

Chapter 4

The Second Law of Thermodynamics

The first law of thermodynamics elucidates the nature of heat and what we mean by the energy of thermal systems as well as the mutual relationship between work and heat. It also requires that all natural processes conserve energy at the end of a cyclic change. This conservation law of energy then demands that the internal energy be a state function, and as a consequence its differential is an exact differential in thermodynamic state space. However, the first law does not tell us whether a natural process is possible to occur spontaneously or not. It merely imposes a restriction with regard to the energy of the system at the end of a process.

In nature, we see that some processes occur spontaneously whereas some others do not. It is an indisputable fact that the river flows downstream, not upstream, unless an external agency intervenes with it to make the reverse process possible by some sort of compensation in energy. Similarly, a vacuum is filled by air if it is connected with a container filled with air, but the vacuum is not created spontaneously in a container filled with gas without a compensation. There are numerous examples of this kind in nature that while some processes can happen spontaneously, their reverse processes are not spontaneously possible, even if they are energetically possible, not being in violation of the first law. Such a directional preference by natural phenomena is made an axiom in the form of the second law of thermodynamics. The second law of thermodynamics was preceded by Carnot's theorem enunciated by Sadi Carnot who, on examination of an idealized cyclic operation characteristic of steam engines, discovered a universal principle for thermal macroscopic processes in 1824. It is perhaps useful to observe that the study of cyclic processes is on the basis of the Carnot theorem and also the second law of thermodynamics. Therefore, it is indispensable to consider them to gain a proper understanding of the essence and evolution of the idea of the second law of thermodynamics.

Carnot originally formulated his theorem on the basis of the caloric theory of heat which was later discarded as an incorrect concept, but the essence of his theorem¹ was found to be correct if the notion of heat (distinguished as *chaleur* from *calorique* by him) was identified with a form of a mechanical energy, as enunciated by Joule, Davy, Count Rumford, and others mentioned in Chapter 3. After examination of Carnot's work, R. Clausius (1850) and W. Thomson (1851) independently were able to modify the Carnot theorem and enunciate the second principle of thermodynamics when systems undergo cyclic processes. Their universal principle is now known as the second law of thermodynamics, and it was stated by them as follows:

Clausius principle: *It is impossible to transfer heat from a colder to a hotter body without converting at the same time a certain amount of work into heat at the end of a cycle of changes.*

W. Thomson (Lord Kelvin) equivalently stated it as follows:

Kelvin principle: *In a cycle of processes it is impossible to transfer heat from a heat reservoir and convert it all into work, without transferring at the same time a certain amount of heat from a hotter to a colder body.*

These statements can be also put in another still equivalent form by M. Planck:

Planck principle: *It is impossible to construct a perpetual machine of the second kind which transfers heat from a colder to a hotter body without a compensation.*

These principles can be shown to be equivalent.² Schematically, the second law states that the following process is not possible unless some work is done: Let the temperatures of two systems be T_1 and T_2 , respectively, and $T_2 < T_1$. Let the amount of heat given up by the system at T_1 to the system at T_2 be Q_1 . Then it is impossible to return all of Q_1 to the system at T_1 without an equivalent amount of work. Similar examples can

¹In Carnot's theory, there appears the notion of *calorique*, which is distinctive from *chaleur*. He did not clarify its true nature, but it is safe to assume it is a quantity associated with heat transfer and equivalent to entropy or, more precisely, calortropy in the present work.

²See, for example, J. G. Kirkwood and I. Oppenheim, *Chemical Thermodynamics* (McGraw-Hill, New York, 1961).

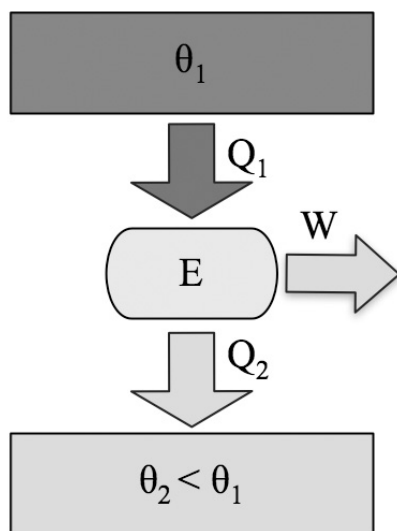


Fig. 4.1 A schematic rendering of the essence of the second law of thermodynamics, which states that Q_2 cannot be equal to zero for a realizable process (engine).

be constructed with the gravitational force and so on. Another schematic way of looking at the essence of the second law is to examine the essential feature of a heat engine depicted in Fig. 4.1. The engine (E) takes heat Q_1 from the high temperature heat reservoir at T_1 and performs work W returning some heat Q_2 to the lower temperature heat reservoir at T_2 . It is impossible to make an engine which converts all of Q_1 into work W without some $Q_2 \neq 0$ emitted to the lower temperature reservoir. That is, it is not possible to have $Q_2 = 0$.

Since the efficiency of the engine in question may be defined by

$$\epsilon = -\frac{W}{Q_1} \quad (4.1)$$

for work done by the system and by the first law of thermodynamics

$$W = -(Q_1 - Q_2) \quad (4.2)$$

for the cyclic process, the efficiency will be unity if $Q_2 = 0$. Therefore the second law of thermodynamics implies that the efficiency of a cycle cannot be unity.

However universal and truthful a principle may be, it is not possible to formulate a physical theory with only a literal statement of it, and it is no exception for the second law of thermodynamics as stated earlier. One of

the statements must be translated into an equivalent mathematical form. Since the two statements are equivalent, it is sufficient to have a mathematical representation for one of them. A mathematical representation of the second law of thermodynamics was made in the form of an inequality by R. Clausius. The inequality, nowadays called the Clausius inequality, was then specialized to the case of reversible processes which Clausius defined as the processes where the uncompensated heat vanishes. He showed that in such processes there exists a quantity (state function) called *entropy*.³ It, however, is a thermodynamic state function defined only for the case of reversible processes. In order to develop this concept we now follow Clausius, who used the Carnot cycle and the Carnot theorem for the purpose.⁴ The restriction of reversible processes can be removed, and the notion of entropy can be generalized to irreversible processes. This will be discussed later. It is interesting to notice that Clausius was able to give the second law of thermodynamics a mathematical representation by using the Carnot theorem. Therefore the important position that Carnot's theorem takes in thermodynamics cannot be overstated.

4.1 Carnot Cycle

In the early 19th century, the industrial revolution, powered by steam engines, was progressing in earnest in England, and it made England dominant, economically and politically, in the world at that time. In the book⁵ entitled "*Réflexions sur la Puissance motrice du Feu et sur les Machines*" published in 1824 Sadi Carnot proposed to study an idealized cyclic process in order to understand steam engines which he called the English machines, since the English were using them to power the industrial revolution and

³It was coined by Clausius from a Greek word root *tropy* to which prefix *en* was added so that it looks akin to the term *energy*. In Greek the term *entropy* means *evolution*. See R. Clausius, *Ann. Phys.* (Leipzig) **125**, 313 (1865).

⁴Later, when statistical mechanics of gases was developed initially by J. C. Maxwell (1867) and L. Boltzmann (1872) followed by J. W. Gibbs (1902), the second law of thermodynamics was given statistical mechanical interpretations along with the statistical mechanical formula for the entropy and its inequality. In some textbooks on thermodynamics the statistical mechanical entropy inequality is used to the exclusion of adequate accounts of its evolution as a law that imposes a limitation upon macroscopic physical processes in nature. Such a treatment of this important physical law is not only unjustifiable, but also detrimental to the development of thermodynamic theory of irreversible processes.

⁵English translation: E. Mendoza, *Reflections on the Motor Power of Fire and on the Machines* (Peter Smith, Gloucester, MA, 1977).

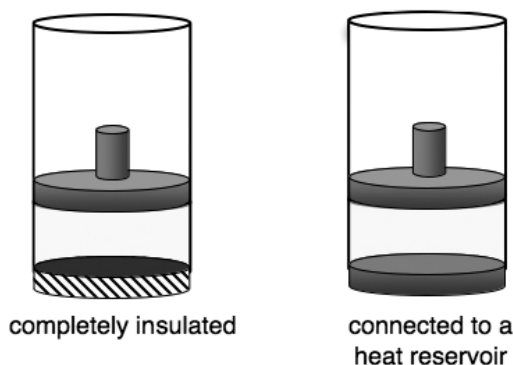


Fig. 4.2 The cylinder on the left is fitted with an insulator (adiabatic wall) at the bottom, and the bottom wall of the cylinder on the right is diathermal. Both pistons and the cylinder wall are adiabatic.

became powerful. This cyclic process, now called the Carnot cycle, does not really represent the working of real engines, but is contrived to capture the essence of their working. As mentioned earlier, Carnot used the notion of heat according to the caloric theory of heat, which was overturned about a quarter century later by Joule, Rumford, and others. Nevertheless, he captured the essential truth for the working of engines and macroscopic processes, physical and biological, in nature. We discuss the essence of his work in the following.

