the cycle. The *p-V* diagram of a typical heat engine is shown in Fig. (4.21).

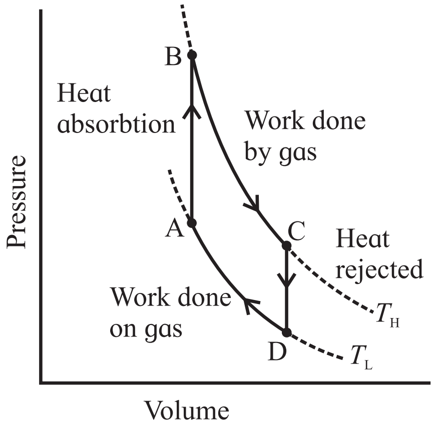


Fig. 4.21: *p-V* diagram of a typical heat engine.

The operating cycle begins at the point A in the cycle. The working substance, the gas in this case, absorbs heat at constant volume and no work is done by the gas or on the gas. The pressure is increased till the point B is reached. The temperature of the gas also increases and its internal energy increases.

The gas starts expanding by pushing the piston away and its volume changes from the point B to the point C. Because the gas expands, its pressure is reduced. The gas does work in this part of the cycle.

When the point C is reached, the excess heat, the heat that is not utilized in doing work by the gas, is rejected. The gas cools down and its internal energy decreases. This process is again at constant volume. The pressure of the gas is reduced and point D on the *p-V* diagram is reached.

The gas is now compressed. Its volume decreases and its pressure increases. The change continues till the point A is reached. The cycle is complete and the system is ready for the next cycle.

Thus, the *p-V* diagram is a visual tool for the study of heat engines. The working substance of a heat engine is usually a gaseous mixture. Study of the *p-V* diagram helps us understand the behavior of the three state variables of a gas throughout the operational cycle.

The operation of a heat engine is a cyclic process therefore, its *p-V diagram is a closed loop*. The area of the loop represents the work done during one complete cycle.

Since work is done by the gas, or on the gas, only when its volume changes, the *p-V* diagram provides a visual interpretation of the work done during one complete cycle. Similarly, the internal energy of the gas depends upon its temperature. Hence, the *p-V* diagram along with the temperatures calculated from the ideal gas law determines the changes in the internal energy of the gas.

We can calculate the amount of heat added or rejected from the first law of thermodynamics.

Thus, a p-V diagram helps us analyze the performance of any heat engine which uses a gas as its working substance.

4.9 Refrigerators and Heat Pumps:

So far, we have discussed a heat engine which takes heat from a source at higher temperature and rejects it to a sink at lower temperature. The input provided to the working substance (a gas or a mixture of gasoline and air) in a heat engine is in the form of heat which is converted into mechanical work as output. Figure 4.20 shows this in the form of an energy flow diagram. *Refrigerators and heat pumps are heat engines that work in backward direction. They convert mechanical work into heat.*

4.9.1 Heat Flow from a Colder Region to a Hotter Region:

According to the second law of thermodynamics (to be discussed in the next article), *heat cannot flow from a region of lower temperature to a region of higher temperature on its own*. We can force heat to flow from a region of lower temperature to a region of higher temperature by doing work on the system (or, on the working substance of a heat engine). Refrigerators or air-conditioners and heat pumps are examples of heat engines which cause heat to be transferred from a cold region to a hot region. Usually, this is achieved with the aid of *phase change* of a fluid, called the refrigerant. The refrigerant is forced to evaporate and then condense by successively decreasing and increasing its pressure. It can, therefore, 'pump' energy from a region at lower temperature to a region of higher temperature. It extracts the heat of vaporization of the refrigerant from the cold region and rejects it to the hotter region outside the refrigerator. This results in cooling down the cold region further.

Figure 4.22 shows the concept of transferring heat from a cold region to a hot region in a schematic way. Heat from the cold region is carried to the hot region by the refrigerant. It extracts heat from a cold region due to forced evaporation. The heat of evaporation of the refrigerant thus absorbed is rejected by compressing and condensing it into liquid at a higher temperature. All this process is carried out in a mechanism involving a compressor and closed tubing such as seen at the back of a house hold refrigerator.

