Chapter

6 Heat and Thermodynamics

Learning Objectives

After studying this chapter, the students will be able to:

- Describe the basic assumptions of the kinetic theory of gasses. [Including understanding the temperature, pressure and density conditions under which an ideal gas is a good approximation of a real gas.]
- State that regions of equal temperature are in thermal equilibrium
- Relate a rise in temperature of an object to an increase in its internal energy
- Apply the equation of state for an ideal gas[expressed as $PV = nRT$, where n = amount of substance (number of moles) and as $PV = Nk_BT$, where N = number of molecules]
- State that the Boltzmann constant k is given by $k_b = R/N_A$
- Use $W = P\Delta V$ for the work done when the volume of a gas changes at constant pressure.
- Describe the difference between the work done by a gas and the work done on a gas.
- Define and use the first law of thermodynamics [$\Delta U = Q - W$ expressed in terms of the increase in internal energy, the heating of the system (energy transferred to the system by heating) and the work done on the system]
- Explain qualitatively, in terms of particles, the relationship between the pressure, temperature and volume of a gas [Specifically the below case:
  (a) pressure and temperature at constant volume
  (b) volume and temperature at constant pressure
  (c) pressure and volume at a constant temperature
- Use the equation, including a graphical representation of the relationship between pressure and volume for a gas at constant temperature.
- Justify how the first law of thermodynamics expresses the conservation of energy.
- Relate a rise in temperature of a body to an increase in its internal energy.
- State the working principle of a heat engine.
- Describe the concept of reversible and irreversible processes.
- State and explain the second law of thermodynamics.
- State the working principle of Carnot's engine
- Describe that refrigerator is a heat engine operating in reverse as that of an ideal heat engine.
- Explain that an increase in temperature, increases the disorder of the system.
- Explain that increase in entropy means degradation of energy.
- Explain that energy is degraded during all natural processes.
- Identifying that system tends to become less orderly over time.
- Explain that Entropy, S is a thermodynamic quantity that relates to the degree of disorder of the particles in a system.
- State that the Carnot cycle sets a limit for the efficiency of a heat engine at the temperatures of its heat reservoir given by; Efficiency = $1 - \frac{T_{\text{cold reservoir}}}{T_{\text{hot reservoir}}}$

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Thermodynamics is the branch of physics that deals with the relationships and conversions between heat and other forms of energy. It encompasses principles governing the behaviour of systems at macroscopic scales, such as temperature, pressure, and volume. Thermodynamics thus plays a key role in technology, since almost all the raw energy available for our use is liberated in the form of heat. In this chapter, we shall study the bebaviour of gases and laws of thermodynamics, their significance and applications.

6.1 ASSUMPTIONS OF THE KINETIC THEORY OF GASES

The kinetic theory of gases is a fundamental theory in physics and chemistry that explains the behaviour of gases based on the motion of their constituent particles. This theory provides a macroscopic understanding of gas properties such as pressure, temperature, and volume. Here are the key assumptions of the kinetic theory of gases.

1. Gas Particles are in Constant, Random Motion

Gas molecules are in perpetual, random motion. They move in straight lines until they collide with either another molecule or the walls of the container.

2. Negligible Volume of Gas Particles

The volume of the individual gas molecules is negligible as compared to the total volume of the gas. This means that the particles are considered point masses with no significant volume.

3. No Intermolecular Forces

There are no attractive or repulsive forces between the gas molecules. The particles do not exert any force on each other except during collisions.

4. Elastic Collisions

The collisions between gas molecules, and with the walls of the container are perfectly elastic. This means that there is no net loss of kinetic energy during collisions. The total kinetic energy is conserved.

5. Large Number of Particles

A gas contains a large number of particles. This large number allows for the use of statistical methods to describe the properties of the gas.

6. Average Kinetic Energy is Proportional to Temperature

The average kinetic energy of gas particles is directly proportional to the absolute temperature of the gas. This implies that as the temperature increases, the speed of the gas particles also increases.

7. Pressure due to Particle Collisions

The pressure exerted by a gas on the walls of its container is due to the collisions of gas

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particles with the walls. The force exerted by the particles during collisions generates pressure.

8. Time of Collisions is Negligible

The time interval of a collision between gas particles is extremely short compared to the time between collisions. This assumption simplifies the analysis of particle dynamics.

Limitations of Kinetic Molecular Theory

Real Gases

The assumptions of the kinetic theory hold true for ideal gases, but real gases exhibit deviations due to intermolecular forces and finite molecular volume, especially at high pressures and low temperatures.

In summary, the kinetic theory of gases provides a macroscopic view of gas behaviour, linking macroscopic properties like pressure and temperature to the motion of gas particles, and serves as a foundational concept in understanding thermodynamics and statistical mechanics.

Equation of State for an Ideal Gas

A gas that obeys kinetic theory of gases is termed as an ideal gas. Ideal gas equation is given by

$$PV = nRT \quad \ldots\ldots (6.1)$$

Here P represents pressure, V is volume, n is number of moles of the gas, R is universal gas constant ($R = 8.3145\ J\ mol^{-1}\ K^{-1}$) and T is the absolute temperature.