Imagine a working substance, for example, steam or air, is contained in a cylinder fitted at one end with a movable, adiabatic piston. The other end of the cylinder can be made perfectly diathermal or adiabatic at will, but the cylinder wall is adiabatic. The following sequence of operations is performed on the substance in the cylinder (see Fig. 4.3.):

First operation. Put the heat conducting wall in contact with the hot reservoir A at temperature⁶ θ_1 and let the piston rise to volume V_2 from V_1 by reducing the external pressure from p_1 to p_2 , see Fig. 4.3.

⁶In the present discussion it is not necessary to specify a particular temperature scale; it is sufficient to have two thermal reservoirs at given temperatures. However, the subsequent calculations using the ideal gas equation of state will make it abundantly clear that the absolute temperature scale is meant by θ . We use the symbol θ to distinguish it from the thermodynamic temperature T which will be introduced later on the basis of the Carnot theorem and the efficiency of a Carnot cycle. This thermodynamic temperature is eventually made coincident with the absolute temperature.

Since the process is an isothermal expansion, heat Q_1 is absorbed from A . The change in the state of the system in this process is from (p_1, V_1, θ_1) to (p_2, V_2, θ_1) .

Second operation. Remove the cylinder from A and insulate the base of the cylinder so that the cylinder is thermally isolated. Then the pressure is reversibly reduced and as a consequence the volume is increased. Since the process is adiabatic, the temperature is decreased. This process is continued until the temperature drops to θ_2 . Assume that the pressure and the volume at that point are p_3 and V_3 , respectively. The change in the state of the system in this process is from (p_2, V_2, θ_1) to (p_3, V_3, θ_2) .

Third operation. The insulating base of the cylinder is removed from the cylinder, and the cylinder is put in thermal contact with the cold reservoir B at temperature θ_2 . Then the pressure is reversibly increased to p_4 and the volume is decreased to V_4 as a consequence. This pressure is taken such that the system returns to state (V_1, p_1, θ_1) at the end of the fourth operation. Since the process is isothermal and the volume is decreased, the substance gets hotter under compression and hence heat Q_2 is transferred to the cold reservoir B . The change in the state of the system in this process is from (p_3, V_3, θ_2) to (p_4, V_4, θ_2) .

Fourth operation. The cylinder is removed from B and the base of the cylinder is thermally insulated, and then the substance is compressed reversibly and adiabatically until the temperature rises to θ_1 . Since p_4 was so chosen as to return the system to its original state, the system will return to (V_1, p_1) at θ_1 . The change in the state of the system in this process is from (p_4, V_4, θ_2) to (p_1, V_1, θ_1) .

Thus the system is returned to the initial state at the end of a cyclic operation. This cyclic reversible process is depicted in four steps in Fig. 4.3. The diagram as in Fig. 4.3 was introduced for the first time by E. Clapeyron, who gave a mathematical analysis of Carnot's *Réflexion* in which mathematical analysis was avoided because the book was intended for popular consumption.

Let us calculate the net amount of work done by the cycle by using a mole of an ideal gas so as to make calculation simple. We will assume that the specific heat is independent of temperature.

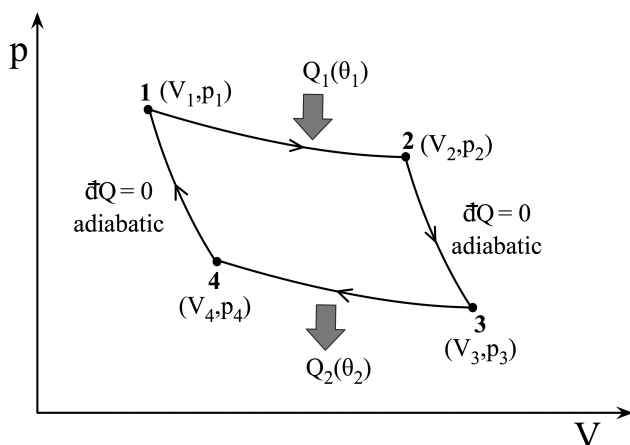


Fig. 4.3 A Carnot cycle in the p - V plane. The four operations are described in the text. The horizontal segments represent isothermal processes, and the vertical segments adiabatic processes.

The work done by the system in the four steps are as follows:

Step 1:

$$W_{12} = -R\theta_1 \ln\left(\frac{V_2}{V_1}\right),$$

Step 2:

$$W_{23} = \int_{\theta_1}^{\theta_2} d\theta c_v(\theta) = c_v(\theta_2 - \theta_1),$$

Step 3:

$$W_{34} = -R\theta_2 \ln\left(\frac{V_4}{V_3}\right),$$

Step 4:

$$W_{41} = \int_{\theta_2}^{\theta_1} d\theta c_v(\theta) = c_v(\theta_1 - \theta_2).$$

The c_v is the molar heat capacity of the working substance, namely, the ideal gas. Note that c_v for the ideal gas is independent of temperature θ . The total work is given by

$$\begin{aligned} W &= W_{12} + W_{23} + W_{34} + W_{41} \\ &= -R\theta_1 \ln\left(\frac{V_2}{V_1}\right) - R\theta_2 \ln\left(\frac{V_4}{V_3}\right). \end{aligned} \quad (4.3)$$

Now recall that for ideal gases in an adiabatic process

$$\theta V^{\gamma-1} = \text{constant}.$$

More explicitly written for Steps 2 and 4,

$$\begin{aligned}\theta_1 V_2^{\gamma-1} &= \theta_2 V_3^{\gamma-1}, \\ \theta_1 V_1^{\gamma-1} &= \theta_2 V_4^{\gamma-1}.\end{aligned}$$

By eliminating θ_1 and θ_2 from the equations we find a relation among volumes:

$$\left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{V_4}{V_3}\right)^{\gamma-1}. \quad (4.4)$$

Use of this relation in Eq. (4.3) gives rise to the net amount of work in a rather simple form:

$$W = -R(\theta_1 - \theta_2) \ln\left(\frac{V_2}{V_1}\right). \quad (4.5)$$

The heat transfers Q_1 and Q_2 during the isothermal processes (i.e., Steps 1 and 3) are easily calculated in the case of an ideal gas. According to the result obtained in Sec. 3.4 they are as follows:

$$\begin{aligned}Q_1 &= -W_{12} = R\theta_1 \ln\left(\frac{V_2}{V_1}\right), \\ Q_2 &= -W_{34} = R\theta_2 \ln\left(\frac{V_4}{V_3}\right) \\ &= R\theta_2 \ln\left(\frac{V_1}{V_2}\right).\end{aligned} \quad (4.6)$$

For the second equality of Q_2 Eq. (4.4) is used.

The efficiency of the Carnot cycle (engine) is defined by the ratio of the work W to the heat supplied Q_1 :

$$\eta = \frac{-W}{Q_1} = \frac{|W|}{Q_1}. \quad (4.7)$$

Since for a cycle the internal energy is conserved, that is,

$$\oint dE = 0,$$

the work done by the reversible Carnot cycle is

$$-W = Q_1 - Q_2 \quad (4.8)$$

and hence we may express the efficiency in terms of heat alone:

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}. \quad (4.9)$$

Upon use of Q_1 and Q_2 in Eq. (4.6) the efficiency for the reversible cycle may be expressed only in terms of temperatures of the reservoirs and no other parameters:

$$\eta = \frac{R(\theta_1 - \theta_2) \ln(V_2/V_1)}{R\theta_1 \ln(V_2/V_1)} = \frac{\theta_1 - \theta_2}{\theta_1} = 1 - \frac{\theta_2}{\theta_1}. \quad (4.10)$$

The temperatures in this expression is in the absolute temperature scale because of the ideal gas equation of state used for calculations involved. We emphasize that this efficiency formula is shown to be valid in the case of an ideal gas undergoing reversible processes. We will see in Sec. 4.4 that it holds in general for real substances, reinforcing the universality of the result as demanded by the Carnot theorem.

4.2 Carnot's Theorem

As a result of the analysis made of the working of a Carnot cycle as an idealization of real engines, Carnot obtained a theorem concerning the efficiency of reversible cycles and its relationship to the efficiency of irreversible cycles. This theorem is now known as Carnot's theorem.

Carnot's theorem: *The efficiency of reversible Carnot cycles is independent of materials and modes of operation, and is maximum. It depends only on the temperatures of the heat reservoirs. In other words, if we denote the efficiencies of reversible cycles by η_{rev} , η'_{rev} , and so on, and that of an irreversible cycle by η_{irr} then it may be stated that*

$$\eta_{rev} = \eta'_{rev} \quad \text{and} \quad \eta_{rev} \geq \eta_{irr}.$$

Moreover, η_{rev} depends only on the temperatures θ_1 and θ_2 of the two heat reservoirs, hot and cold.

