4

Second Law of Thermodynamics

4.1 LIMITATIONS OF THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics deals with energy changes involved in a process. But, it alone cannot answer many questions related to transformation of energy. The first law specifies only this: if energy is produced during a process, it must be compensated with a loss of an exactly equal quantity, so that the total energy before and after the process are the same. It helps us to determine the energy changes involved in a process, but it cannot tell us whether a proposed change would actually occur or not. If it occurs, what is the direction of the change and what are the conditions of equilibrium under which the system undergoes no further change?

The major limitation of the first law of thermodynamics is, therefore, its inability to deal with the direction of the process and the extent of change. Also, according to the first law, all forms of energy are quantitatively equivalent and they are just additive terms in an energy balance. It fails to recognise the qualitative differences between various forms of energy. This difference is apparent when we attempt to convert heat into work by means of a heat engine. Before we embark on the detailed study of the second law of thermodynamics, a discussion on these limitations is quite in order.

4.1.1 Direction of Change

We have seen that the first law of thermodynamics deals with the amount of energy in different forms that are involved in various spontaneous processes, but it is not concerned with the 'direction of change'. For example, when water on the top of a mountain runs to the bottom as a stream or as a waterfall, the initial potential energy of water is converted to the kinetic energy and the first law of thermodynamics is satisfied, because, the total energy remains unchanged. It would equally be satisfied in the reverse process in which the water flows upwards spontaneously. The first law doesn't suggest the impossibility of water flowing upwards spontaneously. However, such an occurrence is contrary to our experience.

Now, let us consider another example. When two bodies at different temperatures are brought into contact, heat energy flows from the body at high temperature to that at low temperature spontaneously. Heat energy will never flow from a lower temperature level to a higher temperature level without applying external work. According to the first law, the energy gained by the cold body should be equal to the energy lost by the hot body. Again, there is nothing in the first law that predicts that the transfer of heat must always be from the hot to the cold body. The first law would be satisfied equally well if the transfer of energy took place in the reverse direction, but such a transfer never happens in nature. Similarly, we never observe a mixture of gases made up of two or more components spontaneously separating into its constituents. Though such a process is against our experience, it would not be inconsistent with the first law of thermodynamics as long as no net change in the total energy is involved. Thus, it is clear that apart from the first law, but complementary to it, there should be some principle to deal with the spontaneous processes and their direction.

The inadequacy of the first law of thermodynamics to explain our general experience with spontaneous processes or tendency to change led to the development of the second law of thermodynamics, which deals with the direction of change. With the help of the tools provided by the second law, we can find answers to many problems that are not answered by the first law. For a chemical reaction occurring from a given initial state of reactants to a given final state of products, the first law can be utilised to estimate the heat of reaction and the effect of temperature and pressure on it. But, will the reaction proceed spontaneously? What is the equilibrium point at which no further change occurs? How is the equilibrium affected by the operating conditions? What is the maximum work available from a process? What is the minimum work required to carry out a process? What is the maximum efficiency with which a process could be carried out? Such questions are answered by the second law of thermodynamics, usually in combination with the first law.

4.1.2 Qualitative Difference between Heat and Work

Another limitation of the first law of thermodynamics is that it does not take into account the difference in quality between heat and work. When we treat heat and work as additive terms in an energy balance, we are in fact ignoring the intrinsic difference between them. It is true that, in the application of the first law this difference is not going to affect our calculations. However when we consider converting heat energy to other forms of energy, the qualitative difference between heat and work would be obvious. It is possible to convert one form of work to another (such as electrical to mechanical) with almost 100 per cent efficiency, provided, the irreversibilities in the apparatus are eliminated. But the efficiency of converting energy transferred to a system as heat into any of the forms of work is limited to very low values. This leads us to the conclusion that heat is a less versatile or more degraded form of energy compared to the other forms of energy or work can be termed energy of a higher quality than heat. During the conversion of heat into work, a portion of the energy becomes *unavailable*, that is, not capable of being transformed into useful form.

The difference between the quality of heat and other forms of energy are accounted for in the second law of thermodynamics. When we say that heat flows always from a higher to a lower temperature we are assigning a characteristic quality as well as quantity to heat, the quality being represented by temperature. We know that the efficiency of a thermal power plant increases as the temperature of the steam in the boiler increases. In the transformation of heat to work, the increase in the efficiency that results from the increase in the temperature of the source clearly establishes the connection between the temperature and the quality of heat.

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4.2 GENERAL STATEMENTS OF THE SECOND LAW THERMODYNAMICS

The second law of thermodynamics is just the generalisation of our experiences with spontaneous processes and can be stated in a number of ways:

1. Heat cannot by itself pass from a cold to a hot body.
2. All spontaneous processes are, to some extent, irreversible and are accompanied by a degradation of energy.
3. Every system, when left to itself, will on the average, change toward a system of maximum probability.
4. *Kelvin–Planck statement.* It is impossible to construct an engine that, operating continuously (in a cycle), will produce no effect other than the transfer of heat from a single thermal reservoir at a uniform temperature and the performance of an equal amount of work. This statement implies that at least two thermal reservoirs of different temperatures are necessary for a heat engine to operate. This is because only part of the heat transferred to the engine from a high temperature reservoir is converted to work; the rest is rejected to a low temperature reservoir. Further, the statement implies that no heat engine can have 100% efficiency because heat cannot be completely converted to work. The word 'continuous' in the Kelvin–Planck statement has an important implication. Consider the isothermal expansion of an ideal gas. The change in internal energy, DU, is zero in this process. This means that the heat absorbed by the gas is completely converted to work. Though it may appear to contradict the second law, in fact, it is not so. What the second law requires is that there should be no change in the system or in the surroundings other than the complete conversion of heat into work. Here, the pressure of the gas has decreased and the process cannot be carried out continuously. The pressure of the gas would soon become equal to that of the surroundings, and further expansion would be impossible. The continuous conversion of heat to work is possible only in a cyclic process. But, in the cyclic process, energy from the surroundings is utilised in the form of work, in order to compress the gas back to its original pressure.
5. *Clausius statement.* It is impossible to construct a heat pump that, operating continuously, will produce no effect other than the transfer of heat from a lower temperature body to a higher temperature one. In other words, any process, which consists solely in the transfer of heat from one temperature to a higher one, is impossible. It means that energy in the form of work must be supplied to the heat pump in order to transfer heat from a cold body to a hot body. Therefore, the coefficient of performance of a heat pump can never be infinity.