Equation (6.1) implies that product of pressure and volume is directly proportional to the absolute temperature for an ideal gas.

Real Gas to Behave Like an Ideal Gas

According to kinetic theory of gases, a gas has no intermolecular interaction and molecules are far apart from each other. For a real gas to behave like an ideal gas, some conditions must be satisfied. *P.E.* of the gas molecules is negligible and this have only *K.E.*

Number of moles 'n' can be given by

$$n = \frac{\text{Mass of gas}}{\text{Molar mass of gas}} = \frac{m}{M}$$

So, Eq. (6.1) becomes: $PV = \frac{m}{M}RT$ or $PM = (\frac{m}{V})RT$

We know that density; $\rho = \frac{m}{V}$, So, $\rho = \frac{PM}{RT}$ as $\frac{M}{R}$ is constant $\therefore \rho \propto \frac{P}{T}$

The density of a gas will be low at low pressure and high temperature due to which molecules of the gas will be at large distance from each other and the intermolecular

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forces will be negligible. So, the real gas behaves like an ideal gas at low pressure and high temperature.

Ideal Gas Equation in Terms of Boltzmann Constant

From ideal gas equation:

$$PV = nRT \quad \ldots\ldots\ldots\ldots \text{(i)}$$

A mole can be defined as the number of atoms or molecules per unit Avogadro's number ($N_A = 6.02 \times 10^{23}$).

Mathematically:

$$n = \frac{N}{N_A} \quad \ldots\ldots\ldots\ldots \text{(ii)}$$, N is number of atoms or molecules

Substituting Eq. (ii) in Eq. (i), we have

$$PV = \frac{N}{N_A}RT \quad \ldots\ldots\ldots\ldots \text{(iii)}$$

For your information

Real gases approach ideal behaviour under:

(i) low pressure

(ii) high temperature

The term $\frac{R}{N_A}$ is termed as Boltzmann constant k_B, i.e.,

$$k_B = \frac{R}{N_A} \quad \ldots\ldots\ldots\ldots \text{(6.2)}$$

Substituting the values of R and N_A, we have

$$k_B = 1.38 \times 10^{-23}\ \text{J K}^{-1}$$

Substituting Eq. (6.2) in Eq. (iii),

$$PV = N k_B T \quad \ldots\ldots\ldots\ldots \text{(6.3)}$$

Equation (6.3) gives ideal gas equation in terms of Boltzmann constant k_B.

Example 6.1 One mole of an ideal gas is at a temperature of 300 K. If the Boltzmann constant is $1.38 \times 10^{-23}\ \text{J K}^{-1}$, calculate the volume of the gas at a pressure of 1 atom. [1atm = 101325 Pa]

Solution We know that:

$$PV = nRT$$

$$R = N_A \times k_B \quad \text{where} \quad k_B = \frac{R}{N_A}$$

Here $$V = \frac{nN_A k_B T}{P}$$

$$V = \frac{1\ \text{mol} \times 6.02 \times 10^{23}\ \text{mol}^{-1} \times 1.38 \times 10^{-23}\ \text{J K}^{-1} \times 300\ \text{K}}{101325\ \text{Pa}}$$

$$V \approx 0.0245\ \text{m}^3$$

Thus, volume of gas would be $0.0245\ \text{m}^3$.

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Gas Laws

There are some variables (state functions) which describe quantity of gas which includes pressure, volume, and temperature (P, V, and T) with change in one variable, the second variable changes while the third is kept constant. The laws that relate these variables mutually for an ideal gas are termed as gas laws.

Boyle's Law

This law was introduced by Robert Boyle in 1662, and it provides a relationship between pressure and volume of a gas at constant temperature. It sates that for a fixed mass of an ideal gas, the pressure P exerted by a gas varies inversely with volume V occupied by the gas at constant temperature.

Mathematically;

$$P \propto \frac{1}{V} \quad \text{at constant } T$$

$$P = \text{constant} \frac{1}{V} \quad \text{or} \quad PV = \text{constant}$$

or $P_1V_1 = P_2V_2$

Graphical representation of Boyle's law is shown in Fig. 6.1.

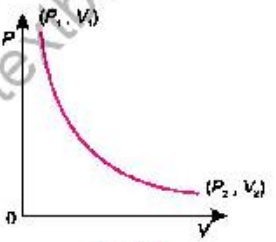

Fig. 6.1

Charles' Law

Charles' law relates volume and temperature of an ideal gas for a fixed mass at constant pressure. This law was formulated in 1870 by a French Physicist Jacques Charles. It states that the volume of given mass of gas at constant pressure is directly proportional to the absolute temperature.

Mathematically;

$$V \propto T \quad \text{at constant } P$$

or $$\frac{V}{T} = \text{constant}$$

or $$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Graphically, it can be shown in Fig. 6.2.

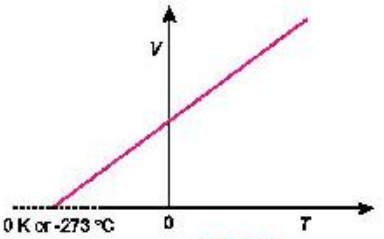

Fig. 6.2

Joseph lussac's Law

It states that for a fixed mass of an ideal gas, the pressure exerted by a gas varies directly with absolute temperature of the gas at constant volume.