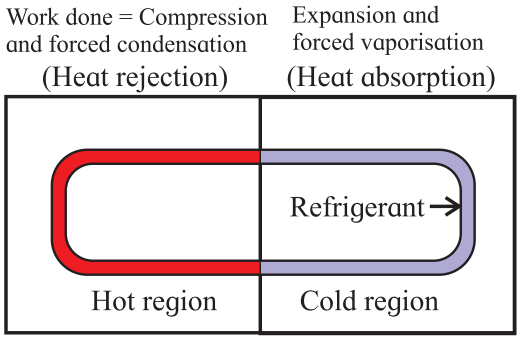


Fig. 4.22: Schematic diagram of transferring heat from a cold region to a hot region.

4.9.2 Refrigerator:

Refrigeration is a process of cooling a space or substance of a system and/or to maintain its temperature below its ambient temperature. *In simple words, refrigeration is artificial cooling.*

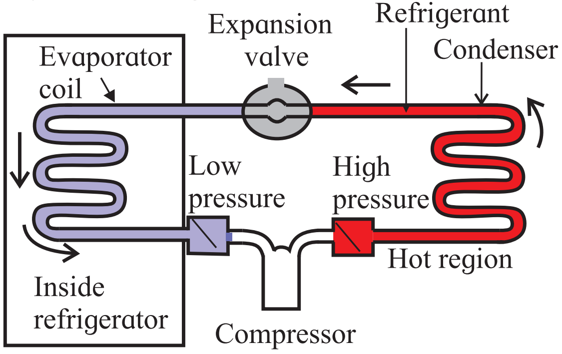


Fig. 4.23 (a): Schematics of a refrigerator.

A refrigerator extracts heat from a cold region (inside the chamber, or the compartments) and delivers it to the surrounding (the atmosphere) thus, further cooling the cold region. That's the reason why if you place your hand behind a working refrigerator, you can feel the warm air. But the interior of the refrigerator is cold. An air conditioner also works on similar principles.

Figure 4.23 (a) shows the schematics of the mechanism used in a typical refrigerator. It consists of a compressor, an expansion valve, and a closed tube which carries the refrigerant. Part of the tube, called the cooling coil, is in the region which is to be cooled at lower temperature and lower pressure. The other part which is exposed to the surrounding (generally, the atmosphere) is at a higher temperature and higher pressure. A fluid such as isobutane is used as refrigerant. Normally, the cold and the hot part of the coil contain the refrigerant as a mixture of liquid and vapour phase in equilibrium.

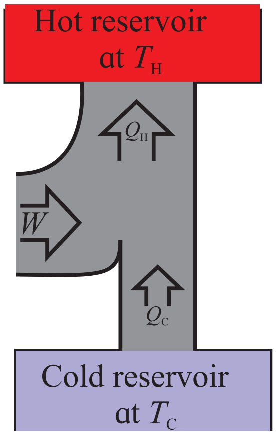


Fig. 4.23 (b): Energy flow diagram of a refrigerator.

Figure 4.23 (b) shows the energy flow diagram of a refrigerator. As you can see, the heat extracted from a cold reservoir is supplemented by the mechanical work done (on the refrigerant) by the compressor and the total energy is rejected at the hot reservoir. The refrigerant goes through the following steps in one complete cycle of refrigeration.

Step 1: The fluid passes through a nozzle and expands into a low-pressure area. Similar to the way carbon dioxide comes out of a fire extinguisher and cools down, the fluid turns into a gas and cools down. This is essentially an adiabatic expansion.

Step 2: The cool gas is in thermal contact with the inner compartment of the fridge. It heats up as heat is transferred to it from the contents of the fridge. This takes place at constant pressure, so it's an isobaric expansion.

Step 3: The gas is transferred to a compressor, which does most of the work in this process. The gas is compressed adiabatically, heating it and turning it back to a liquid.

Step 4: The hot liquid passes through coils on the outside of the fridge, and heat is transferred to the atmosphere. This is an isobaric compression process.

The compressor is driven by an external energy source and it does the work $|W|$ on the working substance during each cycle.

4.9.3 Performance of a Refrigerator:

Consider the energy flow diagram of a refrigerator Fig. 4.23 (b). It shows the relation between the work and heat involved in transferring heat from a low temperature region to a high temperature region. This is a cyclic process in which the working substance, the refrigerant in this case, is taken back to the initial state.

