Eq. (12.1), the total heat absorbed equals the work done by the system.

12.9 HEAT ENGINES

Heat engine is a device by which a system is made to undergo a cyclic process that results in conversion of heat to work.

(1) It consists of a **working substance**–the system. For example, a mixture of fuel vapour and air in a gasoline or diesel engine or steam in a steam engine are the working substances.

(2) The working substance goes through a cycle consisting of several processes. In some of these processes, it absorbs a total amount of heat Q_1 from an external reservoir at some high temperature T_1.

(3) In some other processes of the cycle, the working substance releases a total amount of heat Q_2 to an external reservoir at some lower temperature T_2.

(4) The work done (W) by the system in a cycle is transferred to the environment via some arrangement (e.g. the working substance may be in a cylinder with a moving piston that transfers mechanical energy to the wheels of a vehicle via a shaft).

The basic features of a heat engine are schematically represented in Fig. 12.9.

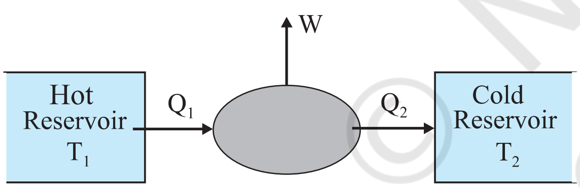


Fig. 12.9 *Schematic representation of a heat engine. The engine takes heat Q_1 from a hot reservoir at temperature T_1, releases heat Q_2 to a cold reservoir at temperature T_2 and delivers work W to the surroundings.*

The cycle is repeated again and again to get useful work for some purpose. The discipline of thermodynamics has its roots in the study of heat engines. A basic question relates to the efficiency of a heat engine. The efficiency (η) of a heat engine is defined by

$$\eta = \frac{W}{Q_1} \quad (12.18)$$

where Q_1 is the heat input i.e., the heat absorbed by the system in one complete cycle and W is the work done on the environment in a cycle. In a cycle, a certain amount of heat (Q_2) may also be rejected to the environment. Then, according to the First Law of Thermodynamics, over one complete cycle,

$$W = Q_1 - Q_2 \quad (12.19)$$

i.e.,

$$\eta = 1 - \frac{Q_2}{Q_1} \quad (12.20)$$

For $Q_2 = 0$, $\eta = 1$, i.e., the engine will have 100% efficiency in converting heat into work. Note that the First Law of Thermodynamics i.e., the energy conservation law does not rule out such an engine. But experience shows that such an ideal engine with $\eta = 1$ is never possible, even if we can eliminate various kinds of losses associated with actual heat engines. It turns out that there is a fundamental limit on the efficiency of a heat engine set by an independent principle of nature, called the Second Law of Thermodynamics (section 12.11).

The mechanism of conversion of heat into work varies for different heat engines. Basically, there are two ways : the system (say a gas or a mixture of gases) is heated by an external furnace, as in a steam engine; or it is heated internally by an exothermic chemical reaction as in an internal combustion engine. The various steps involved in a cycle also differ from one engine to another.

12.10 REFRIGERATORS AND HEAT PUMPS

A refrigerator is the reverse of a heat engine. Here the working substance extracts heat Q_2 from the cold reservoir at temperature T_2, some external work W is done on it and heat Q_1 is released to the hot reservoir at temperature T_1 (Fig. 12.10).

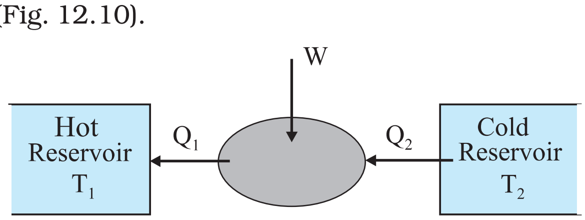
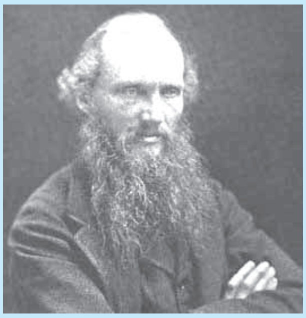
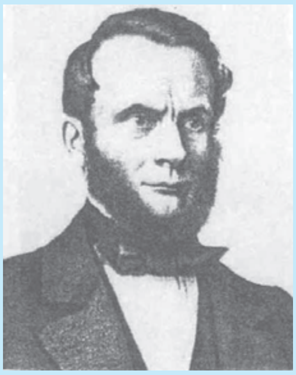