Mathematically;

$$P \propto T \quad \text{at constant } V$$

or $$P = \text{constant} \times T$$

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or $$\frac{P}{T} = \text{constant}$$

or $$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Graphically, Joseph lussac's law is shown in Fig. 6.3.

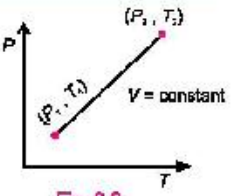

Fig. 6.3

Thermal Equilibrium

When two bodies are at the same temperature, the thermal energy (which is related to the kinetic energy of particles) of each body is equal. As a result, there is no driving force for heat transfer between them, and thus they remain in thermal equilibrium.

Example

When we put a metal spoon into a hot cup of coffee:

(i) initially, the coffee is hotter than the spoon.

(ii) over time, heat flows from the coffee to the spoon.

(iii) eventually, the coffee and spoon reach at the same temperature.

Thermal equilibrium is achieved at this point, there is no net heat flow between the coffee and the spoon, and they are said to be in thermal equilibrium.

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6.2 INTERNAL ENERGY

The sum of all forms of molecular energies (kinetic and potential) of a substance is termed as its internal energy. In the study of thermodynamics, usually ideal gas is considered as a working substance. The molecules of an ideal gas are mere mass points which exert no forces on one another. So, the internal energy of an ideal gas system is generally the translational *K.E.* of its molecules. Since the temperature of a system is defined as the average *K.E.* of its molecules, thus for an ideal gas system, the internal energy is directly proportional to its temperature.

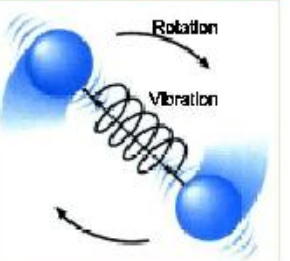
According to the kinetic theory of gases, the average kinetic energy of gas molecules is given by

$$\langle K.E \rangle = \frac{3}{2} k_B T \text{ or } \left\langle \frac{1}{2} mv^2 \right\rangle = \frac{3}{2} k_B T$$

where k_B is Boltzmann constant.

Therefore, the rise in temperature of an object reflects an increase in the internal kinetic energy of its particles. This increase in internal energy can

Do you know?



A diatomic gas molecule has both translational and rotational energy. It also has vibrational energy associated with the spring like bond between its atoms.

Tidbit

Different processes can lead to changes in internal energy and temperature, such as heating (adding heat), adiabatic compression or expansion (no heat exchange), or phase changes (where heat energy changes the state of matter without changing temperature).

occur due to the absorption of heat energy, which raises the average kinetic energy of the particles and thus increases the temperature of the object.

6.3 HEAT AND WORK

We know that both heat and work correspond to transfer of energy by some means. The idea was first applied to the steam engine where it was natural to transfer heat in and get work out. Consequently, it made a sense to define both heat in and work out as positive quantities. Hence, work done by the system on its environment is considered positive while work done on the system by the environment is taken as negative. If an amount of heat Q enters the system, it could manifest itself as either an increase in internal energy or as a resulting quantity of work performed by the system on the surrounding or both.

We can express the work in terms of directly measurable variables. Consider the gas enclosed in the cylinder with a moveable, frictionless piston of cross-sectional area A as shown in Fig.6.4(a). In equilibrium, the system occupies volume V and exerts a pressure P on the walls of the cylinder and its piston. The force F exerted by the gas on the piston is PA.

We assume that the gas expands through ΔV very slowly, so that it remains in equilibrium as shown in Fig. 6.4(b). As the piston moves up through a small distance Δy, the work W done by the gas is:

$$W = F\Delta y = PA\Delta y$$

Since $A\Delta y = \Delta V$ (Change in volume)

Hence $W = P\Delta V$ ..... (6.4)

The work done can also be calculated by area of the curve under P-V graph as shown in Fig. 6.5.

For your information

Internal energy is a function of state. Consequently, it does not depend on path but depends on initial and final states of the system. Thus, internal energy is similar to the gravitational P.E. So, like the potential energy, it is the change in internal energy and not its absolute value, which is important.

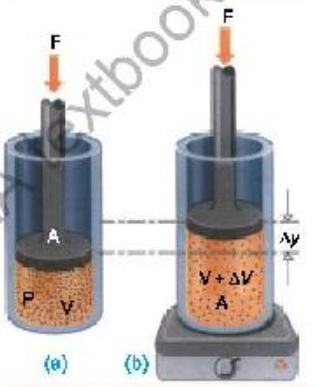


Fig. 6.4

A gas is sealed in a cylinder by a weightless, frictionless piston. The constant downward applied force F equals PA, and when the piston is displaced, downward work is done on the gas.

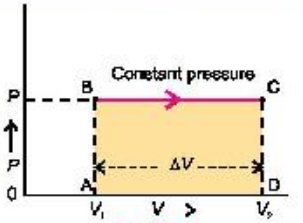


Fig. 6.5

Knowing the details of the change in internal energy and the mechanical work done, we are in a position to describe the general principles which deal with heat energy and its transformation into mechanical energy. These principles are known as laws of thermodynamics.