For a refrigerator, the heat absorbed by the working substance is Q_C and the heat rejected by it is Q_H. A refrigerator absorbs heat at lower temperature and rejects it at higher temperature, therefore, we have, $Q_C > 0$, $Q_H < 0$, and $W < 0$. Hence, we write, $|W|$ and $|Q_H| = -Q_H$. In this case, we apply the first law of thermodynamics to the cyclic process. For a cyclic process, the internal energy of the system in the initial state and the final state is the same, therefore, from Eq. (4.21), we have,

$$Q_H + Q_C = W \text{, or } Q_H + Q_C - W = 0$$

$$\therefore -Q_H = Q_C - W$$

For a refrigerator, $Q_H < 0$, and $W < 0$, therefore,

$$|Q_H| = |Q_C| + |W| \qquad \text{---(4.26)}$$

From the Fig.4.23 (b), we realize that the heat $|Q_H|$ rejected by the working substance at the hot reservoir is always greater than the heat Q_C received by it at the cold reservoir. Note that the Eq. (4.26), derived for a refrigerator and the Eq. (4.23), derived for a heat engine, are the same. They are valid for a heat engine and also for a refrigerator.

The ratio $\frac{|Q_C|}{|W|}$ indicates the performance of a refrigerator and is called the *coefficient of performance (CoP), K, or quality factor, or Q-value of a refrigerator*. Larger is the ratio, better is the refrigerator. That means a refrigerator has the best performance when the heat extracted by the refrigerant at the cold reservoir is maximum by doing minimum work in one operating cycle.

From Eq. (4.26), $|W| = |Q_C| - |Q_H|$

$$\therefore K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_C| - |Q_H|} \quad \text{--- (4.27)}$$

All the quantities on the right side of Eq. (4.27) represent energy and are measured in the same energy units. The coefficient of performance, K of a refrigerator is, therefore, a dimensionless number. For a typical household refrigerator, $K \approx 5$.

Remember this

Refrigerator transfers heat from inside a closed space to its external environment so that inside space is cooled to temperature below the ambient temperature.

Do you know?

Capacity of a refrigerator is expressed in litre. It is the volume available inside a refrigerator.

4.9.4 Air conditioner:

Working of an air conditioner and a refrigerator is exactly similar. It differs from a refrigerator only in the volume of the chamber/room it cools down. For an air conditioner, the evaporator coils are inside the room that is to be cooled and the condenser is outside the room. The air cooled by the evaporator coils inside the room is circulated by a fan placed inside the air conditioning unit. The performance of an air conditioner is defined by $K = \frac{|Q_C|}{|W|}$. It is important to consider the rate of heat removed H and the power P required for removing the heat.

We define the rate of heat removed as the heat current $H = \frac{|Q_C|}{t}$, where, t is the time in which heat $|Q_C|$ is removed. Therefore, the coefficient of performance of an air conditioner can be calculated as,

$$K = \frac{|Q_C|}{|W|} = \frac{Ht}{Pt} = \frac{H}{P} \quad \text{--- (4.28)}$$

Typical values of K are 2.5 to 3.0 for room air conditioners.

Do you know?

Capacity of an air conditioner is expressed in tonne. Do you know why?

Before refrigerator and AC was invented, cooling was done by using blocks of ice. When cooling machines were invented, their capacity was expressed in terms of the equivalent amount of ice melted in a day (24 hours). The same term is used even today.

4.9.5 Heat Pump:

Heat pump is a device which works similar to a refrigerator. It is used to heat a building or a similar larger structure by cooling the air outside it. A heat pump works like a refrigerator operating inside out. In this case, the evaporator coils are outside and absorb heat from the cold air from outside. The condenser coils are inside the building. They release the absorbed heat to the air inside the room thus, warming the building.

Remember this

Heat flow from a hot object to a cold object is spontaneous whereas, work is always required for the transfer of heat from a colder object to a hotter object.

4.10 Second Law of Thermodynamics:

4.10.1 Limitations of the First Law of Thermodynamics:

The First law of thermodynamics tells us that heat can be converted into work and work can also be converted into heat. It is merely a quantitative statement of the equivalence of heat and work. It has the following limitations.

(a) It does not tell us whether any particular process can actually occur. According to the first law of thermodynamics, heat may, on its own, flow from an object at higher temperature to one at lower temperature and it can also, on its own, flow from an object at lower temperature to one at higher temperature. We know that practically, heat cannot flow from an object at lower temperature to another at higher temperature. The First law of thermodynamics does not predict this practical observation.

(b) According to the First law, we could convert all (100%) of the heat available to us into work. Similarly, all the work could be converted into heat. Again, we know that practically this is not possible.

Thus, the First law of thermodynamics does not prevent us from converting heat entirely into work or work entirely into heat. These limitations lead to the formulation of another law of thermodynamics called the Second law of thermodynamics. We will discuss this at a later stage in this chapter.