Proof. In order to prove the first part of the theorem we first consider two reversible engines operating between two heat reservoirs at temperatures θ_1 and θ_2 ($\theta_1 \geq \theta_2$). Engine En' takes heat Q'_1 from the hotter reservoir and converts part of it into work W and emits heat Q'_2 to the colder reservoir. The other engine En takes heat Q_1 from the hotter reservoir and converts part of it into work W and emits heat Q_2 to the colder reservoir. The two engines are now coupled such that engine En' is a prime

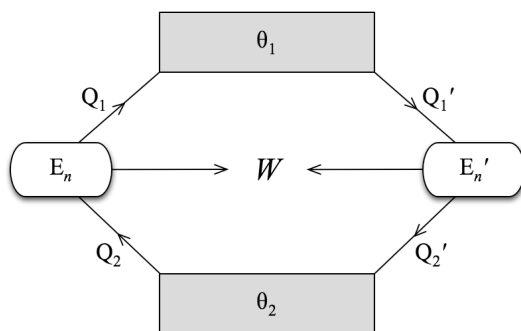


Fig. 4.4 Coupling of a prime mover and a refrigerator as a device to prove Carnot's theorem.

mover and the other engine E_n is a refrigerator; see Fig. 4.4. Engine E_n thus operates reversely to the mode by which the engine E_n' operates, pumping heat Q_2 from the colder reservoir and returning heat Q_1 to the hotter reservoir at the expense of work W . Now assume that

$$\eta'_{rev} > \eta_{rev}.$$

By the definition of efficiency, this may be written equivalently as

$$\frac{-W}{Q'_1} > \frac{-W}{Q_1},$$

which means the inequality

$$Q_1 - Q'_1 > 0.$$

This implies that heat $\Delta Q = Q_1 - Q'_1$ is transferred at the end of the cycle from the colder to the hotter reservoir without a compensation. This is against the second law of thermodynamics. Therefore the assumption is false.

Let us then assume that the reverse is true, that is,

$$\eta'_{rev} < \eta_{rev}.$$

By reversing the cycle, that is, by considering E_n as a prime mover and E_n' as a refrigerator, we reach the same conclusion as before. Therefore we must conclude that

$$\eta'_{rev} = \eta_{rev}. \quad (4.11)$$

Since the same argument can be carried out with another engine E_n'' instead of E_n' , the first part of the theorem is proved.

In order to prove the second part of the theorem we regard En' as an irreversible prime mover and En as a reversible refrigerator. Now suppose that

$$\eta_{irr} > \eta_{rev}.$$

Then, by the definition of efficiency

$$\frac{-W}{Q'_1} > \frac{-W}{Q_1},$$

which means

$$Q_1 - Q'_1 > 0.$$

This again contradicts the second law of thermodynamics, since it implies that heat is transferred from the colder body to a hotter one at the end of a cycle without a compensation. Therefore, we must conclude that the assumption is false, and

$$\eta_{rev} \geq \eta_{irr}. \quad (4.12)$$

The reverse process is not possible, since it involves an irreversible engine.

We now prove⁷ the last part of the theorem: *that the reversible efficiency depends only on the temperatures of the two heat reservoirs, hot and cold.*

The reversible Carnot cycle is entirely determined when the adiabatics and isotherms of the cycle are known. If the working substance is specified so that the constitutive relations of the substance are given, the isotherms are determined by the temperatures θ_1 and θ_2 , and the adiabatics by some independent variables, say, v_1 and v_2 corresponding to the temperatures. The efficiency of the reversible Carnot cycle is then thought to be a function of θ_1 , θ_2 , v_1 , and v_2 and of the working substance C . Let us therefore assume

$$\frac{-W}{Q_1} = f(\theta_1, \theta_2, v_1, v_2, C). \quad (4.13)$$

This is a continuous function of the variables. The Carnot theorem states that f depends only on θ_1 and θ_2 . Consider two bodies C and C' which transform between the same heat reservoirs and describe cycles En and En' , respectively, the former being a prime mover and the latter working in the reverse sense—a refrigerator. For this to be possible the temperatures must satisfy certain inequalities. Let θ_1 and θ_2 be the temperatures of two reservoirs, hot and cold; and θ'_1 and θ'_2 be the temperatures of the isotherms

⁷See H. Poincaré, *Thermodynamique* (Georges Carré, Paris, 1892).

of the cycle En ; and θ_1'' and θ_2'' the temperatures of the isotherms of the cycle En' . Then for the coupled cycles to be possible the inequalities of temperatures must hold

$$\theta_1'' > \theta_1 > \theta_1' > \theta_2' > \theta_2 > \theta_2''.$$

Denote by W the work produced by the cycle En , Q_1 the heat that is taken from the hot reservoir, Q_2 the heat that it cedes to the cold reservoir. And by W' , Q_1' , and Q_2' similar quantities corresponding to cycle En' . Then

$$\frac{-W}{Q_1} \leq \frac{-W'}{Q_1'}. \quad (4.14)$$

This is proved as follows. If m and m' are the masses of bodies C and C' , which are transformed in the cycles, we have for the heat taken from the hot heat reservoir by the combined cycles

$$mQ_1 - m'Q_1'.$$

Since Q_1 and Q_1' are positive, we can take for m and m' values such that

$$mQ_1 - m'Q_1' = 0. \quad (4.15)$$

But then the work

$$-mW + m'W'$$

produced by the two cycles cannot be positive because then we will have a production of work with only one source of heat, contrary to the second law of thermodynamics. Therefore

$$-mW + m'W' \leq 0. \quad (4.16)$$

Replacing m and m' with Q_1^{-1} and $Q_1'^{-1}$ we obtain Inequality (4.14).

Consider now two Carnot cycles En and En' which are, respectively, defined by the variables $\theta_1', \theta_2', v_1',$ and v_2' for the former and by $\theta_1'', \theta_2'', v_1'',$ and v_2'' for the latter. The cycle En runs in the direct sense and the cycle En' in the reverse sense between two same heat reservoirs of temperatures θ_1 and θ_2 , respectively. For this to be possible we must have the inequalities

$$\theta_1' < \theta_1, \quad \theta_2' > \theta_2 \quad \theta_1'' > \theta_1, \quad \theta_2'' < \theta_2.$$

Then it follows from Inequality (4.14) that

$$f(\theta_1', \theta_2', v_1', v_2', C) \leq f(\theta_1'', \theta_2'', v_1'', v_2'', C'). \quad (4.17)$$

If we suppose

$$\theta_1' > \theta_1, \quad \theta_2' < \theta_2 \quad \theta_1'' < \theta_1, \quad \theta_2'' > \theta_2,$$

we can describe the cycle En in the reverse direction and the cycle En' in the direct sense. Then we have the inequality

$$f(\theta'_1, \theta'_2, v'_1, v'_2, C) \geq f(\theta''_1, \theta''_2, v''_1, v''_2, C'). \quad (4.18)$$

Since f is continuous, we can make $\theta'_1, \theta''_1 \rightarrow \theta_1$ and $\theta'_2, \theta''_2 \rightarrow \theta_2$ without changing the sign of Inequalities (4.17) and (4.18). We then have

$$f(\theta_1, \theta_2, v'_1, v'_2, C) \leq f(\theta_1, \theta_2, v''_1, v''_2, C'), \quad (4.19)$$

$$f(\theta_1, \theta_2, v'_1, v'_2, C) \geq f(\theta_1, \theta_2, v''_1, v''_2, C'). \quad (4.20)$$

These inequalities cannot be satisfied simultaneously. Therefore we have

$$f(\theta_1, \theta_2, v'_1, v'_2, C) = f(\theta_1, \theta_2, v''_1, v''_2, C'), \quad (4.21)$$

which means that f is independent of variables v_1 , v_2 , and C . This proves the last part of the Carnot theorem. Therefore the Carnot theorem is completely proved.

The proof presented is in fact seen also as the proof of equivalence of the second law of thermodynamics and the Carnot theorem. The Carnot theorem provides not only the more transparent mathematical representation, but also an important concept that is not transparent in the Clausius and Kelvin principles, since it shows that *the efficiencies of irreversible cycles cannot exceed the efficiency of the reversible cycles*. Furthermore, we now see that the second law of thermodynamics, which is based on everyday experience and therefore less transparent mathematically than the Carnot theorem, is given a clearer mathematical representation by means of Carnot's theorem. We reiterate that both the second law of thermodynamics and the Carnot theorem are phrased about cyclic processes, since cyclic processes are the only kind of processes in which the system is assured of returning to the original state without fail and thus the existence of conserved quantities characteristic of the system is implied without recourse to any other measure to ascertain their conserved nature. And conserved quantities are certainly convenient to use in formulating a theory of macroscopic processes.