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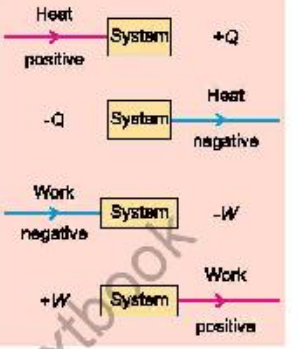
6.4 FIRST LAW OF THERMODYNAMICS

When heat is added to a system there is an increase in the internal energy due to the rise in temperature, an increase in pressure or change in the state. If at the same time, a substance is allowed to do work on its environment by expansion, the heat Q required will be the heat necessary to change the internal energy of the substance from U_1 in the first state to U_2 in the second state plus the work W done on the environment.

Thus $Q = (U_2 - U_1) + W$

or $Q = \Delta U + W$ ..... (6.5)

For your information



Thus the change in internal energy $\Delta U = U_2 - U_1$ is defined as $Q - W$. Since it is the same for all processes concerning the state, the first law of thermodynamics, thus can be stated as,

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

1. **Conservation Principle**: The underlying principle of the first law of thermodynamics is the conservation of energy. It asserts that while energy can change from one form to another (such as from chemical potential energy to thermal energy), the total energy in an isolated system remains constant over time.
2. **Wider Applicability:** Beyond mechanical systems, the first law of thermodynamics applies universally to all forms of energy and all types of processes, including chemical reactions, electrical systems, and nuclear reactions. It provides a foundational understanding that allows scientists and engineers to predict and understand energy transformations in various contexts.

The first law of thermodynamics expresses the law of conservation of energy by affirming that energy is a conserved quantity in isolated systems. It provides a framework to understand how energy is transferred and transformed within systems without violating the fundamental principle that energy neither be created nor be destroyed.

A bicycle pump is a good example of first law of thermodynamics. When we pump on the handle rapidly, it becomes hot due to mechanical work done on the gas, raising thereby its internal energy. One such simple arrangement is shown in Fig. 6.6. It consists of a bicycle pump with a blocked outlet.

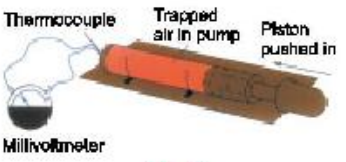


Fig. 6.6

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A thermocouple connected through the blocked outlet allows the air temperature to be monitored. Thermocouple thermometer can detect a minute variation of the temperature. When the piston is rapidly pushed, thermometer shows a temperature rise due to increase of internal energy of the air. The push force does work on the air, thereby, increasing its internal energy, which is shown, by the increase in temperature of the air.

Human metabolism also provides an example of energy conservation. Human beings and other animals do work when they walk, run, or move. Work requires energy. Energy is also needed for growth to make new cells and to replace old cells that have died. Energy transforming processes that occur within an organism are named as metabolism. We can apply the first law of thermodynamics ($\Delta U = Q - W$), to an organism of the human body. Work done will result in the decrease in internal energy of the body. Consequently, the body temperature or in other words internal energy is maintained by the food we eat.

Example 6.2 A gas is enclosed in a container fitted with a piston of cross-sectional area 0.10 m^2. The pressure of the gas is maintained at 8000 N m^{-2}. When heat is slowly transferred, the piston is pushed up through a distance of 4.0 cm. If 42 J heat is transferred to the system during the expansion, what is the change in internal energy of the system?

Solution The work done by the gas is

$$W = P\Delta V = PA\Delta y = 8000 \text{ N m}^{-2} \times 0.10 \text{ m}^2 \times 4.0 \times 10^{-2} \text{ m}$$
$$= 32 \text{ N m} = 32 \text{ J}$$

The change in internal energy is found from first law of thermodynamics

$$\Delta U = Q - W = 42 \text{ J} - 32 \text{ J} = 10 \text{ J}$$

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Isothermal Process

It is a process which is carried out at constant temperature and hence the condition for the application of Boyle's law on the gas is fulfilled. Therefore, when gas expands or compresses isothermally, the product of its pressure and volume during the process remains constant. If P_1, V_1 are initial pressure and volume whereas P_2, V_2 are pressure and volume after the isothermal change takes place (Fig. 6.7-a), respectively, then

$$P_1V_1 = P_2V_2$$

In case of an ideal gas, the *P.E.* associated with its molecules is zero, hence, the internal energy of an ideal gas depends only on its temperature, which in this case remains constant, therefore, $\Delta U = 0$. Hence, the first law of thermodynamics reduces to

$$Q = W$$

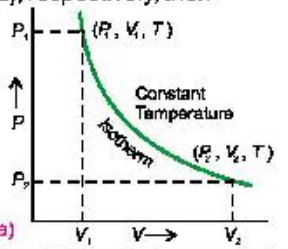

Fig. 6.7(a)

Thus if gas expands and does external work W, an amount of heat Q has to be supplied to the gas in order to produce an isothermal change. Since transfer of heat from one

place to another requires time, hence, to keep the temperature of the gas constant, the expansion or compression must take place slowly. The curve representing an isothermal process is called an isotherm (Fig. 6.7-a).