Fig. 12.10 *Schematic representation of a refrigerator or a heat pump, the reverse of a heat engine.*

Pioneers of Thermodynamics





Lord Kelvin (William Thomson) (1824-1907), born in Belfast, Ireland, is among the foremost British scientists of the nineteenth century. Thomson played a key role in the development of the law of conservation of energy suggested by the work of James Joule (1818-1889), Julius Mayer (1814-1878) and Hermann Helmholtz (1821-1894). He collaborated with Joule on the so-called Joule-Thomson effect : cooling of a gas when it expands into vacuum. He introduced the notion of the absolute zero of temperature and proposed the absolute temperature scale, now called the Kelvin scale in his honour. From the work of Sadi Carnot (1796-1832), Thomson arrived at a form of the Second Law of Thermodynamics. Thomson was a versatile physicist, with notable contributions to electromagnetic theory and hydrodynamics.

Rudolf Clausius (1822-1888), born in Poland, is generally regarded as the discoverer of the Second Law of Thermodynamics. Based on the work of Carnot and Thomson, Clausius arrived at the important notion of entropy that led him to a fundamental version of the Second Law of Thermodynamics that states that the entropy of an isolated system can never decrease. Clausius also worked on the kinetic theory of gases and obtained the first reliable estimates of molecular size, speed, mean free path, etc.

A heat pump is the same as a refrigerator. What term we use depends on the purpose of the device. If the purpose is to cool a portion of space, like the inside of a chamber, and higher temperature reservoir is surrounding, we call the device a refrigerator; if the idea is to pump heat into a portion of space (the room in a building when the outside environment is cold), the device is called a heat pump.

In a refrigerator the working substance (usually, in gaseous form) goes through the following steps : (a) sudden expansion of the gas from high to low pressure which cools it and converts it into a vapour-liquid mixture, (b) absorption by the cold fluid of heat from the region to be cooled converting it into vapour, (c) heating up of the vapour due to external work done on the system, and (d) release of heat by the vapour to the surroundings, bringing it to the initial state and completing the cycle.

The coefficient of performance (α) of a refrigerator is given by

$$\alpha = \frac{Q_2}{W} \qquad (12.21)$$

where Q_2 is the heat extracted from the cold reservoir and W is the work done on the system–the refrigerant. (α for heat pump is defined as Q_1/W) Note that while η by definition can never exceed 1, α can be greater than 1. By energy conservation, the heat released to the hot reservoir is

$$Q_1 = W + Q_2$$

i.e.,
$$\alpha = \frac{Q_2}{Q_1 - Q_2} \qquad (12.22)$$

In a heat engine, heat cannot be fully converted to work; likewise a refrigerator cannot work without some external work done on the system, i.e., the coefficient of performance in Eq. (12.21) cannot be infinite.

12.11 SECOND LAW OF THERMODYNAMICS

The First Law of Thermodynamics is the principle of conservation of energy. Common experience shows that there are many conceivable processes that are perfectly allowed by the First Law and yet are never observed. For example, nobody has ever seen a book lying on a table jumping to a height by itself. But such a thing would be possible if the principle of conservation of energy were the only restriction. The table could cool spontaneously, converting some of its internal energy into an equal amount of mechanical energy of the book, which would then hop to a height with potential energy equal to the mechanical energy it acquired. But this never happens. Clearly, some additional basic principle of nature forbids the above, even though it satisfies the energy conservation principle. This principle, which disallows many phenomena consistent with the First Law of Thermodynamics is known as the Second Law of Thermodynamics.

The Second Law of Thermodynamics gives a fundamental limitation to the efficiency of a heat engine and the co-efficient of performance of a refrigerator. In simple terms, it says that efficiency of a heat engine can never be unity. According to Eq. (12.20), this implies that heat released to the cold reservoir can never be made zero. For a refrigerator, the Second Law says that the co-efficient of performance can never be infinite. According to Eq. (12.21), this implies that external work (W) can never be zero. The following two statements, one due to Kelvin and Planck denying the possibility of a perfect heat engine, and another due to Clausius denying the possibility of a perfect refrigerator or heat pump, are a concise summary of these observations.

Kelvin-Planck statement

No process is possible whose sole result is the absorption of heat from a reservoir and the complete conversion of the heat into work.

Clausius statement

No process is possible whose sole result is the transfer of heat from a colder object to a hotter object.

It can be proved that the two statements above are completely equivalent.