From the Carnot theorem it is possible to deduce that *a reversible work is a maximum work possible*. To show it let us assume that there are two engines operating between two heat reservoirs and both of them absorb heat Q_1 from the hotter reservoir and emit heat Q_2 to the colder reservoir. The work performed by the reversible engine is W and that by the irreversible engine is W' .

Then according to the Carnot theorem there holds the inequality

$$\eta_{rev} = \frac{-W}{Q_1} \geq \frac{-W'}{Q_1} = \eta_{irr}, \quad (4.22)$$

which means that

$$-W \geq -W'. \quad (4.23)$$

This proves the statement. It is seen as a corollary to the Carnot theorem. By the sign convention on work, $-W$ is positive since W is the work performed by the system, and similarly for $-W'$. Therefore, Inequality (4.23) implies that if the process is irreversible there is an amount of work unavailable to the given task of the process. This is related to the energy dissipation accompanying an irreversible process. It is convenient to introduce the unavailable work W_{ua} by the relation

$$W = W' + W_{ua}. \quad (4.24)$$

The precise nature of unavailable work depends on the irreversible process in question and the system as well as the device with which the work is performed. This unavailable work must be elucidated if the theory of irreversible processes is the aim.

4.3 Thermodynamic Temperature

The Carnot theorem makes it possible to give the second law of thermodynamics a mathematical representation. To achieve the desired aim it is necessary to lay foundations for it. First of all, let us consider implications of the Carnot theorem. One of the most important is the notion of thermodynamic temperature which was first deduced from the Carnot theorem by Lord Kelvin. We consider the gist of it here. Since the efficiency of reversible Carnot cycles is independent of materials and the modes of operation, but depends only on the temperatures θ_1 and θ_2 of the heat reservoirs according to Carnot's theorem, we see that the ratio of Q_2 to Q_1 is a function of θ_1 and θ_2 only:

$$\frac{Q_2}{Q_1} = f(\theta_2, \theta_1). \quad (4.25)$$

Since we may write the left-hand side in the form

$$\frac{Q_2}{Q_1} = \frac{Q_2}{Q_0} \cdot \frac{Q_0}{Q_1} = f(\theta_2, \theta_0) f(\theta_0, \theta_1),$$

we conclude that $f(\theta_2, \theta_1)$ is a function with the following property:

$$f(\theta_2, \theta_1) = f(\theta_2, \theta_0)f(\theta_0, \theta_1). \quad (4.26)$$

Let $\theta_2 = \theta_1$. Then

$$f(\theta_1, \theta_0) = \frac{1}{f(\theta_0, \theta_1)}. \quad (4.27)$$

The properties of f described in Eqs. (4.26) and (4.27) imply that there exists a function of θ , $\phi(\theta)$, such that

$$f(\theta_2, \theta_1) = \frac{\phi(\theta_2)}{\phi(\theta_1)} \quad (4.28)$$

and consequently it is possible to write

$$\frac{Q_2}{Q_1} = \frac{\phi(\theta_2)}{\phi(\theta_1)}. \quad (4.29)$$

The function $\phi(\theta)$ is arbitrary. It will be denoted by T :

$$T = \phi(\theta). \quad (4.30)$$

This is called the thermodynamic temperature. The temperature based on the Carnot theorem must be universal since the Carnot theorem is universal owing to the fact that *the reversible efficiencies are independent of the modes of operation and the working substances*. In the manner shown, the Carnot theorem can serve as the basis of introducing a universal thermodynamic temperature.⁸ Since the efficiency calculated for a reversible cycle in Eq. (4.10) is expressed in absolute temperature, it is appropriate to regard θ here as a temperature in the absolute scale. In this event, the efficiency formula for a reversible cycle in Eq. (4.10) suggests that $\phi(\theta)$ must be linearly proportional to θ , and the proportionality constant may be taken such that θ coincides with the thermodynamic temperature T :

$$T = \theta. \quad (4.31)$$

In this manner, the thermodynamic temperature is made to coincide with the absolute temperature based on the ideal gas temperature, and they now can be interchangeably used. It then is possible to express the efficiency of

⁸The existence of universal thermodynamic temperature presupposes a reversible cycle or process. Without it the temperature defined is no longer universal and hence generally dependent on the substance or the system.

a reversible cycle in terms of the absolute temperature (or thermodynamic temperature):

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}. \quad (4.32)$$

It is important to recall that T_1 and T_2 are originally the temperatures of the heat reservoirs and, only in the case of a reversible cycle, can they be regarded as the temperatures of the system which is in thermal equilibrium with the heat reservoirs in various steps of operation in the cycle.

4.4 Entropy and Calortropy

4.4.1 Clausius Inequality

With the Carnot efficiency for reversible cycles expressed in terms of the thermodynamic temperature, the Carnot theorem now acquires a firmer mathematical grip on the second law of thermodynamics. To pursue this line further, which eventually gives rise to the Clausius inequality, it is convenient at this point to adopt a sign convention for heat transfer in a way consistent with the sign convention for work introduced earlier.

Sign convention: *If heat is transferred to the system, Q is taken positive whereas, if it is transferred out of the system, Q is taken negative.*

With this convention, we may write the efficiency of a reversible cycle in the form

$$\frac{Q_1 - (-Q_2)}{Q_1} = \frac{T_1 - T_2}{T_1}.$$

Rearranging the terms in this equation we find for the reversible cycle

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0. \quad (4.33)$$

If the amounts of heat injected into and rejected by or withdrawn from the system (cycle) are infinitesimal, we may write Eq. (4.33) in a differential form in terms of differential elements dQ_i :

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = 0. \quad (4.34)$$

This equation may be further generalized by the following mathematical device. A reversible cycle may be regarded as consisting of a large number

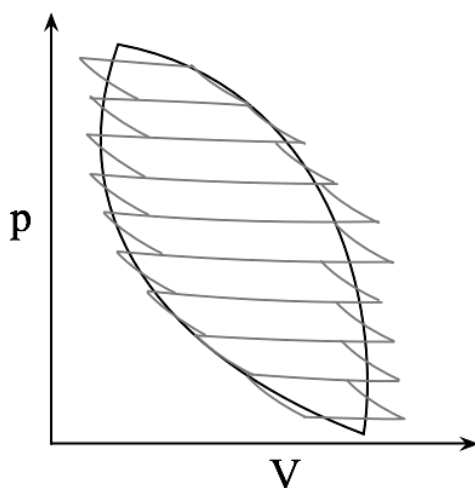


Fig. 4.5 Decomposition of a Carnot cycle into infinitesimal Carnot cycles $\{i\}$. The i th cycle takes heat dQ_i from the adjacent $(i - 1)$ th cycle and emits heat dQ_{i+1} to its immediate neighbor, the $(i + 1)$ th cycle in the sequence.

of infinitesimal reversible cycles as shown in Fig. 4.5. The horizontal lines represent the isotherms, and the vertical lines the adiabats. The cycle i takes an infinitesimal amount of heat dQ_i from the $(i - 1)$ th cycle and emits an infinitesimal amount of heat dQ_{i+1} to the $(i + 1)$ th cycle. The temperatures of the isotherms are denoted by T_i . For the whole collection of the infinitesimal cycles we may then write

$$\sum_i \frac{dQ_i}{T_i} = 0, \quad (4.35)$$

which is a generalization of Eq. (4.34). If the number of infinitesimal cycles is taken to infinity the summation may be replaced with an integral over the whole cycle:

$$\oint \frac{dQ_{rev}}{T} = 0. \quad (4.36)$$

It must be emphasized that this equation holds for reversible cycles only and dQ_{rev} denotes a differential heat transfer in a reversible process. They are cycles in which processes are performed such that the system is in continuous equilibrium with the surroundings or there is no energy dissipation, the meaning of which will be elucidated later more precisely.

Let us now consider a more general case involving an irreversible cycle. In this case, the Carnot theorem reads

$$\eta_{irr} = \frac{Q_1 - Q_2}{Q_1} \leq \frac{T_1 - T_2}{T_1} = \eta_{rev}. \quad (4.37)$$

By applying the same method of reasoning as for that leading to Eq. (4.36) we obtain the inequality

$$-\oint \frac{dQ}{T} \geq 0. \quad (4.38)$$

This inequality, first obtained by Clausius, is called the Clausius inequality. It is important to remember that T is the temperature associated with the reversible cycle and thus equilibrium, and even if the process in question is irreversible the temperature factor T in the inequality is still that of the reversible process corresponding to the irreversible process of interest; see Eq. (4.37).