Adiabatic Process

An adiabatic process is the one in which no heat enters or leaves the system. Therefore, $\Delta Q = 0$ and the first law of thermodynamics gives: $W = -\Delta U$

Brain teaser!

Why does the internal energy of an ideal gas remain constant during isothermal expansion?

Thus, if the gas expands and does external work, it is done at the expense of the internal energy of its molecules and, hence, the temperature of the gas falls. Conversely, an adiabatic compression causes the temperature of the gas to rise because of the work done on the gas.

Adiabatic change occurs when the gas expands or compressed rapidly, particularly when the gas is contained in an insulated cylinder. The examples of adiabatic process are:

(i) The rapid escape of air from a burst tyre.

(ii) The rapid expansion and compression of air through which a sound wave is passing.

(iii) Cloud formation in the atmosphere.

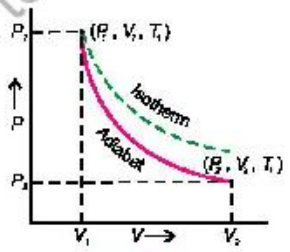

Fig. 6.7(b)

As the temperature of the gas does not remain constant, so it has been seen that;

$$PV^{\gamma} = \text{constant}$$

where γ is the ratio of the molar specific heat of the gas at constant pressure to molar specific heat at constant volume ($\gamma = \frac{C_P}{C_V}$). The curve representing an adiabatic process is called an adiabat (Fig.6.7-b).

6.5 REVERSIBLE AND IRREVERSIBLE PROCESSES

A reversible process is one which can be retraced in exactly reverse order, without producing any change in the surroundings. In the reverse process, the working substance passes through the same stages as in the direct process but thermal and mechanical effects at each stage are exactly reversed. If heat is absorbed in the direct process, it will be given out in the reverse process and if work is done by the substance in the direct process, work will be done on the substance in the reverse process. Hence, the working substance is restored to its original conditions.

A succession of events which brings the system back to its initial condition is called a cycle. A reversible cycle is the one in which all the changes are reversible.

Although no actual change is completely reversible but the processes of liquification and evaporation of a substance, performed slowly, are practically reversible. Similarly the

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slow compression of a gas in a cylinder is reversible process as the compression can be changed to expansion by slowly decreasing the pressure on the piston to reverse the operation.

> If a process cannot be retraced in the backward direction by reversing the controlling factors, it is an irreversible process.

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

Do you know?

First practical steam-engine was designed by John Braithwaite and John Ericsson in England around 1829.

6.6 HEAT ENGINE

A heat engine converts some thermal energy to mechanical work. Usually, the heat comes from the burning of a fuel. The earliest heat engine was the steam engine. It was developed on the fact that when water is boiled in a vessel covered with a lid, the steam inside tries to push the lid off showing the ability to do work. This observation helped to develop a steam engine.

The working principle of a heat engine is based on the conversion of heat energy into mechanical work through a cyclic process. Here is how a heat engine typically operates. The working principle of a heat engine involves the cyclic transfer of heat energy from a high temperature reservoir to a low temperature reservoir, with the objective of converting as much heat as possible into mechanical work. This process is governed by principles of thermodynamics and is essential in various applications where mechanical energy is required from heat sources.

6.7 SECOND LAW OF THERMODYNAMICS

First law of thermodynamics tells us that heat energy can be converted into equivalent amount of work, but it is silent about the conditions under which this conversion takes place. The second law is concerned with the circumstances in which heat can be converted into work and direction of flow of heat.

Before initiating the discussion on formal statement of the second law of thermodynamics, let us analyze briefly the factual operation of an engine. The engine or the system (Fig. 6.8) absorbs a quantity of heat Q_1 from the heat source at temperature T_1. It does work W and expels heat Q_2 to low temperature reservoir at temperature T_2. As the

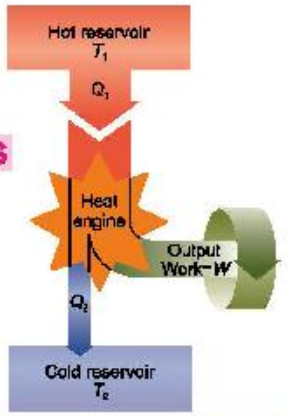

Fig. 6.8

Schematic representation of a heat engine. The engine absorbs heat Q_1 from the hot reservoir, expels heat Q_2 to the cold reservoir and does work W.

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working substance goes through a cyclic process, in which the substance eventually returns to its initial state, the change in internal energy is zero. Hence, from the first law of thermodynamics, net work done should be equal to the net heat absorbed. i.e.,

$$W = Q_1 - Q_2$$

In practice, the petrol engine of a motor car extracts heat from the burning fuel and converts a part of this energy to mechanical energy or work and expels the rest to the atmosphere. It has been observed that petrol engines convert roughly 25% and diesel engines 35 to 40% available heat energy into work.

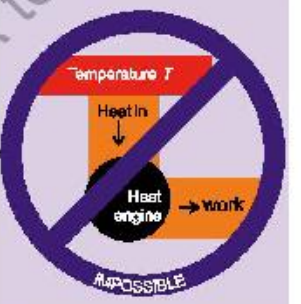
The second law of thermodynamics is a formal statement based on these observations. It can be stated in a number of different ways:

According to Lord Kelvin's statement based on the working of a heat engine:

> It is impossible to devise a process which may convert heat, extracted from a single reservoir, entirely into work without leaving any change in the working system.