4.2.1 The Equivalence of the Kelvin and Clausius Statements

All the statements of the second law are equivalent and mean the same thing. Any device that violates any one of these statements will violate all other statements. Figure 4.1 shows an engine, which violates Kelvin–Planck statement by absorbing heat from a single thermal reservoir and producing an equivalent amount of work. The work output of this engine ($W = Q_1$) is used to drive a heat pump which transfers an amount of heat Q_2 from a low temperature reservoir and an amount ($Q_1 + Q_2$) to a high temperature reservoir. The combined system shown by the dotted lines in the figure then act as heat pump which transfers an amount of heat Q_2 from a lower temperature to a higher temperature reservoir without using any external work. This is a violation of Clausius statement.

Now consider a heat pump, which violates the Clausius statement, by absorbing heat Q_2 from a low temperature reservoir and transferring it to a high temperature reservoir (Fig. 4.2). Let a heat engine work between these two reservoirs by absorbing heat Q_1 ($Q_1 > Q_2$) delivering work W ($W = Q_1 - Q_2$) and rejecting heat Q_2 to the low temperature reservoir. Since this process does not affect the low-temperature reservoir, the net effect is a heat engine operating with a single thermal reservoir absorbing heat $Q_1 - Q_2$ and converting it completely to work. This is a violation of the Kelvin–Planck statement.

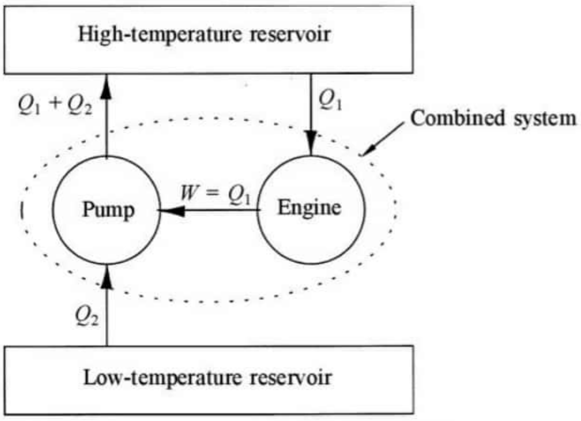

Fig. 4.1 A heat engine that violates the Kelvin–Planck, statement.

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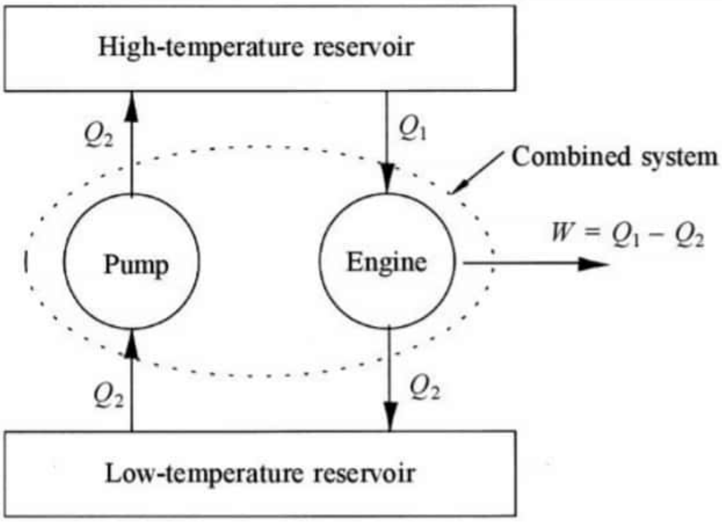

Fig. 4.2 A heat pump that violates the Clausius statement.

4.3 ENTROPY

4.3.1 Why the Concept of Entropy?

The second law of thermodynamics states that all spontaneous processes are, to some extent, irreversible and are accompanied by a degradation of energy. It also means that it is impossible for any self-acting machine to transfer energy from a given state to a higher state of availability. To make these statements quantitative there is required some function that always changes in a certain way during a spontaneous process and therefore, will characterise such a change. Internal energy was defined to give quantitative significance to the first law. Internal energy does not change in any characteristic way in a spontaneous process, and it does not help in any way in the development of the second law. The function that is fundamental in the development of the second law is *entropy*, which means transformability (change) in Greek, introduced by Clausius in 1851. Later in this chapter, we will show that the second law of thermodynamics necessitates that all spontaneous processes result in an increase in the entropy and no process is possible that results in a decrease in entropy.

Consider an imaginary process for gas separation as illustrated in Fig. 4.3. Assuming that the gases behave ideally, the change in the internal energy, $DU = 0$. On the basis of the first law, the process is not an impossible one. With the aid of the entropy function it can readily be shown that the imagined process is impossible, because, it would involve a net decrease in entropy of the system with no corresponding increase in the entropy of the surroundings.

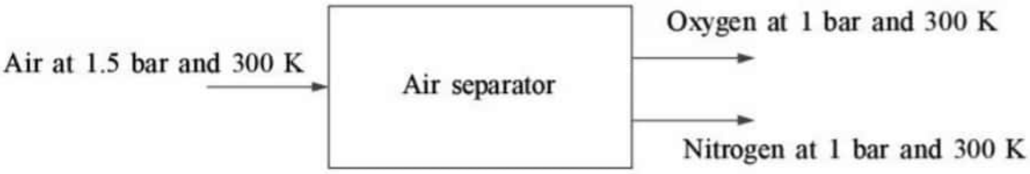

Fig. 4.3 A process that is permitted by the first law, but that violates the second law.

We have seen that although there is an exact quantitative equivalence among the different forms of energy, there is a marked difference in the availability of these forms for useful work. Heat represents the least 'available' form of energy and transformation of other forms into heat represents a degradation of energy. Entropy is the thermodynamic property, which serves as a measure of the unavailability or degradation of energy. An increase in unavailability of the total energy of a system is quantitatively expressed by a corresponding increase in its entropy. Entropy, being an intrinsic property of matter, is not affected by the external position of the body or its motion relative to other bodies. The entropy of unit mass of water at the top of the mountain is equal to the entropy of the same amount of water at the bottom of the falls, if the temperature and pressure are the same. Similarly, the entropy of unit mass of water in the flowing stream will be equal to the entropy of water in a stagnant pool, provided that the conditions such as the temperature and pressure are the same in both the cases. The entropy of a system is affected only by the nature of matter under consideration and by the state in which it exists.