Clausius called dQ the compensated heat since it is a heat transfer between the system and the surroundings (heat reservoirs) that occurs irreversibly. He also identified another basic quantity that he called the uncompensated heat, and denoted it by N . This quantity, which is always positive and vanishes if the process is reversible, is equal in value to the closed contour integral (simply called the circular integral) in the inequality (Eq. (4.38)):

$$N = -\oint \frac{dQ}{T} \geq 0. \quad (4.39)$$

Before we examine this form of the Clausius inequality in detail, it is useful in historical deference to the development made by Clausius regarding a special case of his inequality. This special case gives rise to equilibrium thermodynamics.

4.4.2 Entropy

Let us return to Eq. (4.36), which holds for reversible processes. Although Clausius discovered the existence of uncompensated heat N , its precise nature was not known sufficiently well to him at that time.⁹ To make some

⁹In connection with this line of work and much before he put forward the notion of entropy, Clausius had made use of the notion of *disgregation*, which appeared to be akin to a quantity he later called *entropy*. However, he never developed and quantified the notion beyond the entropy and into the regime of irreversible processes.

progress in the absence of the detailed knowledge of N Clausius considered the case of reversible processes¹⁰ for which $N = 0$ identically. Since the line integral of the compensated heat thus obtained is nothing other than Eq. (4.36) and meets the mathematical criterion for exact differentials, it led him to conclude that there exists an exact differential dS such that

$$dS = \frac{dQ_{rev}}{T} \quad (4.40)$$

in the space of thermodynamic variables characteristic of the system for the reversible process considered. Moreover, it can be shown that there exists such a function S for any reversible process since the Carnot theorem holds for all reversible processes. Clausius called S the entropy¹¹ of the system, and it is a state function in the space of thermodynamic variables for the system, which is spanned by the internal energy and volume and, in the case of a mixture, also by the concentrations of species.

The second law of thermodynamics, expressed by Eq. (4.36) for a reversible process, is now represented by the vanishing circular integral

$$\oint dS = 0. \quad (4.41)$$

It should be emphasized that this vanishing integral is true only if the process is reversible. It must be also noted that dQ_{rev} denotes a non-exact differential for heat change although the symbol δ is not used in place of the symbol d . When dQ_{rev} is divided by the absolute temperature the result becomes an exact differential. Such factors which make non-exact differentials exact are called integrating factors, and $1/T$ is an integrating factor in the case of dQ_{rev} . Therefore the entropy change for a reversible process $A \rightarrow B$ is obtained on integration of Eq. (4.40):

$$\Delta S = S_B - S_A = \int_A^B dS = \int_A^B \frac{dQ_{rev}}{T}, \quad (4.42)$$

where the integration is over the reversible path. For an isolated system there is no heat put in or taken out of the system and hence

$$dQ_{rev} = 0,$$

¹⁰Reversible processes may be defined as the processes in which the uncompensated heat N vanishes everywhere. This definition is preferable to the definition based on the process of continuous quasi-equilibrium introduced in Section 2.5.

¹¹See Footnote 3 for the reference.

which then implies

$$\Delta S = 0.$$

In other words,

$$S_A = S_B$$

for isolated systems at equilibrium. It should be clearly understood that the entropy S is defined for reversible processes only.

The differential for S given in Eq. (4.40) can be combined with the first law of thermodynamics to yield the fundamental relation for thermodynamics of reversible processes or equilibrium

$$dE = T dS - p dV, \quad (4.43)$$

in the case of pressure–volume work alone. If there are other kinds of work besides the pressure–volume work then the differential form for energy may be written as

$$dE = TdS - pdV + \sum_i X_i dx_i, \quad (4.44)$$

where X_i are forces and x_i are displacements whose examples were given in Chapter 2. We will consider thermodynamics in the cases of such forms of work in later chapters. The differential forms (Eqs. (4.43) or (4.44)) are often referred to the mathematical expression for the second law of thermodynamics, but it is only for reversible processes or systems in equilibrium.

4.4.3 Calortropy

Before we discuss the application of the notion of entropy in thermodynamics it is useful to examine more closely the form of the Clausius inequality (Eq. (4.39)), to learn about the nature of the uncompensated heat N . It must be associated with the unavailable work appearing in Eq. (4.24) since the numerator in the right member of Eq. (4.14) is equal to $-W'$ which is less than the work $-W$ performed by the reversible cycle corresponding to the right member of Inequality (4.37). By adding a term $-W_{ua}/Q_1$ to the left member of Inequality (4.37), which thereby is made an equation, we can cast Inequality (4.37) in the form of an equation

$$-\frac{W_{ua}}{T_2} = -\oint \frac{dQ}{T}. \quad (4.45)$$

If the left-hand side is identified with the uncompensated heat

$$N \equiv -\frac{W_{ua}}{T_2} \geq 0, \quad (4.46)$$

then the Clausius inequality (Eq. (4.39)) is recovered and a little more definite meaning of the uncompensated heat is attained. Clearly, the uncompensated heat so identified is always positive in the sign convention adopted for work and vanishes only if the process is reversible. This consideration made here indicates that *the compensated and uncompensated heats are two independent physical quantities which exactly balance each other for the cycle*. In other words, we may write Eq. (4.45) in the form

$$\oint \frac{dQ}{T} + N = 0. \quad (4.47)$$

The compensated and uncompensated heats are characteristic of the system and the surroundings in a given heat transfer process involved between them. The symbol N clearly is not another way of writing the circular integral on the right-hand side of Eq. (4.45), which appears to be an identity at a quick glance. Neither is the circular integral on the right-hand side of Eq. (4.45) the definition of N , which should be elucidated on its own right if an irreversible process was an object of study. It is important to recognize that the Clausius inequality is derived from the Carnot theorem. Therefore the temperature T appearing in the Clausius inequality or Eq. (4.47) is the temperature expressing the efficiency of the reversible cycle with which the efficiency of an irreversible cycle is compared.

The uncompensated heat may be expressed as an integral over the path of the cycle

$$N = \oint dN \geq 0, \quad (4.48)$$

where dN is such that $(dN/dt) \geq 0$ everywhere in the cycle, since otherwise it is possible to construct a cycle, which contravenes the positivity of the integral and thus the second law of thermodynamics. Then the Clausius inequality can be written as

$$\oint \left(\frac{dQ}{T} + dN \right) = 0. \quad (4.49)$$

This is a mathematical representation for the second law of thermodynamics, which was literally stated in the forms of the Clausius and Kelvin principles. It now is written in a form of equation instead of an inequality initially obtained by Clausius, and such an equation is realized by treating

the compensated and uncompensated heats as two independent physical quantities on the equal footing. Although it may look as a simple and trivial rewriting of the Clausius inequality, it provides a *fresh way of looking at the thermodynamics of irreversible processes and generalizing the classical equilibrium thermodynamics to nonequilibrium*. We now examine how the classical thermodynamics of reversible processes or equilibrium can be recovered and made free from the troublesome features, especially the one related to the concept of entropy, which is defined only when the system is in equilibrium, but, as will be shown below, has been nevertheless used in the context in which the system is away from equilibrium.

As in the case of Eq. (4.36) holding for reversible processes, Eq. (4.49) implies that even if the process is irreversible there still exists a state function Ψ in the space of thermodynamic variables whose differential form is given by

$$d\Psi = \frac{dQ}{T} + dN \quad (4.50)$$

and vanishes on integration over the cycle:

$$\oint d\Psi = 0. \quad (4.51)$$

This is reminiscent of the vanishing circular integral of dS in Eq. (4.41). The vanishing circular integral (Eq. (4.51)) implies that $d\Psi$ is an exact differential in the thermodynamic space which may be spanned by the internal energy, volume, concentrations of species, and macroscopic variables characteristic of the nonequilibrium system in which irreversible processes occur. The precise nature of the thermodynamic space should be elucidated upon detailed examination of the irreversible processes in hand, but it is clear that the space should be spanned by macroscopic variables describing the irreversible process in hand in addition to the usual variables characterizing the equilibrium system of temperature T , such as the internal energy, volume, and concentrations of species involved. This state function is called the calortropy.¹² Since the process is irreversible Ψ is a generalized form of the Clausius entropy S , which holds for reversible

¹²It is a composite word meaning heat (*calor*) evolution (*tropy*). It is akin to Carnot's *calorique*, which he used in his *Réflexion* to mean a quantity that is similar to heat, but not quite the same as heat. Since *calorie* is already in use, the term *calorique* is inappropriate to use. The term coined thus seems to be suitable. Some research workers in irreversible thermodynamics use the term nonequilibrium entropy to mean what is essentially the calortropy here, but the latter is simpler and more concise than the former.