This means that a single heat reservoir, no matter how much energy it contains, cannot be made to perform any work. This is true for oceans and our atmosphere which contain a large amount of heat energy but cannot be converted into useful mechanical work. As a consequence of second law of thermodynamics, two bodies at different temperatures are essential for the conversion of heat into work. Hence, for the working of heat engine there must be a source of heat at a high temperature and a sink at low temperature to which heat may be expelled. The reason for our inability to utilize the heat contents of oceans and atmosphere is that there is no reservoir at a temperature lower than any one of the two.

Tidbits



According to the Kelvin statement of the second law of thermodynamics, the process pictured here is impossible. Heat from a source at a single temperature cannot be converted entirely into work.

6.8 CARNOT ENGINE AND CARNOT'S THEOREM

Sadi Carnot in 1824 described an ideal engine using only isothermal and adiabatic processes. He showed that a heat engine operating in an ideal reversible cycle between two heat reservoirs at different temperatures, would be the most efficient engine. A Carnot cycle using an ideal gas as the working substance is shown on *PV* diagram (Fig. 6.9). It consists of following four steps:

1. The gas is allowed to expand isothermally at temperature T_1, absorbing heat Q_1 from the hot

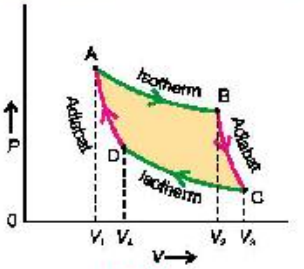


Fig. 6.9

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reservoir. The process is represented by the curve AB.

2. The gas is then allowed to expand adiabatically until its temperature drops to T_2. The process is represented by the curve BC.
3. The gas at this stage is compressed isothermally at temperature T_2 rejecting heat Q_2 to the cold reservoir. The process is represented by the curve CD.
4. Finally the gas is compressed adiabatically to restore its initial state at temperature T_1. The process is represented by the curve DA.

Thermal and mechanical equilibrium is maintained all the time so that each process is perfectly reversible. As the working substance returns to the initial state, there is no change in its internal energy i.e., $\Delta U = 0$.

The net work done during one cycle equals to the area enclosed by the path ABCDA of the PV diagram. It can also be estimated from net heat ΔQ absorbed in one cycle.

$$Q = Q_1 - Q_2$$

From 1st law of thermodynamics:

$$Q = \Delta U + W$$

or $$W = Q_1 - Q_2 \qquad (\because \Delta U = 0)$$

The efficiency η of the heat engine is defined as:

$$\eta = \frac{\text{Output (Work)}}{\text{Input (Energy)}}$$

Thus $$\eta = \frac{Q_1 - Q_2}{Q_1} \quad \ldots\ldots\ldots \quad (6.6)$$

The energy transfer in an isothermal expansion or compression turns out to be proportional to kelvin temperature. So Q_1 and Q_2 are proportional to kelvin temperatures T_1 and T_2 respectively and hence,

$$\eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1} \quad \ldots\ldots\ldots \quad (6.7)$$

Interesting information

A waterfall analogy for the heat engine.

The efficiency is usually taken in percentage, in that case:

$$\text{Percentage efficiency} = \left(1 - \frac{T_2}{T_1}\right) \times 100$$

Thus, the efficiency of Carnot engine depends on the temperature of hot and cold reservoirs. It is independent of the nature of working substance. The larger the temperature difference of two reservoirs, the greater is the efficiency. But it can never be one or 100% unless cold reservoir is at absolute zero temperature ($T_2 = 0$ K).

Such reservoirs are not available and hence the maximum efficiency is always less than

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one. Nevertheless, the Carnot cycle establishes an upper limit on the efficiency of all heat engines. No practical heat engine can be perfectly reversible and also energy dissipation is inevitable. This fact is stated in Carnot's theorem:

> No heat engine can be more efficient than a Carnot engine operating between the same two temperatures.

The Carnot's theorem can be extended to state that:

> All Carnot's engines operating between the same two temperatures have the same efficiency, irrespective of the nature of working substance.

In most practical cases, the cold reservoir is near room temperature. So, the efficiency can only be increased by raising the temperature of hot reservoir. All real heat engines are less efficient than Carnot engine due to friction and other heat losses.

Example 6.3 The turbine in a steam power plant takes steam from a boiler at 427 °C and exhausts into a low temperature reservoir at 77 °C. What is the maximum possible efficiency?