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degradation of energy is measured by a net increase in the entropy. In this case, the increase in entropy was due to the degeneration of mechanical energy into heat. In general, an increase in entropy results from the addition of heat into the system through the degradation of energy in any form or, by the direct supply of heat to the system. In short, *the entropy of the system is increased by the addition of heat through any mechanism or from any source.* The increase in entropy is proportional to the heat exchanged but not equal to it, since, it is necessary to consider the temperature of the system when the heat is transferred.

4.3.3 Entropy and Temperature

The amount of heat added to a system is only a partial measure of the magnitude of its entropy increase. It also depends upon the temperature of the system to which heat is added. Consider a system consisting of a weight and two separate reservoirs, one at temperature T_h and the other at a lower temperature T_C. The weight is first allowed to fall to the high-temperature reservoir, transferring to it certain quantity of heat in the process. The heat so transferred is then made to flow into the reservoir at T_C. These two irreversible processes result in a net increase in entropy which would be the same as the increase in entropy that would result if the weight were allowed to fall directly to the reservoir at T_C. This is so, because, the initial and the final conditions are the same in both cases. Entropy, as will be shown later, is a thermodynamic property that depends only on the terminal states and not on the path followed. Therefore, the change in entropy would be the same in both cases. In the first instance, it is the sum of two contributions: one, the entropy change that resulted by the dropping of the weight to the hot reservoir; and the other by the transfer of heat to the cold reservoir. Since, these two together equal the entropy change resulted by the dropping of the weight to the cold reservoir, we can conclude that the change in entropy due to the lowering of weight to a reservoir at a high temperature is less than that resulted when the weight was lowered to the reservoir at a low temperature. It means that the transfer of energy to a low temperature leads to a greater degradation than that resulted by the transfer of the same quantity to a higher temperature. The greater the degradation of the energy, the greater would be the irreversibility of the process. Entropy, being a thermodynamic function, used to measure the degree of degradation or the extent of irreversibility, should therefore, be related not to Q, but to Q/T, where Q is the heat received by the reservoir and T is its temperature.

In conclusion, *the transfer of heat within an isolated system to a region of lower temperature increases the unavailability of energy and the entropy of the system. The addition of heat to a system at a lower temperature leads to a greater degradation of energy than that resulted by the addition at a higher temperature.*

4.3.4 Entropy and the Nature of the Process

We have seen that a quantitative description for entropy should take into account the heat transferred and the temperature level at which it is transferred. In addition, in order to complete the definition of entropy, the nature of the process should also be specified. For example, a gas may be expanded freely to a lower pressure within a closed system, which is completely isolated from the surroundings thermally and mechanically. This is an irreversible process resulting in degradation of energy of the system and consequently an increase in its entropy. However, no heat is added, no work is done, and for an ideal gas, the process is isothermal. How is then the increase in entropy for this process measured? Consider an engine operating within the system that continuously converts the work done into heat by means of friction. In this case, heat is added to the system by degradation of mechanical work. The amount of heat added increases with the efficiency of the engine, and reaches a maximum when the engine operates reversibly. But the change in entropy (being a state function) accompanying a process, is dependent only on the initial and final states and not on the path. So, when we take the amount of heat transferred to measure the increase in entropy through the term Q/T, the nature of the process should be specified. The logical choice, thus, is the maximum possible degradation of higher forms of energy into heat, which is possible only in a reversible process. Entropy change should therefore be measured as Q_R/T, where Q_R is the heat transferred when the process is occurring reversibly.

To summarise, the quantitative definition of entropy requires the following specifications:

1. The amount of heat transferred.
2. The temperature level at which the transfer occurs
3. The nature of the process, whether reversible or irreversible.

To comply with these requirements, we define entropy change in a process as

$$\boxed{dS = \frac{dQ_R}{T}} \tag{4.1}$$

In Eq. (4.1), S denotes the entropy, Q the heat transferred, T the absolute temperature, and the suffix R indicates the reversibility of the process.

4.4 THE CARNOT PRINCIPLE

Nicolas Sadi Carnot (1824) introduced the concept of cyclic operations and was among the first to study the principles of the second law of thermodynamics. He devised a classical ideal cycle named after him that formed the basis for the mathematical statement of second law of thermodynamics.

The *Carnot cycle* consists of an alternate series of two reversible isothermal processes and two reversible adiabatic processes as shown in Fig. 4.4.

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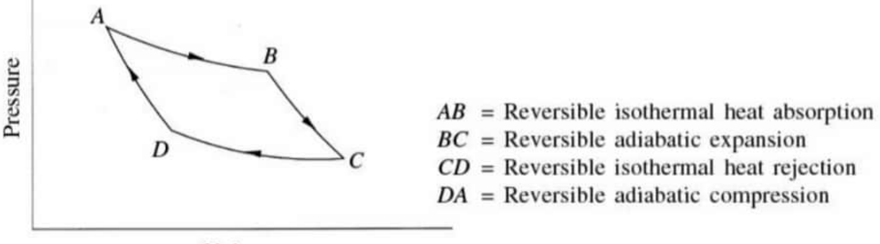

Fig. 4.4 *P-V* diagram for the Carnot cycle.

During the process *AB*, heat is transferred reversibly and isothermally to the working substance from the high-temperature reservoir (HTR) at temperature T_1 and the system performs an amount of work which is given by the area under the curve *AB* on the *PV* diagram. During the reversible adiabatic expansion (*BC*), the temperature of the system decreases from T_1 to T_2. The area under the curve *BC* gives the net work obtained from this step. During process *CD*, the system rejects heat Q_2 to a low-temperature reservoir (LTR) at a constant temperature T_2. The area on the *PV* diagram under the curve *CD* is the net work done on the system during this step. The final step is a reversible adiabatic compression (*DA*) during which the temperature rises from T_2 to T_1 and the original conditions are restored to the system. The area under the curve *DA* is the work done on the system for this change. The enclosed area *ABCD* represents the net work delivered by the engine.

The *Carnot principle* involves the following two propositions.

1. No heat engine operating in a cycle between two constant temperature reservoirs can be more efficient than a reversible engine working between the same two reservoirs.
2. All reversible engines working between two constant temperature reservoirs have the same efficiency irrespective of the working substance, and this efficiency is dependent only on the temperature levels.