processes only. The vanishing circular integral (Eq. (4.51)) is a mathematical representation of the second law of thermodynamics for the irreversible cyclic process under consideration. For the same cyclic process the first law of thermodynamics is also expressible as a vanishing circular integral

$$\oint dE = 0. \quad (4.52)$$

This pair of circular line integrals is over the same irreversible path in the thermodynamic space for the system. We recall that although dW and dQ are not exact differentials, their sum dE is an exact differential. It is then interesting to see that, just as in the case of the first law of thermodynamics, although dQ/T and dN are not exact differentials if the process is irreversible, their sum $d\Psi$ is an exact differential, and the first and second laws of thermodynamics are mathematically expressible as a pair of vanishing circular integrals if the process is cyclic. We summarize these results as a theorem:

Theorem. *In the case of a cyclic process, regardless of whether it is reversible or irreversible, the first and second laws of thermodynamics are, respectively, expressible as a pair of vanishing cyclic integrals in the thermodynamic space:*

$$\oint dE = 0, \quad (4.53)$$

$$\oint d\Psi = 0. \quad (4.54)$$

4.4.4 Inequalities of Entropy and Calortropy

Since $(dN/dt) \geq 0$ where dt is an infinitesimal time interval, for an infinitesimal interval of the cycle there holds the inequality

$$d\Psi \geq \frac{dQ}{T}. \quad (4.55)$$

Since $(dN/dt) = 0$ if the process is reversible, not only the equality holds in Eq. (4.55) but also $d\Psi$ becomes identical with dS , namely,

$$\begin{aligned} d\Psi_{rev} &= \frac{dQ_{rev}}{T} \\ &= dS, \end{aligned} \quad (4.56)$$

where Ψ_{rev} and Q_{rev} are the calortropy and heat transfer accompanying the reversible process.

If Inequality (4.55) is integrated over a finite irreversible process from state 1 to state 2 there follows the inequality

$$\Delta\Psi \geq \int_{1(irr)}^2 \frac{dQ}{T}, \quad (4.57)$$

where

$$\Delta\Psi = \int_{1(irr)}^2 d\Psi. \quad (4.58)$$

Inequality (4.57) also follows directly from Eq. (4.50) if the latter is integrated over the same interval:

$$\begin{aligned} \Delta\Psi &= \int_{1(irr)}^2 \frac{dQ}{T} + \int_{1(irr)}^2 dN \\ &\geq \int_{1(irr)}^2 \frac{dQ}{T}. \end{aligned} \quad (4.59)$$

The equality holds, only if the process is reversible in which case we may write

$$\Delta\Psi_{rev} = \Delta S = \int_{1(rev)}^2 \frac{dQ_{rev}}{T}. \quad (4.60)$$

If the system is isolated, then there is no heat exchange between the system and the surroundings. In this case, dQ vanishes identically over the process and Inequality (4.57) gives rise to the inequality for the calortropy

$$\Delta\Psi \geq 0, \quad (4.61)$$

where the equality holds, only if the process is reversible. This is a special case of Eq. (4.60) for which

$$\Delta\Psi_{rev} = \Delta S = 0. \quad (4.62)$$

For irreversible processes in an isolated system

$$\Delta\Psi > 0. \quad (4.63)$$

Therefore the calortropy tends toward a maximum and attains a maximum value identical with the entropy at equilibrium. This conclusion should be compared with the famous statement for the second law of thermodynamics made by Clausius in 1865: *The entropy of the world tends towards a maximum*. Since by definition the entropy is an attribute of the system at equilibrium, it makes sense that calortropy should replace the term entropy in the statement in our opinion. We elaborate on this assertion with the following examination.

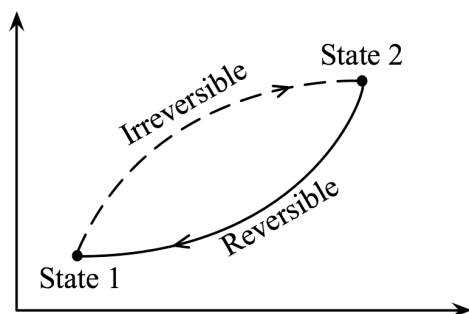


Fig. 4.6 A cyclic path consisting of an irreversible and a reversible segment.

Suppose a system has irreversibly and spontaneously reached a final state from an initial state as in Fig. 4.6. If the system is not closed, it is always possible to make the system return to the original state through a reversible path, provided that the system is properly compensated to do so. For such a system it is always possible to construct a cyclic process consisting of two segments, one irreversible and the other reversible, as depicted in Fig. 4.6, and find from Eq. (4.51)

$$\Delta\Psi = \int_{1(irr)}^2 d\Psi = \int_{1(rev)}^2 d\Psi = \Delta S. \quad (4.64)$$

This equation together with Inequality (4.57) implies the inequality

$$\Delta S \geq \int_{1(irr)}^2 \frac{dQ}{T}. \quad (4.65)$$

This is the Clausius–Duhem inequality known in thermodynamics as a mathematical form of the second law of thermodynamics. This means that Inequality (4.57) implies the Clausius–Duhem inequality. We emphasize that Eq. (4.64) holds only if there exists a reversible segment in the cycle, which in this particular case requires that the system be not closed since some sort of compensation is necessary for the system to return to the original state from which it irreversibly departed. An isolated system that has irreversibly and spontaneously reached a final state cannot spontaneously return to the initial state since the necessary compensation can only come from the surroundings for the system to do so. The Clausius–Duhem inequality (Eq. (4.65)) is mathematically and conceptually impeccable, but it does not mean that for an isolated system there holds the inequality

$$\Delta S \geq 0, \quad (4.66)$$

since there does not exist a complementary reversible process Γ_{rev} that makes up a cycle with irreversible process Γ_{irr} , if the system is isolated. The existence of such a path Γ_{rev} implies that there is a mode of compensation from the surroundings. If so, the system is no longer isolated and inequality $\Delta S > 0$ is misleading.

Inequality (4.66), in fact, causes a considerable conceptual difficulty when closely examined, since ΔS is not defined if the process is irreversible, and $\Delta S = 0$ for a reversible process in an isolated system, since

$$\Delta S = \int_{1(rev)}^2 \frac{dQ_{rev}}{T} = 0 \quad (4.67)$$

identically because $dQ_{rev} = 0$ for an isolated system. Therefore it cannot be concluded that $\Delta S > 0$ if there is an irreversible process in an isolated system. The confusing part of Inequality (4.66) is the conclusion that $\Delta S > 0$ although the system is isolated so that $dQ_{rev} = 0$ and thus, by definition, $\Delta S = 0$. This difficulty disappears if ΔS is replaced by $\Delta\Psi$ so that Inequality (4.61) holds for the case of an isolated system undergoing an irreversible process; Inequality (4.61) has no such problem as for Inequality (4.66) for the reason that it is not equal to zero even if the system is isolated and thus $dQ_{rev} = 0$ because of a nonvanishing uncompensated heat for an irreversible process.

The laxity of the Clausius statement has been a source of debate¹³ and confusion in the fine points of thermodynamics, but we now seem to have a way to avoid such confusions. The discussion presented here on the basis of Eq. (4.64) and Inequality (4.65) suggests that the conventional Clausius–Duhem inequality for the Clausius entropy should be phrased in terms of the calortropy over the irreversible segment as in Inequality (4.57) and, in the case of an isolated system, as in Inequality (4.61). Inequality (4.61) is easier to comprehend than the Clausius–Duhem inequality for an isolated system because it does not present a difficulty that there holds Eq. (4.67) for a reversible process in an isolated system. We further elaborate on this point.

Inequality (4.66) may be understood in the following sense. Suppose the irreversible process Γ_{irr} in Fig. 4.6 occurs when the system is isolated and the reversible process Γ_{rev} occurs when the system is not isolated. In other words, after the irreversible process Γ_{irr} is completed, the system

¹³See, for example, J. Kestin, *The Second Law of Thermodynamics* (Dowden, Hutchinson, & Ross, Stroudsburg, PA, 1976).

is allowed to interact with its surroundings and made to return reversibly from state B to state A . In this case

$$\Delta S = \Delta \Psi (\Gamma_{irr}) = \int_{A(irr)}^B dN \geq 0,$$

where the equality holds if Γ_{irr} is reversible. This equation, as Eq. (4.64), allows to calculate $\Delta \Psi (\Gamma_{irr})$ in terms of ΔS over a complementary reversible process, but only implies that if an irreversible process occurs in an isolated system then the ΔS of a reversible process that is complementary to the irreversible process in question and occurs in interaction with the surroundings is positive. This is probably what Clausius should have meant by Inequality (4.66).