Solution Maximum efficiency for any engine operating between temperatures T_1 and T_2 is

$$\%\eta = \frac{T_1 - T_2}{T_1} \times 100\% \quad \text{where} \quad T_1 = 427 + 273 = 700\ \text{K}$$

and $$T_2 = 77 + 273 = 350\ \text{K}$$

So $$\eta = \frac{T_1 - T_2}{T_1} = \frac{700\ \text{K} - 350\ \text{K}}{700\ \text{K}} = \frac{350\ \text{K}}{700\ \text{K}} = \frac{1}{2} = 0.5 \quad \text{or} \quad \%\eta = 0.5 \times 100 = 50\%$$

6.9 REFRIGERATOR

Refrigerator is a device which maintains the temperature of a body below that of its surrounding. It operates in a cyclic process but in reverse as that of the heat engine as shown in Fig.6.10. A refrigerator absorbs heat from a cold reservoir and gives it off to a hot reservoir. This shows that in a refrigerator, the work is done on the system while in a heat engine work is done by the system.

A refrigerator works on the basis of Clausius statement of second law of thermodynamics, i.e., a heat engine is operating in reverse. Heat Q_c is drawn from Low Temperature Reservoir (LTR) T_1 by compressor and is thrown into High Temperature Reservoir (HTR) T_2 with the help of external work done. The heat rejected to HTR (Q_h) is given by

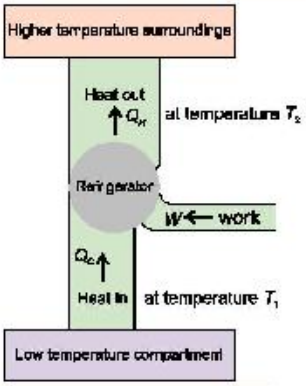

Fig. 6.10
A refrigerator transfers heat from a low-temperature compartment to higher-temperature surroundings with the help of external work. It is a heat engine operating in reverse order.

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$$Q_c + W = Q_H \quad \text{or} \quad W = Q_H - Q_c$$

The main purpose of refrigerator is to extract as much heat Q_c as possible from LTR with the expenditure of as little work W as possible.

Coefficient of Performance of Refrigerator

The ratio of heat removed from LTR (Q_c) to the work done (W) is called coefficient of performance of a refrigerator.

A better refrigerator will remove a greater amount of heat from inside the refrigerator for the expenditure of a smaller mechanical work or electrical energy. The coefficient of performance of a refrigerator can be given by

$$E = \frac{Q_c}{W} = \frac{Q_c}{Q_H - Q_c}$$

The coefficient of performance in terms of temperature, where $Q \propto T$ is:

$$E = \frac{T_1}{T_2 - T_1} \quad \ldots\ldots\ldots \quad (6.8)$$

Example 6.4

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

Solution

Coefficient of performance $E = 8$

Temperature of cold reservoir (freezer) $T_1 = -23°C = -23 + 273 = 250\ K$

Temperature of hot reservoir (room) $T_2 = ?$

Coefficient of performance $= \dfrac{T_1}{T_2 - T_1}$

Substituting the values $8 = \dfrac{250\ K}{T_2 - 250\ K}$

or $8\,(T_2 - 250\ K) = 250\ K$ or $T_2 - 250\ K = \dfrac{250\ K}{8}$

or $T_2 = 31.25\ K + 250\ K = 281.25\ K = 8.25\ °C$

6.10 ENTROPY

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

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$$\Delta S = \frac{\Delta Q}{T} \quad \ldots\ldots\ldots \quad (6.9)$$

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

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

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

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

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

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

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

Every time entropy increases, the opportunity to convert some heat into work is lost. For example, there is an increase in entropy when hot and cold waters are mixed. Finally, the warm water cannot be separated into a hot layer and a cold layer. There has been no loss of energy but some of the energy is no longer available for conversion into work. Therefore, increase in entropy means degradation of energy from a higher level where more work can be extracted to a lower level at which less or no useful work can be done. The energy in a sense is degraded, going from more orderly form to less orderly form, eventually ending up as thermal energy.

In all real processes where heat transfer occurs, the energy available for doing useful

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work decreases, eventually, the entropy increases. Even if the temperature of some system decreases, thereby decreasing the entropy, it is at the expense of net increase in entropy for some other system. When all the systems are taken together as the universe, the entropy of the universe always increases.

Example 6.5 Calculate the entropy change when 1.0 kg ice at 0 °C melts into water at 0 °C. Latent heat of fusion of ice $L_f = 3.36 \times 10^5$ J kg^{-1}.

Solution

$m = 1$ kg

$T = 0\,°C = 273$ K

$L_f = 3.36 \times 10^5$ J kg^{-1}

As $\Delta S = \frac{\Delta Q}{T}$

where $\Delta Q = mL_f$

So $\Delta S = \frac{mL_f}{T}$

Substituting the values

$$\Delta S = \frac{1.00\text{ kg} \times 3.36 \times 10^5\text{ J kg}^{-1}}{273\text{ K}}$$

$$\Delta S = 1.23 \times 10^3\text{ J K}^{-1}$$

Thus, entropy increases as it changes to water. The increase in entropy in this case is a measure of increase in the disorder of water molecules that change from solid to liquid state.

Brain teaser!

Why does a deck of cards become more disordered when shuffled?

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QUESTIONS

Multiple Choice Questions

Tick (✓) the correct answer.