The first proposition can be easily verified by considering a reversible engine (*R*) and an irreversible engine (*I*) operating between two heat reservoirs as shown in Fig. 4.5. Assume that the irreversible engine is more efficient than the reversible one. Let the work output of both the engines be *W*. Since, the efficiency is defined as the ratio of the work output to the heat input, then for engine *I*, both the heat absorbed $Q_{1,I}$ and the heat rejected $Q_{2,I}$ are less than the corresponding values $Q_{1,R}$ and $Q_{2,R}$ for the reversible engine.

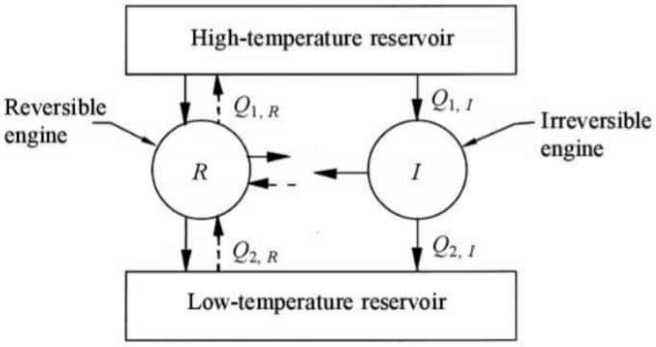

Fig. 4.5 The proof of Carnot's principle.

Since the reversible engine can be operated as a heat pump as shown by the dotted arrows in Fig. 4.5, the work output from engine (*I*) can be utilised to pump heat $Q_{2,R}$ from the LTR, thereby, rejecting heat $Q_{1,R}$ to the HTR. The net effect of the combined system would be the transfer of heat ($Q_{2,R} - Q_{2,I}$) from a cold body to the hot one without the aid of an external agency. As this is a violation of the second law of thermodynamics, an irreversible engine cannot be more efficient than a reversible one.

To prove the second proposition, assume that the irreversible engine (*I*) in Fig. 4.5 be replaced by a reversible engine (*R*☐). Let this engine be more efficient than the engine *R*. By reasoning on the same lines as in the preceding paragraph, we can show that the engine *R* can be reversed to run as a heat pump, producing a net effect of transfer of energy from a lower to a higher temperature without any work. Since this is contrary to the second law, *R*☐ cannot be more efficient than *R* and vice versa. This means that neither *R* nor *R*☐ can be more efficient than each other, i.e., both must have same efficiency. Since, no restrictions were placed on the working fluid in the engine, this efficiency is independent of the working substance and depends only on the temperature levels between which the system is operating.

Denoting the efficiency of the Carnot engine by h,

$$h = f(T_1, T_2)$$

Since the efficiency is defined as the ratio of *W* to Q_1, and *W* by the first law of thermodynamics is equal to $Q_1 - Q_2$, we can write the above equation as

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Denoting the efficiency of the Carnot engine by h,

$$h = f(T_1, T_2)$$

Since the efficiency is defined as the ratio of W to Q_1, and W by the first law of thermodynamics is equal to $Q_1 - Q_2$, we can write the above equation as

$$\frac{Q_1 - Q_2}{Q_1} = f(T_1, T_2) \tag{4.2}$$

or

$$\frac{Q_2}{Q_1} = \phi(T_1, T_2) \tag{4.3}$$

Equation (4.3) means that the ratio of heat rejected to the heat absorbed by a reversible engine is a function only of the temperatures of the heat source and sink.

4.4.1 Thermodynamic Temperature Scale

The fact that the efficiency of a Carnot engine is independent of the working fluid enables us to define a universal scale of temperature independent of the individual properties of the thermometric substance and of the arbitrary nature of the method of measurement. Lord Kelvin proposed an absolute thermodynamic scale of temperature such that the functional relationship in Eq. (4.3) could be written as

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \tag{4.4}$$

Equation (4.4) means that if an ideal Carnot engine be constructed and Q_1 and Q_2 are measured, their ratio would be the ratio of the absolute thermodynamic temperature of the heat source to that of the sink. The choice of the function $f(T_1, T_2)$ as T_1/T_2 is arbitrary. We could have chosen this function as equal to T_2/T_1, or exp $(T_1 - T_2)$ instead of T_1/T_2. But the present choice is found to be convenient, because by this choice, the absolute temperature coincides with the temperature in the ideal gas equation. The unit of absolute temperature is defined by choosing a single fixed point, the triple point of water as $T_t = 273.16$ K. If a heat engine has a heat source at this temperature, the temperature of the cold sink—the object, whose temperature we want to measure—can be found by measuring Q_1 and Q_2 and using

$$T_2 = \frac{Q_2}{Q_1} \times T_t$$

With the above choice of the thermodynamic temperature, the efficiency (h) of an ideal Carnot engine, Eq. (4.2), becomes

$$\boxed{\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}} \tag{4.5}$$

and Eq. (4.3) becomes

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

The absolute zero or the zero of the thermodynamic temperature scale is the value of T_2 at which the Carnot efficiency becomes equal to unity. Equation (4.5) gives the maximum efficiency of a heat engine operating between two thermal reservoirs at thermodynamic temperatures T_1 and T_2. In the following section, we consider the efficiency of an ideal Carnot engine using an ideal gas as the working fluid and show that the thermodynamic temperature and the ideal gas temperature are the same.

4.4.2 Ideal Gas as the Carnot Engine Working Substance

Consider an ideal Carnot engine cycle as depicted in Fig. 4.4 with an ideal gas as the working substance. Let P_A, P_B, P_C and P_D denote the pressures of the gas at the various states represented by points A, B, C and D respectively. The isothermal expansion step AB and isothermal compression step CD are carried out at constant temperatures T_1 and T_2 respectively. The net work done by the engine

$$W_{net} = W_{AB} + W_{BC} + W_{CD} + W_{DA} \tag{4.6}$$

The work done during the reversible adiabatic operations BC and DA are equal to $-$ DU. It follows from the first law, Eq. (2.4), D$U = Q - W$, in which $Q = 0$