We have seen earlier in section 4.7.3 that an irreversible process defines the preferred direction of an irreversible process. It is also found that it is impossible to build a heat engine that has 100% efficiency Eq. (4.25). *That is, it is not possible to build a heat engine that can completely convert heat into work.*

Similarly, for a refrigerator it is impossible to remove heat without doing any work on a system. That is, the coefficient of performance, Eq. (4.28) of a refrigerator can never be infinite.

These practical observations form the basis of a very important principle of thermodynamics, the Second law of thermodynamics.

The Second law of thermodynamics is a general principle which puts constraints upon the direction of heat transfer and the efficiencies that a heat engine can achieve.

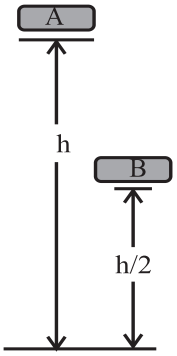


Fig. 4.24 (a): Energy of an object at two different hights.

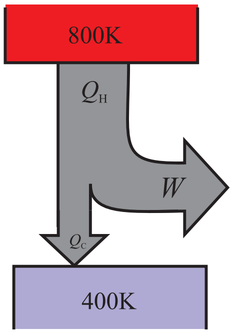


Fig. 4.24 (b): Limitations on efficiency of a heat engine.

Consider an object A at certain height of h above the ground and another object B of the same mass a height of h/2 as shown in Fig. 4.24 (a). We know that potential energy of the object B is half that of the object A. That means we can extract only half the energy from the object B. Similarly, if a heat engine as shown in Fig. 4.24 (b) operates between the temperatures of 800 K and 400 K, i.e., if it receives heat at 800 K and rejects it at 400 K, its maximum efficiency can be 50%.

4.10.2 The second law of thermodynamics, statement:

We now know that heat can be converted into work by using a heat engine. However, our practical experience says that entire heat supplied to the working substance can never be converted into mechanical work. Second law of thermodynamics helps us to understand this. According to the second law of thermodynamics, "*It is impossible to extract an amount of heat Q_H from a hot reservoir and use it all to do work W. Some amount of* *heat Q_C must be exhausted to a cold reservoir. This prohibits the possibility of a perfect heat engine*".

Sometimes it is also called as the 'Engine Law' or the 'Engine Statement' of the Second law of thermodynamics.

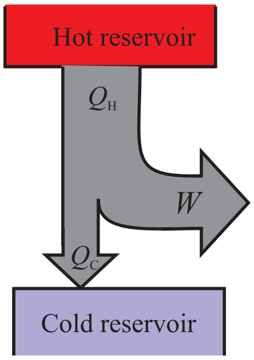


Fig. 4.25 (a): Second law of thermodynamics.

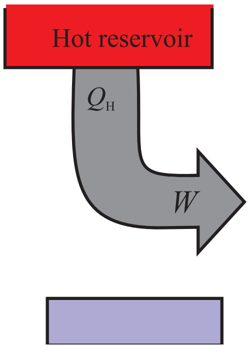


Fig. 4.25 (b): Energy flow diagram of Engine statement.

Figure 4.25 is a diagrammatic representation of the application of the Second law of thermodynamics to a heat engine. As you can see from the diagram, Fig. 4.25 (a), all heat engines lose some heat to the environment of a perfect heat engine. All the heat Q_H, extracted can not be used to do work. Figure 4.25 (b) shows the energy flow diagram for such a situation.

This form of statement of the Second law of thermodynamics is called as the **Kelvin-Planck statement** or the '*First form*' of the Second law of thermodynamics.

We have seen how the efficiency of a heat engine is restricted by the second law of thermodynamics. Heat engine is one form of 'heat – work conversion'. Let us see what happens in case of a refrigerator, the other form of 'work – heat conversion'.

"*It is not possible for heat to flow from a colder body to a warmer body without any work having been done to accomplish this flow*".

This means that energy will not flow spontaneously from an object at low temperature to an object at a higher temperature. This rules out the possibility of a perfect refrigerator. The statements about refrigerators are also applicable to air conditioners and heat pumps, which work on the same principles.

This is the '*Second form*' or **Clausius statement** of the Second law of thermodynamics. Sometimes it is also called as the 'Refrigerator Law' or the 'Refrigerator Statement' of the Second law of thermodynamics.