12.12 REVERSIBLE AND IRREVERSIBLE PROCESSES

Imagine some process in which a thermodynamic system goes from an initial state i to a final state f. During the process the system absorbs heat Q from the surroundings and performs work W on it. Can we reverse this process and bring both the system and surroundings to their initial states with no other effect anywhere ? Experience suggests that for most processes in nature this is not possible. The spontaneous processes of nature are irreversible. Several examples can be cited. The base of a vessel on an oven is hotter than its other parts. When the vessel is removed, heat is transferred from the base to the other parts, bringing the vessel to a uniform temperature (which in due course cools to the temperature of the surroundings). The process cannot be reversed; a part of the vessel will not get cooler spontaneously and warm up the base. It will violate the Second Law of Thermodynamics, if it did. The free expansion of a gas is irreversible. The combustion reaction of a mixture of petrol and air ignited by a spark cannot be reversed. Cooking gas leaking from a gas cylinder in the kitchen diffuses to the entire room. The diffusion process will not spontaneously reverse and bring the gas back to the cylinder. The stirring of a liquid in thermal contact with a reservoir will convert the work done into heat, increasing the internal energy of the reservoir. The process cannot be reversed exactly; otherwise it would amount to conversion of heat entirely into work, violating the Second Law of Thermodynamics. Irreversibility is a rule rather an exception in nature.

Irreversibility arises mainly from two causes: one, many processes (like a free expansion, or an explosive chemical reaction) take the system to non-equilibrium states; two, most processes involve friction, viscosity and other dissipative effects (e.g., a moving body coming to a stop and losing its mechanical energy as heat to the floor and the body; a rotating blade in a liquid coming to a stop due to viscosity and losing its mechanical energy with corresponding gain in the internal energy of the liquid). Since dissipative effects are present everywhere and can be minimised but not fully eliminated, most processes that we deal with are irreversible.

A thermodynamic process (state $i \rightarrow$ state f) is reversible if the process can be turned back such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe. From the preceding discussion, a reversible process is an idealised notion. A process is reversible only if it is quasi-static (system in equilibrium with the surroundings at every stage) and there are no dissipative effects. For example, a quasi-static isothermal expansion of an ideal gas in a cylinder fitted with a frictionless movable piston is a reversible process.

Why is reversibility such a basic concept in thermodynamics ? As we have seen, one of the concerns of thermodynamics is the efficiency with which heat can be converted into work. The Second Law of Thermodynamics rules out the possibility of a perfect heat engine with 100% efficiency. But what is the highest efficiency possible for a heat engine working between two reservoirs at temperatures T_1 and T_2? It turns out that a heat engine based on idealised reversible processes achieves the highest efficiency possible. All other engines involving irreversibility in any way (as would be the case for practical engines) have lower than this limiting efficiency.

12.13 CARNOT ENGINE

Suppose we have a hot reservoir at temperature T_1 and a cold reservoir at temperature T_2. What is the maximum efficiency possible for a heat engine operating between the two reservoirs and what cycle of processes should be adopted to achieve the maximum efficiency ? Sadi Carnot, a French engineer, first considered this question in 1824. Interestingly, Carnot arrived at the correct answer, even though the basic concepts of heat and thermodynamics had yet to be firmly established.

We expect the ideal engine operating between two temperatures to be a reversible engine. Irreversibility is associated with dissipative effects, as remarked in the preceding section, and lowers efficiency. A process is reversible if it is quasi-static and non-dissipative. We have seen that a process is not quasi-static if it involves finite temperature difference between the system and the reservoir. This implies that in a reversible heat engine operating between two temperatures, heat should be absorbed (from the hot reservoir) isothermally and released (to the cold reservoir) isothermally. We thus have identified two steps of the reversible heat engine : isothermal process at temperature T_1 absorbing heat Q_1 from the hot reservoir, and another isothermal process at temperature T_2 releasing heat Q_2 to the cold reservoir. To complete a cycle, we need to take the system from temperature T_1 to T_2 and then back from temperature T_2 to T_1. Which processes should we employ for this purpose that are reversible? A little reflection shows that we can only adopt reversible adiabatic processes for these purposes, which involve no heat flow from any reservoir. If we employ any other process that is not adiabatic, say an isochoric process, to take the system from one temperature to another, we shall need a series of reservoirs in the temperature range T_2 to T_1 to ensure that at each stage the process is quasi-static. (Remember again that for a process to be quasi-static and reversible, there should be no finite temperature difference between the system and the reservoir.) But we are considering a reversible engine that operates between only two temperatures. Thus adiabatic processes must bring about the temperature change in the system from T_1 to T_2 and T_2 to T_1 in this engine.