If the nature of uncompensated heat is elucidated in detail, it should be possible to calculate $\Delta \Psi$. We briefly comment on this aspect. Let us imagine that there is a finite segment of an irreversible process $1 \rightarrow 2$. Then, on integrating Eq. (4.50), there follows

$$\Delta \Psi = \int_{1(irr)}^2 \frac{dQ}{T} + \Xi_g, \quad (4.68)$$

where

$$\Xi_g = \int_{1(irr)}^2 dN \geq 0. \quad (4.69)$$

This inequality is a form of the second law of thermodynamics. If it is possible to take the system to the initial state 1 through a reversible process then the entropy change for the reversible process ΔS is given by the equation

$$\Delta S = \int_{1(irr)}^2 \frac{dQ}{T} + \Xi_g \quad (4.70)$$

as was originally suggested by Clausius. Provided we know how to compute Ξ_g for the process, it is possible to compute the integral in Eq. (4.70) by computing ΔS for a reversible process complementary to the irreversible process in question, or Ξ_g from the knowledge of the integral in Eq. (4.70) and ΔS .

Let us examine the significance of Eq. (4.70) with the following example. A metal bar at temperature T_2 is separated by an insulator C from another of the same metal at temperature T_1 , which is lower than T_2 . The insula-

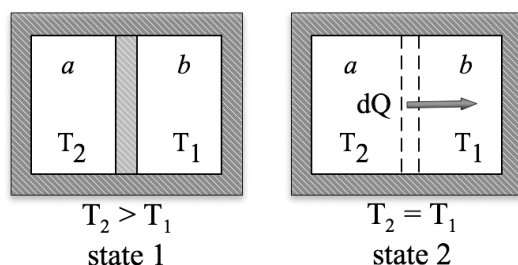


Fig. 4.7 Two metal bars in contact at two different temperatures which go through an irreversible process of heat transfer.

tor is then removed and the metal bars are allowed to interact thermally (Fig. 4.7). They will reach equilibrium at which point the temperature will be $\frac{1}{2}(T_1 + T_2)$. The systems are subsequently brought to the original states by a reversible process by making them interact with the surroundings. This reversible process is accompanied by an entropy change ΔS in the system. Since the irreversible process occurs in an isolated condition the integral in Eq. (4.70) is equal to zero and ΔS is given by

$$\Delta S = \Xi_g \geq 0. \quad (4.71)$$

The entropy change ΔS for the reversible process can be easily calculated:

$$\Delta S = C_p \ln \left(\frac{T_1 + T_2}{2\sqrt{T_1 T_2}} \right), \quad (4.72)$$

for which we have assumed, for the simplicity of the result, that the specific heat C_p is independent of temperature. Since there holds the inequality

$$\frac{1}{4} (T_1 + T_2)^2 \geq T_1 T_2,$$

we conclude that indeed

$$\Delta S \geq 0$$

and Inequality (4.71) is satisfied, indicating that the irreversible process in question is spontaneous with the value of the global uncompensated heat estimated for the irreversible process as in Eq. (4.72). Therefore, we see that Eq. (4.70) can be used for estimating the uncompensated heat Ξ_g from the knowledge of ΔS for a reversible process complementary to the irreversible process in question. We emphasize that ΔS in

Eq. (4.72) is for a reversible process in a system interacting with the surroundings.

4.5 Carnot's Theorem and Real Gases

We have calculated the efficiency of a reversible Carnot cycle when the working substance is ideal. However, the working substance is not ideal in practice but real, since the molecules do interact with each other and the ideal gas equation of state holds only in the low pressure limit. If a real gas is taken for the working substance, some steps in the calculation we have performed for the Carnot cycle are not valid. There then arises the question as to the generality of the result obtained for the efficiency. The result, however, holds in general for real working substances, and we would like to prove this statement for the Carnot cycle depicted in Fig. 4.4 in the following.

The equation of state for 1 mole of a real gas may be given in the form

$$p = \frac{RT}{V} + f(V, T), \quad (4.73)$$

where $f(V, T)$ is a function of V and T which we do not have to specify except that it is a well-behaved function and piecewise integrable. Note that in the case of real gases

$$\left(\frac{\partial E}{\partial V}\right)_T \neq 0.$$

This requires a new mode of calculation for the heat change accompanying an isothermal expansion, which is different from that used for an ideal gas.

The work of isothermal expansion is

$$W_{ij} = - \int_{V_i}^{V_j} p dV \quad (i = 1, 3; j = 2, 4), \quad (4.74)$$

which may be explicitly calculated if the integration is performed with Eq. (4.73) substituted into it. Such calculation, however, is not necessary for our purpose here.

By regarding the internal energy as a function of V and T we may write

$$\begin{aligned} dQ &= dE + p dV \\ &= C_v dT + \left[T \left(\frac{\partial p}{\partial T} \right)_V - p \right] dV + p dV. \end{aligned} \quad (4.75)$$

Therefore, since $dQ = 0$ for an adiabatic process, the work of adiabatic expansion (or compression) may be written in the form

$$W_{23} = - \int_{V_2}^{V_3} p dV = - \int_{T_1}^{T_2} C_v dT + \int_{V_2}^{V_3} \left[p - T \left(\frac{\partial p}{\partial T} \right)_V \right]_{T_2} dV, \quad (4.76)$$

$$W_{41} = - \int_{V_4}^{V_1} p dV = \int_{T_1}^{T_2} C_v dT + \int_{V_4}^{V_1} \left[p - T \left(\frac{\partial p}{\partial T} \right)_V \right]_{T_1} dV. \quad (4.77)$$

The total work is then the sum of the four components calculated above:

$$\begin{aligned} W &= W_{12} + W_{23} + W_{34} + W_{41} \\ &= - \int_{V_1}^{V_2} p(T_1) dV - \int_{V_3}^{V_4} p(T_2) dV + \int_{V_2}^{V_3} \left[p - T \left(\frac{\partial p}{\partial T} \right)_V \right]_{T_2} dV \\ &\quad + \int_{V_4}^{V_1} \left[p - T \left(\frac{\partial p}{\partial T} \right)_V \right]_{T_1} dV. \end{aligned} \quad (4.78)$$

By the first law of thermodynamics

$$\oint dE = 0$$

for the cycle, and we obtain

$$-W = Q_1 - Q_2.$$

Therefore the efficiency is

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

which takes the same form as for the ideal working substance. We would like to show that, as is for the ideal gas, the efficiency for the real gas is still given by

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

For the purpose we first observe that for an isothermal process

$$dQ = T \left(\frac{\partial p}{\partial T} \right)_V dV,$$

which follows from Eq. (4.75) if $dT = 0$. Therefore the heat changes accompanying the isothermal expansion and compression in the cycle are

$$\begin{aligned} Q_1 &= \int_1^2 dQ = \int_{V_1}^{V_2} dV T_1 \left(\frac{\partial p}{\partial T} \right)_V (T_1), \\ Q_2 &= \int_4^3 dQ = \int_{V_4}^{V_3} dV T_2 \left(\frac{\partial p}{\partial T} \right)_V (T_2), \end{aligned} \quad (4.79)$$

where we have used the sign convention on heat emission and absorption. Along the adiabatics

$$\frac{C_v}{T} dT + \left(\frac{\partial p}{\partial T} \right)_V dV = 0, \quad (4.80)$$

which follows from Eq. (4.75) if $dQ = 0$. Moreover, since

$$dC_v(T, V) = \left(\frac{\partial C_v}{\partial V} \right)_T dV \text{ at } T = \text{constant},$$

we obtain

$$\begin{aligned} C_v(T, V) &= C_v^0 + \int^V dV \left(\frac{\partial C_v}{\partial V} \right)_T \\ &= C_v^0 + \int^V dV T \left(\frac{\partial^2 p}{\partial T^2} \right)_V \\ &= C_v^0 + \int^V dV T \left(\frac{\partial^2 f}{\partial T^2} \right)_V (T = \text{constant}), \end{aligned} \quad (4.81)$$

where C_v^0 is generally a function of T , but we will consider the case of constant C_v^0 . Substitution of Eq. (4.81) into Eq. (4.80) and use of the equation of state (Eq. (4.73)) yield

$$d \left[R \ln(T^\alpha V) + \int^V dV \left(\frac{\partial f}{\partial T} \right)_V \right] = 0, \quad (4.82)$$

where $\alpha = C_v/R$. Integrating it, we obtain

$$R \ln(T^\alpha V) + \int^V dV \left(\frac{\partial f}{\partial T} \right)_V = \text{constant}. \quad (4.83)$$

Since from the equation of state

$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{R}{V} + \left(\frac{\partial f}{\partial T} \right)_V,$$

using Eqs. (4.79) and (4.83) we find

$$Q_1 = RT_1 \ln \left(\frac{T_2}{T_1} \right)^\alpha, \quad Q_2 = RT_2 \ln \left(\frac{T_2}{T_1} \right)^\alpha \quad (4.84)$$

and consequently

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}. \quad (4.85)$$

Finally, we thus find

$$\eta = 1 - \frac{T_2}{T_1}, \quad (4.86)$$

even if the working substance is real. This result also holds even if the assumption on constant C_v is removed. For the following holds true:

$$\int^T \frac{C_v^0}{T} dT + \int^V dV \left(\frac{\partial p}{\partial T} \right)_V (T) = \text{constant}. \quad (4.87)$$

By the calculation performed above, we have proved that the efficiency of a reversible Carnot cycle of a real fluid for the working substance obeying the equation of state (Eq. (4.73)) still depends only on the temperatures of the heat reservoirs between which the cycle operates.