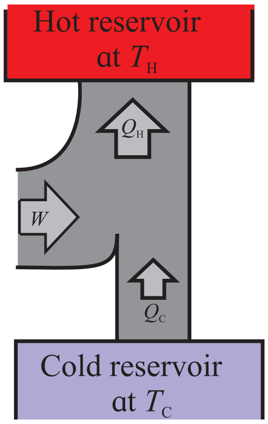


Fig. 4.26 (a): Energy flow diagram of a practical refrigerator.

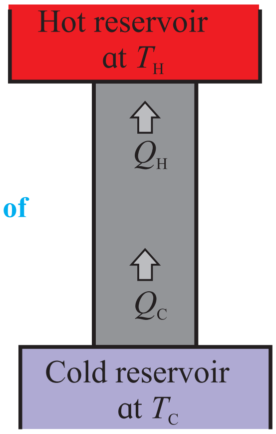


Fig. 4.26 (b): Energy flow of prefect refrigerator.

Figure 4.26 is a diagrammatic representation of the application of the Second law of thermodynamics to a refrigerator. As you can see form the energy flow diagram, Fig. 4.26 (a), a practical refrigerator requires work W to be done to extract heat Q_H from a cold reservoir and reject it to a hot reservoir. *The statement means that spontaneous flow of heat from an object at cold temperature is not possible* Fig. 4.26 (b).

Remember this

When we say that energy will not flow *spontaneously* from a cold object to a hot object, we are referring to the *net transfer of energy*. Energy can transfer from a cold object to a hot object either by transfer of energetic particles or electromagnetic radiation. However, in any spontaneous process, the net transfer of energy will be from the hot object to the cold object. *Work is required to transfer net energy from a cold object to a hot object.*

4.11 Carnot Cycle and Carnot Engine:

In section 4.7.3, we have discussed the concept of a reversible and an irreversible process at length. Now we will discuss why reversibility is such a basic and important concept in thermodynamics.

4.11.1 Significance of Reversibility in Thermodynamics:

We know that a reversible process is a ‘bidirectional’ process, i.e., it follows exactly the same steps in either direction. This requires the process to take place in infinitesimally small steps. Also, the difference between the state variables in the two infinitesimally close states should be very small. This would be possible if the system is in thermodynamic equilibrium with its environment throughout the change.

An irreversible process, on the contrary, is a unidirectional process. It can take place in only in one direction. Any irreversible process is not in thermal equilibrium with its environment.

4.11.2 Maximum Efficiency of a Heat Engine and Carnot’s Cycle:

We know that conversion of work to heat (refrigerator, section 4.9.2) is an irreversible process. A heat engine would convert maximum heat into work if all irreversible processes could be avoided. In that case, the efficiency of the heat engine can be maximum. Sadi Carnot, French engineer and scientist, proposed a hypothetical ideal engine in 1824 which has the maximum efficiency.

In a carnot engine, there are basically two processes:

(i) Exchange of heat (steps A to B and C to D in the Fig. 4.21). For this to be reversible, *the heat exchange must be isothermal*. This is possible if the working substance is at the temperature T_H of the source while absorbing heat. The working substance should be at the temperature of the cold reservoir T_C, while rejecting the heat.

(ii) Work done (steps B to C and D to A). For work done to be reversible, *the process should be adiabatic.*

Thus, the cycle includes two isothermal and two adiabatic processes for maximum efficiency. The corresponding *p*-*V* diagram will then be as shown in the Fig. 4.27.

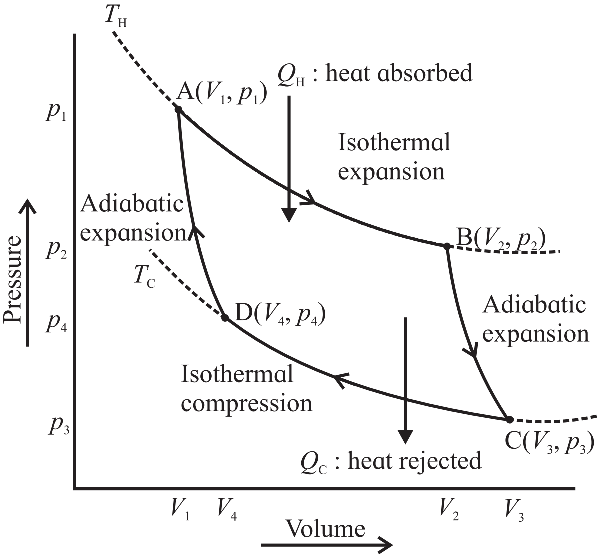


Fig. 4.27: Carnot cycle AB: Isothermal expansion, BC: Adiabatic expansion, CD: Isothermal compression, DA Adiabatic compression.