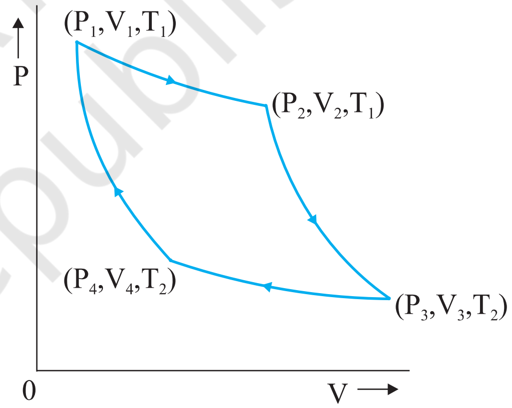


Fig. 12.11 *Carnot cycle for a heat engine with an ideal gas as the working substance.*

A reversible heat engine operating between two temperatures is called a Carnot engine. We have just argued that such an engine must have the following sequence of steps constituting one cycle, called the Carnot cycle, shown in Fig. 12.11. We have taken the working substance of the Carnot engine to be an ideal gas.

(a) *Step* 1 → 2 Isothermal expansion of the gas taking its state from (P_1, V_1, T_1) to (P_2, V_2, T_1).

The heat absorbed by the gas (Q_1) from the reservoir at temperature T_1 is given by

Eq. (12.12). This is also the work done ($W_{1\to 2}$) by the gas on the environment.

$$W_{1\to 2} = Q_1 = \mu R T_1 \ln\left(\frac{V_2}{V_1}\right) \qquad (12.23)$$

(b) *Step* $2 \to 3$ Adiabatic expansion of the gas from (P_2, V_2, T_1) to (P_3, V_3, T_2) Work done by the gas, using Eq. (12.16), is

$$W_{2\to 3} = \frac{\mu R\left(T_1 - T_2\right)}{\gamma - 1} \qquad (12.24)$$

(c) *Step* $3 \to 4$ Isothermal compression of the gas from (P_3, V_3, T_2) to (P_4, V_4, T_2).

Heat released (Q_2) by the gas to the reservoir at temperature T_2 is given by Eq. (12.12). This is also the work done ($W_{3\to 4}$) on the gas by the environment.

$$W_{3\to 4} = Q_2 = \mu R T_2 \ln\left(\frac{V_3}{V_4}\right) \qquad (12.25)$$

(d) *Step* $4 \to 1$ Adiabatic compression of the gas from (P_4, V_4, T_2) to (P_1, V_1, T_1).

Work done on the gas, [using Eq.(12.16), is

$$W_{4\to 1} = \mu R\left(\frac{T_1 - T_2}{\gamma - 1}\right) \qquad (12.26)$$

From Eqs. (12.23) to (12.26) total work done by the gas in one complete cycle is

$$W = W_{1\to 2} + W_{2\to 3} - W_{3\to 4} - W_{4\to 1}$$

$$= \mu R T_1 \ln\left(\frac{V_2}{V_1}\right) - \mu R T_2 \ln\left(\frac{V_3}{V_4}\right) \qquad (12.27)$$

The efficiency η of the Carnot engine is

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

$$= 1 - \left(\frac{T_2}{T_1}\right)\frac{\ln\left(\frac{V_3}{V_4}\right)}{\ln\left(\frac{V_2}{V_1}\right)} \qquad (12.28)$$

Now since step $2 \to 3$ is an adiabatic process,

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

i.e. $$\frac{V_2}{V_3} = \left(\frac{T_2}{T_1}\right)^{1/(\gamma-1)} \qquad (12.29)$$

Similarly, since step $4 \to 1$ is an adiabatic process

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

i.e. $$\frac{V_1}{V_4} = \left(\frac{T_2}{T_1}\right)^{1/\gamma-1} \qquad (12.30)$$

From Eqs. (12.29) and (12.30),

$$\frac{V_3}{V_4} = \frac{V_2}{V_1} \qquad (12.31)$$

Using Eq. (12.31) in Eq. (12.28), we get

$$\eta = 1 - \frac{T_2}{T_1} \quad \text{(Carnot engine)} \qquad (12.32)$$

We have already seen that a Carnot engine is a reversible engine. Indeed it is the only reversible engine possible that works between two reservoirs at different temperatures. Each step of the Carnot cycle given in Fig. 12.11 can be reversed. This will amount to taking heat Q_2 from the cold reservoir at T_2, doing work W on the system, and transferring heat Q_1 to the hot reservoir. This will be a reversible refrigerator.