6.1 In an isothermal change, internal energy:

(a) decreases (b) increases (c) remains the same (d) becomes zero

6.2 First law of thermodynamics is based upon law of conservation of:

(a) mass (b) energy (c) momentum (d) charge

6.3 A device which converts thermal energy into mechanical energy is called:

(a) heat engine (b) Carnot engine (c) refrigerator (d) turbine

6.4 When two objects are made in thermal contact having same temperature, then they are at:

(a) thermal Equilibrium (b) chemical Equilibrium

(c) mechanical Equilibrium (d) physical Equilibrium

6.5 When the system is expanded by adding heat energy, then the work done will be:
(a) positive and on the system (b) negative and on the system
(c) positive and by the system (d) negative and by the system

6.6 Entropy of a system in reversible process:
(a) decreases (b) increases (c) is Infinite (d) is zero

6.7 What happens to internal energy of an object when its temperature:
(a) decreases (b) remains Constant (c) Increases (d) fluctuates

6.8 The value of Boltzmann constant is:
(a) 1.38×10^{-23} J K^{-1} (b) 1.38×10^{23} J K^{-1}
(c) 1.38×10^{29} J K^{-1} (d) 1.38×10^{-29} J^{-1} K^{-1}

6.9 In an adiabatic process, there is no:
(a) change in temperature (b) exchange of heat
(c) change in internal energy (d) work done

6.10 Thermodynamics mostly deals with:
(a) measurement of quantity of heat
(b) transfer of quantity of heat
(c) change of state
(d) Conversion of heat to other forms of energy

Short Answer Questions

6.1 What is meant by thermal equilibrium? Explain briefly.

6.2 What is meant by internal energy? How is it related to temperature of an ideal gas?

6.3 State 2nd law of thermodynamics in two different forms.

6.4 Is it possible to construct a heat engine of 100% efficiency? Explain.

6.5 Differentiate between reversible and irreversible processes.

6.6 Why adiabat is steeper than isotherm? Explain.

6.7 A refrigerator transforms heat from cold to hot body. Does this violate the second law of thermodynamics? Justify your answer.

6.8 Explain briefly heat death of universe in terms of entropy.

6.9 Is it possible for a cyclic reversible heat engine to absorb heat at constant temperature and transforms it completely into work without rejecting some heat at low temperature? Explain.

6.10 How does behaviour of real gases differ from ideal gas at high pressure and low temperature? Identify the reasons behind these differences based on kinetic theory of gases.

6.11 Show that area under *P-V* graph is equal to work done.

6.12 How is work done (i) by a gas (ii) on a gas?

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Constructed Response Questions

6.1 Explain how thermodynamics relates to the concept of energy conservation.

6.2 Explain how thermodynamics applies to biological systems, such as human body.

6.3 A gas is expanding adiabatically. Explain what happens to temperature and pressure of the the gas.

6.4 A coffee cup is left on a table, and overtime coffee cup cools down. Explain thermodynamics processes occurring during this process.

6.5 How can we explain different weather patterns through thermodymical processes like wind, rain, etc.

Comprehensive Questions

6.1 What are the postulates of kinetic theory of gases? Derive a relation for ideal gas equation in the form $PV=Nk_BT$ from general gas equation.

6.2 State and explain various gas laws.

6.3 Explain first law of thermodynamics in detail. Give an example in support of your explanation. Give its two applications.

6.4 What is a refrigerator? Explain its working. Derive an expression for its co-efficient of performance.

6.5. What is Carnot engine? Describe Carnot cycle. State Carnot theorem and derive an expression for efficiency of Carnot engine.

6.6 Define and explain the term "Entropy".

Numerical Problems

6.1 A gas occupies 6.0 L of volume at a pressure of 12 atm. What will be the volume of gas if the pressure is increased by 2.0 atm, assuming that temperature remains constant? (Ans: 5.14 L)

6.2 In a vaccum chamber which is connected to a cryogenic pump, pressure as low as 1.00 nPa is being attained. Calculate the number of molecules in 1.00 m^3 vessel at this pressure and temperature of 300 K. (Ans: 2.41×10^{14} molecules)

6.3 A gas undergoes a thermodynamic process where it absorbs 500 J of heat energy and performs 300 J work on its surroundings. Calculate the change in internal energy of the gas. (Ans: 200 J)

6.4 A Carnot engine is operating between a high temperature reservoir at 600 K and a low temperature reservoir at 300 K. Calculate:

(i) the maximum possible efficiency

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(ii) the amount of work output if the engine absorbs 500 J of heat from the high temperature reservoir. [Ans: (i) 50% (ii) 250 J]

6.5 A refrigerator extracts 1200 J of heat from its interior (the cold reservoir) and releases 1800 J of heat to the surrounding environment (the hot reservoir) during each cycle. Calculate:

(i) the work input required per cycle.

(ii) the coefficient of performance (COP) of the refrigerator.

[Ans: (i) 600 J (ii) 2]

6.6 Calculate the entropy change when 1.0 mole of ice at 0°C melts to form liquid water at the same temperature. (Heat of fusion of ice per mole = 6.01×10^3 J)

(Ans: 22.0 J K^{-1})

6.7 A gas occupies 400 mL at 20 °C. What volume will it occupy at 80 °C, assuming constant pressure? (Ans: 482 mL)

6.8 A gas has a pressure of 2 atm at 300 K. What pressure will it have at 450 K, assuming constant volume? (Ans: 3 atm)

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