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$$W_{BC} = -\Delta U_{BC} = -\int_{T_1}^{T_2} C_V \, dT \qquad (4.7)$$

$$W_{DA} = -\Delta U_{DA} = -\int_{T_2}^{T_1} C_V \, dT \qquad (4.8)$$

Equations (4.7) and (4.8) reveal that W_{BC} and W_{DA} are numerically equal and opposite in sign so that they cancel each other in Eq. (4.6). Therefore,

$$W_{\text{net}} = W_{AB} + W_{CD} \qquad (4.9)$$

The change in internal energy in an isothermal process involving ideal gases = 0. Therefore, $W = Q$. The work done and the heat absorbed (Q_1) during the isothermal expansion AB are given by

$$W_{AB} = Q_1 = RT_1 \ln \frac{P_A}{P_B} \qquad (4.10)$$

The work done during the isothermal compression CD is given by

$$W_{CD} = RT_2 \ln \frac{P_C}{P_D} \qquad (4.11)$$

Substituting Eqs. (4.10) and (4.11) into Eq. (4.9), we get

$$W_{\text{net}} = RT_1 \ln \frac{P_A}{P_B} + RT_2 \ln \frac{P_C}{P_D} \qquad (4.12)$$

Equations (4.10) and (4.12) lead to the following equation for the efficiency of the engine:

$$\eta = \frac{W_{\text{net}}}{Q_1} = \frac{RT_1 \ln(P_A/P_B) + RT_2 \ln(P_C/P_D)}{RT_1 \ln(P_A/P_B)} = 1 + \frac{T_2 \ln(P_C/P_D)}{T_1 \ln(P_A/P_B)} \qquad (4.13)$$

For the adiabatic processes BC and DA, the temperatures and pressures are interrelated as given below.

$$\frac{T_1}{T_2} = \left(\frac{P_A}{P_D}\right)^{(\gamma-1)/\gamma} \quad \text{for process } DA \qquad (4.14)$$

$$\frac{T_1}{T_2} = \left(\frac{P_B}{P_C}\right)^{(\gamma-1)/\gamma} \quad \text{for process } BC \qquad (4.15)$$

Comparing Eqs. (4.14) and (4.15), we see that

$$\frac{P_A}{P_B} = \frac{P_D}{P_C} \qquad (4.16)$$

Substituting Eq. (4.16) into Eq. (4.13), we get

$$\eta = 1 - \frac{T_2}{T_1} = \frac{(T_1 - T_2)}{T_1} \qquad (4.17)$$

By the first law of thermodynamics $W_{\text{net}} = Q_1 - Q_2$. Therefore, Eq. (4.17) can be written as

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \qquad (4.18)$$

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

Comparison of Eq. (4.18) with Eq. (4.5) shows that the ideal gas temperature and the absolute thermodynamic temperature are identical.

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where Q_1 is the heat absorbed and Q_2 is the heat rejected by the system. The heat absorbed by the system is positive and heat rejected is negative as per the sign convention we have adopted so that the above equation should be written as

$$\frac{Q_1}{T_1} = -\frac{Q_2}{T_2} \tag{4.20}$$

or

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \tag{4.21}$$

Equation (4.21) means that the sum of the quantities Q_1/T_1 and Q_2/T_2 for a reversible heat engine is zero. Any reversible cyclic operation like the one represented on the *P-V* diagram in Fig. 4.6 may be regarded as made up of a large number of imaginary Carnot cycles and for each such cycle we can write equation similar to Eq. (4.21) as

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = 0 \tag{4.22}$$

where dQ_1 and dQ_2 are the heat absorbed and heat rejected respectively during one such an imaginary cycle.

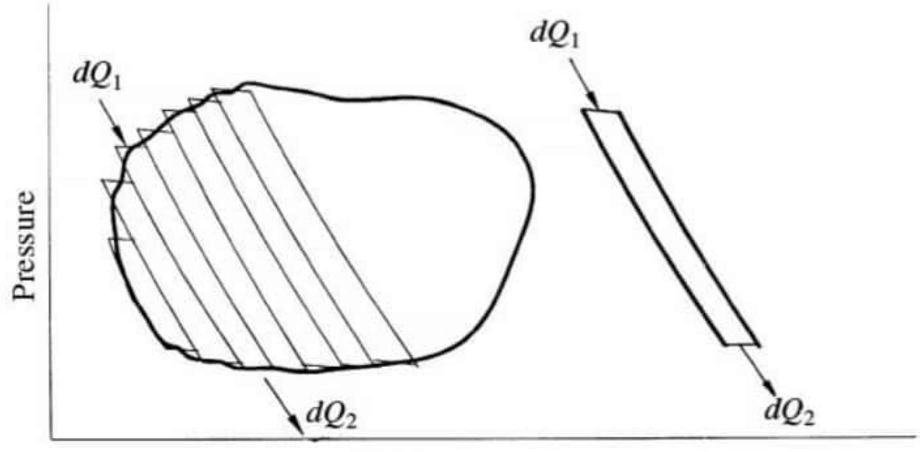

Fig. 4.6 A reversible cycle divided into a number of Carnot's cycles.

Combining all such equations that are written for the separate Carnot cycles into which the original reversible cycle is divided, we get

$$\oint \frac{dQ_R}{T} = 0 \tag{4.23}$$

where the subscript *R* refers to the reversible process and the cyclic integral limits the equation to the cyclic operation. We have defined entropy change in a process by Eq. (4.1). Substituting Eq. (4.1) into Eq. (4.23) we see that

$$\oint dS = (\Delta S)_{\text{cycle}} = 0 \tag{4.24}$$

where *S* is the entropy of the system. We have characterised the thermodynamic property of a system as a quantity that undergoes no net change in a cyclic operation. Equation (4.24) means that the entropy change D*S* for the cyclic operation is equal to zero; or, in short, entropy *S* as defined by Eq. (4.1) is a thermodynamic property of the system. It reveals an interesting fact: *whereas the heat transferred in a process is a path function, the ratio of the heat transferred to the temperature at which it is transferred is a state function.*

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4.6 CALCULATION OF ENTROPY CHANGES

The entropy change as defined by Eq. (4.1), accompanying a process is applicable for a reversible process. In practice, processes are never carried out reversibly. Entropy being a state function depends only on the end states. The entropy change in an irreversible process occurring between any two states would be the same as the entropy change in a reversible process occurring between them, the latter being evaluated by Eq. (4.1). Thus, the entropy change in any irreversible process can be evaluated by devising an imaginary reversible process for accomplishing the same change and calculating the entropy change in the latter.

If the process involves only the direct transfer of heat or the degradation of higher forms of energy into heat, the restriction of reversibility in Eq. (4.1) may be ignored. Thus, entropy change due to the addition of heat can always be calculated by Eq. (4.1), whether the transfer is accomplished reversibly or irreversibly. Similarly, for processes involving the changes in the relative position or movements of matter (as in the case of a falling object) the heat added, even if the process is highly irreversible, measures the entropy change. However, if a process is irreversible because of a finite difference in another driving force, such as pressure, calculation of entropy change is done by devising a reversible process for accomplishing the change. Thus, we see that in the evaluation of entropy changes, the reversibility restriction is to be strictly followed only for processes involving changes in the intrinsic state of the matter.