We next establish the important result (sometimes called Carnot's theorem) that (a) working between two given temperatures T_1 and T_2 of the hot and cold reservoirs respectively, no engine can have efficiency more than that of the Carnot engine and (b) the efficiency of the Carnot engine is independent of the nature of the working substance.

To prove the result (a), imagine a reversible (Carnot) engine R and an irreversible engine I working between the same source (hot reservoir) and sink (cold reservoir). Let us couple the engines, I and R, in such a way so that I acts like a heat engine and R acts as a refrigerator. Let I absorb heat Q_1 from the source, deliver work W' and release the heat Q_1- W' to the sink. We arrange so that R returns the same heat Q_1 to the source, taking heat Q_2 from the sink and requiring work $W = Q_1 - Q_2$ to be done on it.

Now suppose $\eta_R < \eta_I$ i.e. if R were to act as an engine it would give less work output than that of I i.e. $W < W'$ for a given Q_1. With R acting like a refrigerator, this would mean $Q_2 = Q_1 - W > Q_1 - W'$. Thus, on the whole, the coupled I-R system extracts heat $(Q_1 - W) - (Q_1 - W') = (W' - W)$ from the cold reservoir and delivers the same amount of work in one cycle, without any change in the source or anywhere else. This is clearly against the Kelvin-Planck statement of the Second Law of Thermodynamics. Hence the assertion $\eta_I > \eta_R$ is wrong. No engine can have efficiency greater

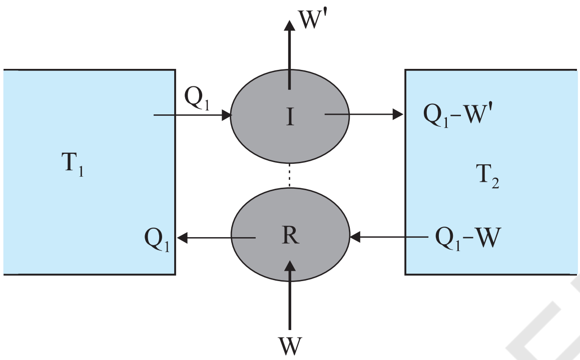


Fig. 12.12 *An irreversible engine (I) coupled to a reversible refrigerator (R). If W ′ > W, this would amount to extraction of heat W′ – W from the sink and its full conversion to work, in contradiction with the Second Law of Thermodynamics.*

than that of the Carnot engine. A similar argument can be constructed to show that a reversible engine with one particular substance cannot be more efficient than the one using another substance. The maximum efficiency of a Carnot engine given by Eq. (12.32) is independent of the nature of the system performing the Carnot cycle of operations. Thus we are justified in using an ideal gas as a system in the calculation of efficiency η of a Carnot engine. The ideal gas has a simple equation of state, which allows us to readily calculate η, but the final result for η, [Eq. (12.32)], is true for any Carnot engine.

This final remark shows that in a Carnot cycle,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \qquad (12.33)$$

is a universal relation independent of the nature of the system. Here Q_1 and Q_2 are respectively, the heat absorbed and released isothermally (from the hot and to the cold reservoirs) in a Carnot engine. Equation (12.33), can, therefore, be used as a relation to define a truly universal thermodynamic temperature scale that is independent of any particular properties of the system used in the Carnot cycle. Of course, for an ideal gas as a working substance, this universal temperature is the same as the ideal gas temperature introduced in section 12.11.

SUMMARY

1. The zeroth law of thermodynamics states that '*two systems in thermal equilibrium with a third system separately are in thermal equilibrium with each other*'. The Zeroth Law leads to the concept of temperature.
2. Internal energy of a system is the sum of kinetic energies and potential energies of the molecular constituents of the system. It does not include the over-all kinetic energy of the system. Heat and work are two modes of energy transfer to the system. Heat is the energy transfer arising due to temperature difference between the system and the surroundings. Work is energy transfer brought about by other means, such as moving the piston of a cylinder containing the gas, by raising or lowering some weight connected to it.
3. The first law of thermodynamics is the general law of conservation of energy applied to any system in which energy transfer from or to the surroundings (through heat and work) is taken into account. It states that

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

where ΔQ is the heat supplied to the system, ΔW is the work done by the system and ΔU is the change in internal energy of the system.