By using the expression for work done during an adiabatic and an isothermal process Eq. (4.7) and (4.20), we can derive an expression for the efficiency of a Carnot cycle/engine as,

$$\eta = \frac{W}{Q_H} = 1 - \frac{|Q_c|}{|Q_H|} = 1 - \frac{T_C}{T_H} \qquad \text{--- (4.29)}$$

Thus, while designing a heat engine for maximum efficiency, the source temperature T_H should be as high as possible and the sink temperature T_C should be as low as possible.

Use your brain power

Suggest a practical way to increase the efficiency of a heat engine.

Remember this

Always Remember for a Carnot Engine:

1. Carnot engine is a hypothetical concept.
2. Every process must be either isothermal or adiabatic.
3. The system must maintain thermodynamic equilibrium throughout the cycle so that it is reversible.
4. The efficiency of a Carnot engine can never be 100% unless $T_C = 0$. We know that this is not possible practically. That means even an ideal heat engine, the Carnot engine, cannot have 100% efficiency.

4.11.3 Carnot Refrigerator:

We know that a refrigerator is nothing but a heat engine operated in the reverse direction. Because each step in the Carnot cycle is reversible, the entire Carnot cycle is reversible. If we operate the Carnot engine in the reverse direction, we get the Carnot refrigerator. Using the Eq. (4.28), we can write the coefficient of performance of a Carnot refrigerator as,

$$K = \frac{|Q_C|}{|Q_C| - |Q_H|} = \frac{\frac{|Q_C|}{|Q_H|}}{1 - \frac{|Q_C|}{|Q_H|}} \qquad \text{--- (4.30)}$$

Using $\frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H}$, in Eq. (4.30) we have, the coefficient of performance of a Carnot refrigerator as,

$$K = \frac{T_C}{T_H - T_C} \qquad \text{--- (4.31)}$$

Equation (4.31) gives the coefficient of performance of an ideal refrigerator or, the Carnot refrigerator. It says that *the coefficient of performance of a Carnot refrigerator also depends on only the temperature difference of the hot and the cold reservoir*. When the temperature difference is very small, the coefficient is very large. In this case, a large quantity of heat can be removed from the lower temperature to the higher temperature by doing very small amount of work. The coefficient of performance is very small when the temperature difference is large. That means a small quantity of heat will be removed even when a large amount of work is done.

Example 4.10: Carnot engine:

A Carnot engine receives 2.0 kJ of heat from a reservoir at 500 K, does some work, and rejects some heat to a reservoir at 350 K. (a) How much work does it do? (b) how much heat is rejected. (c) what is its efficiency?

Solution: The heat Q_C rejected by the engine is given by

$$Q_C = -Q_H \frac{T_C}{T_H} = -(2000\ \text{J})\frac{350\text{K}}{500\text{K}}$$

$$= -1400\ \text{J}$$

From the First law, the work W done by the engine is,

$$W = Q_H + Q_C = 2000\ \text{J} + (-1400\ \text{J})$$

$$= 600\ \text{J}$$

Efficiency of the Carnot engine is,

$$\eta = 1 - \frac{T_C}{T_H} = 1 - \frac{350\text{K}}{500\text{K}} = 0.30 = 30\%$$

Is there any simple way to calculate efficiency?

4.11.4 The Second Law of Thermodynamics and the Carnot Cycle:

"The Carnot engine is the most efficient heat engine. Also, all Carnot engines operating between the same two temperatures have the same efficiency, irrespective of the nature of the working substance".

We have made two very important statements here.

1. Carnot engine is the most efficient heat engine, and

2. Efficiency of a Carnot engine is independent of its working substance.

We can also show that "*A Carnot refrigerator has a greater coefficient of performance among all the refrigerators working between the same two temperatures*."