4.6.1 Phase Change

The entropy change in phase transitions like fusion, vaporisation, or transition from one crystalline form to another can be evaluated from the values of the latent heat of phase change and the temperature at which the change is carried out. The phase changes can be treated as changes occurring reversibly at constant temperature. For example, the entropy of vaporisation DS_V is found out as

$$\boxed{\Delta S_V = \frac{\Delta H_V}{T}} \qquad (4.25)$$

***EXAMPLE* 4.6** Calculate the entropy of evaporation of dry saturated steam at 500 kPa.

Data: From the steam tables, latent heat of vaporisation, DH_V = 2106 kJ/kg; Saturation temperature of steam = 425 K.

Solution By Eq. (4.25), entropy change accompanying vaporisation is DS_V = 2106/425 = 4.96 kJ/kg K

4.6.2 Processes involving Ideal Gases

For a differential change in the thermodynamic state of a closed system, the first law of thermodynamics [Eq. (2.5)] can be written as

$$dQ = dU + dW$$

When the process is reversible and the work involved is only work of expansion ($P\,dV$), the above equation can be modified as

$$dQ_R = dU + P\,dV$$

Since this infinitesimal change in the state of the system can be assumed to occur at constant temperature T, the entropy change by Eq. (4.1) is

$$dS = \frac{dU + P\,dV}{T} \qquad (4.26)$$

For an ideal gas, $dU = C_V\,dT$ and $P = RT/V$.

$$dS = \frac{C_V\,dT + RT\,(dV/V)}{T} = C_V\frac{dT}{T} + R\frac{dV}{V}$$

Assuming that C_V is independent of temperature, this equation can be integrated for a finite change from state 1 to state 2 giving for one mole of an ideal gas,

$$\boxed{\Delta S = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}} \qquad (4.27)$$

where the suffixes 1 and 2 indicate the properties of the gas at state 1 and state 2 respectively. Equation (4.27) can be used for the evaluation of entropy change accompanying the change in states of ideal gases. It can be put in another form also. We know that for ideal gases,

$$C_V = C_P - R \qquad (4.28)$$

and

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$$dS = \frac{dU + P\,dV}{T} \tag{4.26}$$

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$$C_V = C_P - R \tag{4.28}$$

and

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}\frac{T_2}{T_1} \tag{4.29}$$

Substituting Eqs. (4.28) and (4.29) into Eq. (4.27), we obtain the following:

$$\boxed{\Delta S = C_P \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}} \tag{4.30}$$

Referring to Eqs. (4.27) and (4.30), we see that for constant volume process

$$\boxed{\Delta S = C_V \ln\frac{T_2}{T_1}} \tag{4.31}$$

For constant pressure process, we have

$$\boxed{\Delta S = C_P \ln\frac{T_2}{T_1}} \tag{4.32}$$

For an isothermal process, we obtain

$$\boxed{\Delta S = R\ln\frac{V_2}{V_1} = R\ln\frac{P_1}{P_2}} \tag{4.33}$$

Though the above equations are derived on the premise that the processes are reversible, they can be used for irreversible processes occurring between the same terminal conditions as well. This is because the change in entropy depends only on the end states and not on the history of the system.

***EXAMPLE* 4.7** Determine the change in entropy when 2 kg of a gas at 277 K is heated at constant volume to a temperature of 368 K. Take the specific heat at constant volume = 1.42 kJ/kg K.

Solution Entropy change accompanying a constant volume process is given by Eq. (4.31). For $m = 2$ kg,

$$\Delta S = mC_V \ln\frac{T_2}{T_1} = 2.0(1.42)\ln\frac{368}{277} = 0.8067 \text{ kJ/K}$$

***EXAMPLE* 4.8** Calculate the entropy change when 1 kmol of an ideal gas at 300 K and 10 bar expands through a throttle to a pressure of 1 bar, both pressures being maintained constant during the process by suitable means.

Solution During throttling enthalpy is unchanged. For an ideal gas enthalpy being a function of temperature alone, the temperature remains unchanged during the process. Therefore, entropy change accompanying the process can be computed by Eq. (4.33).

$$\Delta S = R\ln\frac{P_1}{P_2} = 8.314\ln\frac{10}{1} = 19.14 \text{ kJ/kmol K}$$

***EXAMPLE* 4.9** What is the change in entropy when 1 kmol of an ideal gas at 335 K and 10 bar is expanded irreversibly to 300 K and 1 bar? $C_P = 29.3$ kJ/kmol K.

Solution The entropy change in this process is given by Eq. (4.30)

$$\Delta S = C_P \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}$$

$$= (29.3)\ln\frac{300}{335} - 8.314\ln\frac{1}{10} = 15.91 \text{ kJ/kmol K}$$

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4.6.3 Adiabatic Mixing Process

When two substances at different temperatures are mixed together adiabatically, both will attain an intermediate temperature, say, T. The change in entropy of each is calculated as

$$\Delta S = \int \frac{dQ_R}{T} = \int_{T_1}^{T} C_P \frac{dT}{T} \tag{4.34}$$

where T_1 denotes its initial temperature. The total entropy change is then obtained by adding the individual changes. Equation (4.34) can be used for the calculation of change in entropy in processes like mixing of two fluid streams or quenching of metallic bodies in liquids.

***EXAMPLE* 4.10** Ten kilograms water at 375 K is mixed adiabatically with 30 kg water at 275 K. What is the change in entropy? Assume that the specific heat of water is 4.2 kJ/kg K and is independent of temperature.

Solution Let T be the final temperature attained by the system. Then the heat balance gives

$$10(375 - T) = 30(T - 275)$$

Solving this, $T = 300$ K. Let ΔS_1 be the change in entropy of the hot water and let ΔS_2 be that of cold water. Then by Eq. (4.34),

$$\Delta S_1 = 10 \times 4.2 \times \ln \frac{300}{375} = -9.37 \text{ kJ/K}$$

$$\Delta S_2 = 30 \times 4.2 \times \ln \frac{300}{275} = 10.96 \text{ kJ/K}$$

The total entropy change is

$$\Delta S = \Delta S_1 + \Delta S_2 = 1.59 \text{ kJ/K}$$

***EXAMPLE* 4.11** A steel casting at a temperature 725 K and weighing 35 kg is quenched in 150 kg oil at 275 K. If there are no heat losses, determine the change in entropy. The specific heat (C_P) of steel is 0.88 kJ/kg K and that of oil is 2.5 kJ/kg K.