4.12 Sterling Cycle:

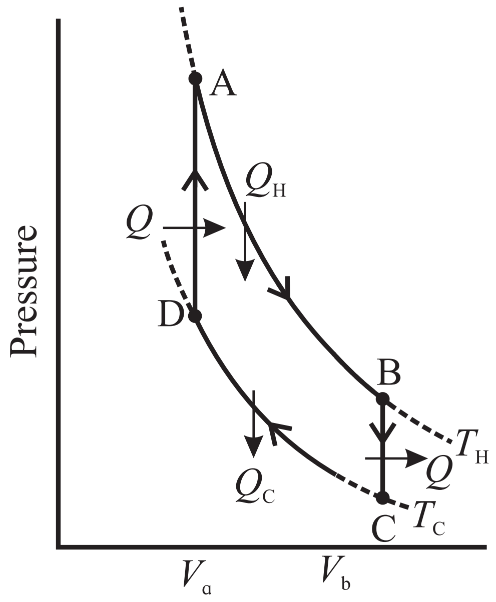


Fig. 4.28: Sterling cycle, *p*-*V* diagram.

This is a closed thermodynamic cycle. The Sterling engine is based on this cycle shown in Fig. 4.28. The working substance used in a Sterling engine is air, helium, hydrogen, nitrogen etc. All the processes in the Sterling cycle are reversible processes. When the gas is heated, the Sterling engine produces useful work. When work is done on the gas, it works as a refrigerator. This is reverse working of a Sterling cycle. The reversed Sterling cycle is extensively used in the field of cryogenics to produce extremely low temperatures or to liquefy air or gases mentioned above.

The ideal Sterling cycle has two isothermal processes AB and CD. Two isobaric processes BC and DA connect the two isothermal processes. Heat is absorbed at constant temperature T_H and rejected at constant temperature T_C. The four processes in a Sterling cycle are described briefly in the following.

- *Isothermal expansion* (AB): The gas is heated by supplying heat Q_H at constant temperature T_H. Useful work is done by the gas in this part of the cycle.
- *Isochoric process* (BC): Part of the heat absorbed (Q_H) by the gas in the previous part of the cycle is released by the gas to the refrigerator. This heat (Q) is used in the next part of the cycle. The gas cools down to temperature T_C.
- *Isothermal compression* (CD): The heat generated in this part of the cycle (Q_C) is rejected to the coolant (sink). The temperature of the gas is maintained at T_C during this process.
- *Isobaric heat absorption* (DA): The compressed gas absorbs heat (Q) during this process. Its temperature is increased to T_H.

The cycle repeats when the process reaches the point A.

Internet my friend

1. https://opentextbc.ca/physicstestbook2/chapter/the-first-law-of-thermodynamics/
2. https://opentextbc.ca/physicstestbook2/chapter/introduction-to-the-second-law-of-thermodynamics-heat-engines-and-their-efficiency/
3. https://opentextbc.ca/physicstestbook2/chapter/the-first-law-of-thermodynamics-and-some-simple-processes/
4. https://courses.lumenlearning.com/boundless-physics/chapter/introduction-8/
5. http://heatengine-sundervallii.blogspot.com/2010/10/everyday-examples-of-heat-engine.html
6. http://hyperphysics.phy-astr.gsu.edu/hbase/heacon.html#heacon
7. http://hyperphysics.phy-astr.gsu.edu/hbase/heacon.html

Exercises

1. Choose the correct option.

i) A gas in a closed container is heated with 10J of energy, causing the lid of the container to rise 2m with 3N of force. What is the total change in the internal energy of the system?

(A) 10J (B) 4J

(C) -10J (D) - 4J

ii) Which of the following is an example of the first law of thermodynamics?

(A) The specific heat of an object explains how easily it changes temperatures.

(B)While melting, an ice cube remains at the same temperature.

(C) When a refrigerator is unplugged, everything inside of it returns to room temperature after some time.

(D) After falling down the hill, a ball's kinetic energy plus heat energy equals the initial potential energy.

iii) Efficiency of a Carnot engine is large when

(A) T_H is large (B) T_C is low

(C) $T_H - T_C$ is large (D) $T_H - T_C$ is small

iv) The second law of thermodynamics deals with transfer of:

(A) work done (B) energy

(C) momentum (D) mass

v) During refrigeration cycle, heat is rejected by the refrigerant in the :

(A) condenser (B) cold chamber

(C) evaporator (D) hot chamber

2. Answer in brief.

i) A gas contained in a cylinder surrounded by a thick layer of insulating material is quickly compressed. (a) Has there been a transfer of heat? (b) Has work been done?

ii) Give an example of some familiar process in which no heat is added to or removed form a system, but the temperature of the system changes.

iii) Give an example of some familiar process in which heat is added to an object, without changing its temperature.

iv) What sets the limits on efficiency of a heat engine?

v) Why should a Carnot cycle have two isothermal two adiabatic processes?