Solution Let T be the final temperature attained by the system. Then the heat balance gives

$$35(0.88)\ (725 - T) = 150(2.5)\ (T - 275)$$

where T is the final temperature attained by the system. Solving this, we get, $T = 309.15$ K. Let ΔS_1 be the change in entropy of the casting and let ΔS_2 be that of oil. Then,

$$\Delta S_1 = 35 \times 0.88 \times \ln \frac{309.15}{725} = -26.25 \text{ kJ/K}$$

$$\Delta S_2 = 150 \times 2.5 \times \ln \frac{309.15}{275} = 43.90 \text{ kJ/K}$$

The entropy change of the casting and oil together is

$$-26.25 + 43.90 \text{ kJ/K} = 17.65 \text{ kJ/K}$$

4.6.4 Isothermal Mixing of Ideal Gases

Consider a mixture of two or more ideal gases at pressure P and temperature T. Let the mole fraction of the components in the mixture be represented by x_i. The entropy change resulting from the irreversible process of mixing of ideal gases in their pure state at temperature T and pressure P to form the mixture at the same temperature and pressure can be computed by the following equation, the proof of which is provided in Chapter 7 [see Eq. (7.122)].

$$DS = -R\,S\,x_i \ln x_i \qquad (4.35)$$

Gibbs paradox. When two distinct intermingling ideal gases are mixed, the resulting entropy change is given by Eq. (4.35). For an equimolar mixture, the entropy change is,

$$DS = -R\,(0.5 \ln 0.5 + 0.5 \ln 0.5) = -R \ln 0.5 = R \ln 2.0$$

This is true as long as the gases are different, no matter how nearly identical they are. But, when the gases are the same, the change in entropy on mixing should be zero. This curious result is known as the *Gibb's paradox*.

***EXAMPLE* 4.12** Assuming that air is a mixture of 21% oxygen and 79% nitrogen by volume, calculate entropy of 1 kmol air relative to pure oxygen and nitrogen, all at the same temperature and pressure.

Solution According to Eq. (4.35), entropy change accompanying the process of mixing pure oxygen and nitrogen to form 1 kmol air is

$$DS = -8.314(0.21 \ln 0.21 + 0.79 \ln 0.79) = 4.27 \text{ kJ/kmol K}$$

This value represents entropy of 1 kmol air relative to pure components.

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4.6.5 Chemical Reactions

The entropy changes accompanying chemical reactions are evaluated through the use of absolute entropies of the various components taking part in the reaction. Let S_P denote the sum of the entropies of the reactants and S_R denotes that of the products. Then the entropy change accompanying the reaction is given by

$$\mathrm{D}S = S_P - S_R \qquad (4.36)$$

***EXAMPLE* 4.13** Calculate the entropy change for the following gas phase reaction occurring at 1 bar and 298 K.

$$\mathrm{CO} + \frac{1}{2}\mathrm{O_2} = \mathrm{CO_2};\ \mathrm{D}H = -2.8318 \,\square\, 10^5 \text{ J/mol}$$

The absolute entropies of CO, oxygen and CO_2 are respectively 198 J/mol K, 205.2 kJ/kmol K and 213.8 J/kmol K. Can you calculate the entropy change as the ratio of heat of reaction to the temperature of the reaction? Why?

Solution Refer Eq. (4.36). The reactants are CO and oxygen. The product is CO_2.

$$S_P = 213.8 \text{ J/K},\ S_R = 198 + 0.5 \,\square\, 205.2 = 300.6 \text{ J/K}$$

$$\mathrm{D}S = 213.8 - 300.6 = -86.8 \text{ J/K}$$

Since the reaction is highly irreversible, entropy change cannot be calculated as the ratio of heat of reaction to the temperature.

$$\Delta S \neq \left(\frac{\Delta H}{T} = \frac{-2.8318 \times 10^5}{298} = -950.27 \text{ J/K} \right)$$

The heat of reaction ($-\mathrm{D}H$) is the heat liberated when the reaction occurred irreversibly. If the reaction were carried out reversibly, for example, in an electrolytic cell with the generation of electric energy, the heat liberated would be ($-T\mathrm{D}S$). Therefore, the difference between these two represents the heat loss because of the irreversible nature of the process, or the heat that could have been utilised for the production of useful work like electrical energy. Thus the energy available for useful work is

$$2.8318 \,\square\, 10^5 - 298 \,\square\, 86.8 = 2.57314 \,\square\, 10^5 \text{ J}$$

4.7 CLAUSIUS INEQUALITY

The Carnot principle states that a reversible heat engine is more efficient than an irreversible engine. The efficiency of a reversible engine is given by Eq. (4.17)

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

Now consider an irreversible engine operating between the same thermal reservoirs. Let dQ_1 be the heat absorbed and dQ_2 be the heat rejected by the engine. The efficiency of the engine is

$$\eta = \frac{dQ_1 - dQ_2}{dQ_1} = 1 - \frac{dQ_2}{dQ_1} \qquad (4.37)$$

Then, by Carnot principle,

$$1 - \frac{dQ_2}{dQ_1} < 1 - \frac{T_2}{T_1} \qquad (4.38)$$

which means

$$-\frac{dQ_2}{dQ_1} < -\frac{T_2}{T_1}$$

or

$$\frac{dQ_1}{T_1} - \frac{dQ_2}{T_2} < 0$$

Adopting the sign convention that the heat rejected dQ_2 is negative, the preceding relation gives

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} < 0 \qquad (4.39)$$

An irreversible cyclic operation can be divided into a number of heat engine cycles involving infinitesimally small heat interactions, as we have done in Fig. 4.6 for the case of a reversible cyclic operation. For each such cycle, it is possible to write equations analogous to Eq. (4.39) so that the net result would be

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$$\oint \frac{dQ}{T} < 0 \tag{4.40}$$

where T is the temperature of the thermal reservoir. Combining Eq. (4.23) for the reversible cyclic operation with Eq. (4.40) for the irreversible process, we get

$$\boxed{\oint \frac{dQ}{T} \le 0} \tag{4.41}$$

which is known as *Clausius inequality*. It states that *in a cyclic operation, the sum of the dQ/T terms around a complete cycle is less than or equal to zero depending on whether the process is irreversible or reversible.*

EXAMPLE 4.14 Using Clausius inequality show that the change in entropy in a process is related to

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4.9 ENTROPY AND IRREVERSIBILITY

The total increase in entropy associated with an actual process is a measure of the loss in capacity of the system and surroundings as a whole to do work. In other words, the increase in entropy accompanying a spontaneous process is a measure of lost work.

Consider an irreversible process in which a quantity of heat Q is transferred from a source at a temperature T_1 to a sink at a lower temperature T_2. The change in total entropy in this process is given by Eq. (4.48).

$$(\Delta S)_{\text{total}} = -\frac{Q}{T_1} + \frac{Q}{T_2} = Q\frac{T_1 - T_2}{T_1 T_2}$$

Now consider a reversible heat engine operating between the same thermal reservoirs receiving the same quantity of heat Q. The efficiency of such an engine is given by Eq. (4.17)

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

The work output of the engine can be calculated as the product of the efficiency and the heat input.

$$W = Q\frac{T_1 - T_2}{T_1} \qquad (4.50)$$

This is the work which would have resulted had the heat transfer process been reversible, but which was lost because of the irreversible nature of the process. Equation (4.50) can be modified as

$$W = T_2 Q\frac{T_1 - T_2}{T_1 T_2} \qquad (4.51)$$

Equation (4.51) can be combined with Eq. (4.48) to give

$$W_{\text{lost}} = T_2(\Delta S)_{\text{total}} \qquad (4.52)$$

Equation (4.52) gives a physical meaning to the total entropy change in an irreversible process. The product of total entropy change and the temperature of the heat sink gives the quantity of heat that is wasted or degraded in an irreversible process. A reversible engine which receives heat Q_1 from the reservoir at temperature T_1 would perform some work rejecting a part of it, say Q_2, to a heat sink at temperature T_2. The heat rejected in the case of an irreversible engine which receives the same amount of heat would be greater by an amount equal to $T_2(DS)_{\text{total}}$. Thus $T_2(DS)_{\text{total}}$ represents heat taken in at a higher temperature that would have been available for doing work had the process been reversible, but that was lost because of the irreversibility of the actual process.

Though Eq. (4.52) is developed for a heat transfer process, it can be shown that it is applicable to any process. We can generalise the equation into the following form

$$W_{\text{lost}} = T_0(DS)_{\text{total}} \qquad (4.53)$$

T_0 is the temperature of the surroundings. In practice, it is approximately equal to the temperature of the atmosphere. The lower the value of T_0, the lesser the work loss due to irreversibility of the process. But, the lowest practicable temperature is that of the atmosphere. To maintain the temperature of a heat sink below that of the atmosphere, work is needed, and this work would be more than that is gained by lowering T_0.

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4.11 THIRD LAW OF THERMODYNAMICS

We have seen in the previous section that the more completely a system is shuffled the greater is its entropy. Entropy is a measure of the randomness of molecular arrangement of a system. An orderly or unmixed configuration results in low entropy. It is natural therefore, to expect a substance to have zero entropy when it reaches a state in which all randomness have disappeared. A perfect crystalline substance at the absolute zero of temperature would meet this requirement and should have zero entropy. Using the experimental data on the heat capacity of perfect crystalline substances at very low temperatures their entropy at 0 K was calculated and it was shown that they all have same entropy values at this temperature. These observations lead to the postulate of the third law of thermodynamics: *The absolute entropy is zero for a perfect crystalline substance at absolute zero of temperatures.*

In comparison with internal energy and enthalpy, which are calculated relative to an arbitrary reference state, entropy is a reference property and is absolute, as are pressure, volume and temperature. Third law of thermodynamics can be utilised to calculate the absolute entropy of substances at a given temperature by assigning the value zero for entropy of the crystalline form of the substance at absolute zero. This is done by measuring the heat capacity at different temperatures and the latent heats of phase transition that the substance must have undergone to arrive at the present state from the initial state of absolute zero of temperature. For example, let the melting point of the substance be T_f and the boiling point be T_b. The entropy at T, where T is above the boiling point may be evaluated as

$$S = \int_0^{T_f} \frac{C_{PS} dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_b} \frac{C_{PL} dT}{T} + \frac{\Delta H_V}{T_b} + \int_{T_b}^{T} \frac{C_{PG} dT}{T} \qquad (4.55)$$

where C_{PS}, C_{PL} and C_{PG} are the specific heats of solid, liquid and gas respectively, and DH_f and DH_V are the latent heats of fusion and vaporisation respectively. The main difficulty in using the above equation is with regards to the measurement of heat capacity at very low temperatures.

***EXAMPLE* 4.21** It is known that the molar heat capacity of a substance at low temperatures can be approximated by the relation $C_P = aT^3$, where a is a constant. Determine the molar entropy of a metal at 10 K if the molar heat capacity at this temperature is 0.45 J/mol K.

Solution The entropy of the solid at 10 K is evaluated using the first integral in Eq. (4.55)

$$S = \int_0^T C_P \frac{dT}{T} = \int_0^T aT^3 \frac{dT}{T} = \frac{1}{3} aT^3$$

At temperature T, $C_P = aT^3$. Therefore,

$$S = C_P/3 = 0.45/3 = 0.15 \text{ J/mol K}$$

***EXAMPLE* 4.22** Calculate the absolute entropy of water vapour at 473 K and 101.3 kPa above 273 K base temperature. Compare this with the value reported in steam tables (S = 7.829 kJ/kg K). The average heat capacity of water = 4.2 kJ/kg K and that of water vapour between 373 K and 473 K = 1.9 kJ/kg K. The latent heat of vaporisation at 373 K = 2257 kJ/kg.

Solution Equation (4.55) is reduced to the following form for the present purpose.

$$S = \int_{T_f}^{T_b} C_{PL} \frac{dT}{T} + \frac{\Delta H_V}{T_b} + \int_{T_b}^{T} C_{PG} \frac{dT}{T}$$

$$= \int_{273}^{373} 4.2 \frac{dT}{T} + \frac{2257}{373} + \int_{373}^{473} 1.9 \frac{dT}{T} = 4.2 \ln \frac{373}{273} + 6.051 + 1.9 \ln \frac{473}{373}$$

S = 7.813 kJ/kg K and it compares favourably with the value reported in the steam tables: S = 7.829 kJ/kg K.

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