3. Answer the following questions.

i) A mixture of hydrogen and oxygen is enclosed in a rigid insulting cylinder. It is ignited by a spark. The temperature and the pressure both increase considerably. Assume that the energy supplied by the spark is negligible, what conclusions may be drawn by application of the first law of thermodynamics?

ii) A resistor held in running water carries electric current. Treat the resistor as the system (a) Does heat flow into the resistor? (b) Is there a flow of heat into the water? (c) Is any work done? (d) Assuming the state of resistance to remain unchanged, apply the first law of thermodynamics to this process.

iii) A mixture of fuel and oxygen is burned in a constant-volume chamber surrounded by a water bath. It was noticed that the temperature of water is increased during the process. Treating the mixture of fuel and oxygen as the system, (a) Has heat been transferred ? (b) Has work been done? (c) What is the sign of ΔU ?

iv) Draw a p-V diagram and explain the concept of positive and negative work. Give one example each.

v) A solar cooker and a pressure cooker both are used to cook food. Treating them as thermodynamic systems, discuss the similarities and differences between them.

4. A gas contained in a cylinder fitted with a frictionless piston expands against a constant external pressure of 1 atm from a volume of 5 litres to a volume of 10 litres. In doing so it absorbs 400 J of thermal energy from its surroundings. Determine the change in internal energy of system. [Ans: -106.5 J]

5. A system releases 130 kJ of heat while 109 kJ of work is done on the system. Calculate the change in internal energy. [Ans: $\Delta U = 21$ kJ]

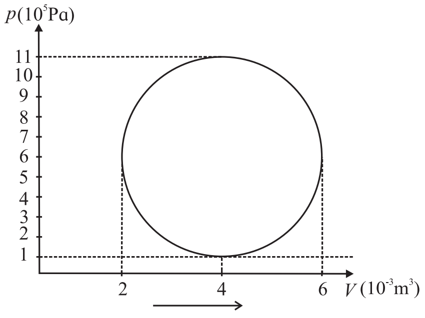
6. Efficiency of a Carnot cycle is 75%. If temperature of the hot reservoir is 727ºC, calculate the temperature of the cold reservoir. [Ans: 23ºC]

7. A Carnot refrigerator operates between 250K and 300K. Calculate its coefficient of performance. [Ans: 5]

8. An ideal gas is taken through an isothermal process. If it does 2000 J of work on its environment, how much heat is added to it? [Ans: 2000J]

9. An ideal monatomic gas is adiabatically compressed so that its final temperature is twice its initial temperature. What is the ratio of the final pressure to its initial pressure? [Ans: 5.656]

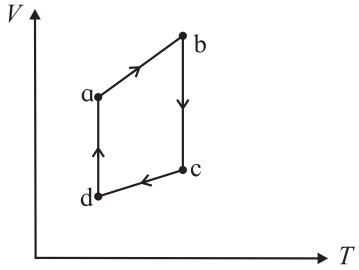
10. A hypothetical thermodynamic cycle is shown in the figure. Calculate the work done in 25 cycles.

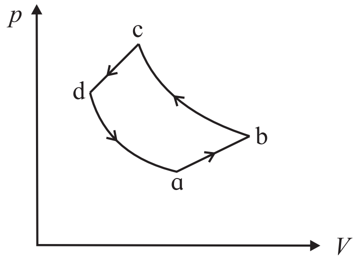


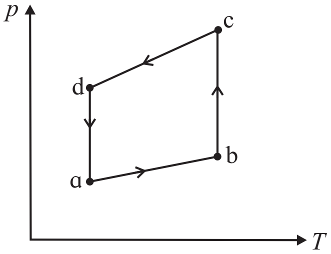
[Ans: 7.855 × 10^4 J]

11. The figure shows the V-T diagram for one cycle of a hypothetical heat engine which uses the ideal gas. Draw the p-V diagram and p-T diagram of the system.

[Ans: (a)]

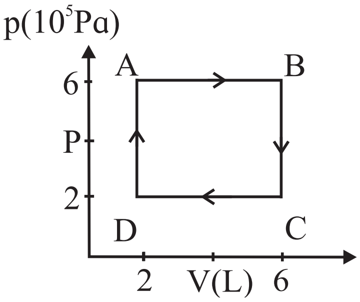






[Ans: (b)]

12. A system is taken to its final state from initial state in hypothetical paths as shown figure. Calculate the work done in each case.



[Ans: AB = 2.4 × 10^6 J, CD = -8 × 10^5 J, BC and DA zero, because constant volume change]

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