4.6 Examples of Other Cycles

Carnot's cycle was the precursor to other cycles invented later. Some examples will be shown in this section. They underlie some of practical engines used in machines including automobiles. The Diesel cycle, for example, is one typical example of application.

4.6.1 Rankine Cycle

The Scottish engineer W. J. M. Rankine, a contemporary of Kelvin and an important pioneer in thermodynamics, invented the Rankine cycle, which basically describes the working of steam engines. It may be schematically represented by the diagram in the p - V plane in Fig. 4.8.

4.6.2 Otto Cycle

The German engineer N. Otto built an engine in 1876 invented by the Frenchman A. Beaudé Rochas in 1862. Otto's engine became the prototype of automobile engines made in the United States. Gasoline engines may be

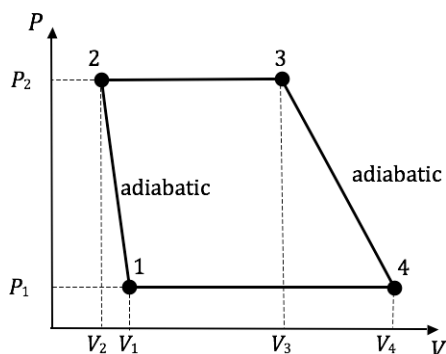


Fig. 4.8 Rankine cycle: step 2-3, isobaric expansion; step 3-4, adiabatic expansion; step 4-1, isobaric compression; step 1-2, adiabatic compression.

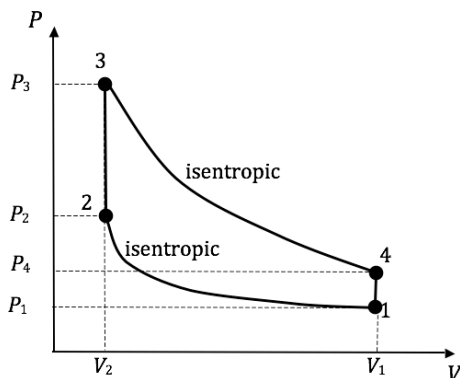


Fig. 4.9 Otto cycle: step 1-2, adiabatic compression (isentropic); step 2-3, constant volume heating; step 3-4, adiabatic expansion (isentropic); step 4-1, constant volume cooling.

represented by the Otto cycle which is described by the diagram in the p - V plane in Fig. 4.9.

4.6.3 Diesel Cycle

In about 1900, the German engineer R. Diesel built engines now known as Diesel engines. The Diesel engines may be described by the following p - V diagram depicted in Fig. 4.10. It is called the Diesel cycle and is currently in use for various automobiles and power generators. The efficiency of the Diesel cycle is greater than the efficiency of an Otto cycle at the same peak pressure.

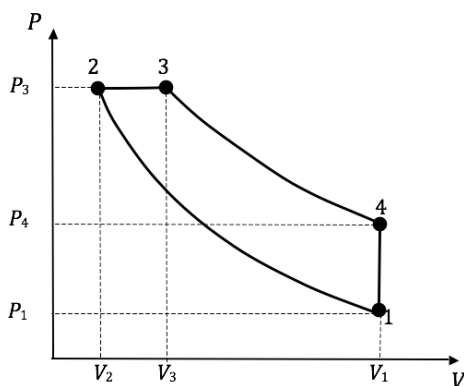


Fig. 4.10 Diesel cycle: step 1–2, adiabatic (isentropic) compression; step 2–3, isobaric expansion (fuel injection and burning at constant pressure); step 3–4, adiabatic (isentropic) expansion; step 4–1, constant volume heat rejection (exhaust and intake of air).

4.7 Calculation of Entropy Change

In this section, we evaluate the entropy changes accompanying some simple reversible processes. More general methods of evaluation will be discussed in later chapters.

4.7.1 Phase Transition and Entropy Change

It is well known that the so-called latent heats are associated with phase transitions, such as the melting of solids or vaporization of liquids and solids. Such heats are called more specifically the heat of fusion (melting), the heat of vaporization, and so on. There are entropy changes associated with such phase transitions. They are called the entropy of fusion, the entropy of vaporization, and so on, and are easily evaluated from the latent heats. Let us recall that since

$$dQ = T dS$$

and

$$H = E + pV,$$

if the process involved is reversible, combining them with the first law of thermodynamics, Eq. (3.9), yields

$$dH = T dS + V dp \quad (4.88)$$

for the enthalpy change.

Using this equation at $p = \text{constant}$, we can calculate the entropy change ΔS_{lat} corresponding to the latent heat ΔH_{lat} of a phase transition at constant p :

$$\Delta S_{lat} = \frac{\Delta H_{lat}}{T}, \quad (4.89)$$

where T is the phase transition temperature. Note that ΔS_{lat} and ΔH_{lat} are discontinuous changes between two phases at T .

4.7.2 Entropy Changes of an Ideal Gas

For reversible processes the entropy change may be written

$$dS = \frac{1}{T}(dE + p dV), \quad (4.90)$$

which results from Fundamental Relation (3.9). Since in the case of an ideal gas E is a function of T only, Eq. (4.90) may be cast in the form

$$dS = \frac{1}{T}c_v dT + RV^{-2} dV. \quad (4.91)$$

Here we are considering 1 mole of an ideal gas and c_v denotes the molar specific heat at constant volume. Suppose a reversible process takes the system from state (T_1, V_1) to state (T_2, V_2) . The entropy change for this process may be evaluated as follows: The temperature of the system is increased from T_1 to T_2 at $V = V_1$ and then the volume is increased from V_1 to V_2 at $T = T_2$. This process is depicted in Fig. 4.11. The entropy change for the isochoric process $(T_1, V_1) \rightarrow (T_2, V_1)$ is

$$\begin{aligned} (\Delta S)_{isochoric} &= \int_{T_1}^{T_2} dT \frac{c_v(T)}{T} \\ &= c_v \ln\left(\frac{T_2}{T_1}\right), \end{aligned} \quad (4.92)$$

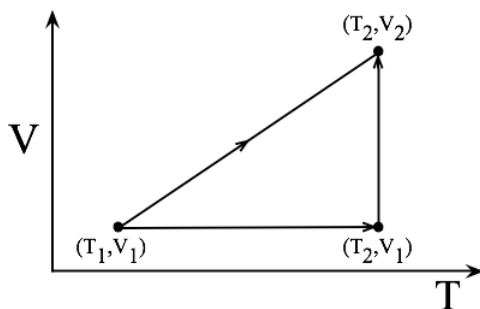


Fig. 4.11 A reversible path in T - V plane and its distortion into an isochoric and an isothermal path.

where the second line holds if C_v is independent of T . The entropy change for the isothermal process $(T_2, V_1) \rightarrow (T_2, V_2)$ is

$$(\Delta S)_{isothermal} = R \int_{V_1}^{V_2} dV \frac{1}{V} = R \ln \left(\frac{V_2}{V_1} \right). \quad (4.93)$$

Combining Eqs. (4.92) and (4.93) yields the entropy change for the process $(T_1, V_1) \rightarrow (T_2, V_2)$:

$$\begin{aligned} \Delta S &= (\Delta S)_{isochoric} + (\Delta S)_{isothermal} \\ &= \int_{T_1}^{T_2} dT \frac{c_v(T)}{T} + R \ln \left(\frac{V_2}{V_1} \right) \\ &= c_v \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{V_2}{V_1} \right), \end{aligned} \quad (4.94)$$

where the third line holds if c_v is independent of T . Since $c_p = c_v + R$ for a mole of an ideal gas, we may write Eq. (4.94) to obtain ΔS in the form

$$\begin{aligned} \Delta S &= \int_{T_1}^{T_2} dT \frac{c_p(T)}{T} + R \ln \left(\frac{p_1}{p_2} \right) \\ &= c_p \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{p_1}{p_2} \right), \end{aligned} \quad (4.95)$$

the second line holding for the case of c_p independent of T .

Let us now remove the assumption of a constant specific heat, since the specific heats for ideal diatomic and polyatomic gases generally depend on temperature. The temperature dependence of c_v may be represented by the expansion

$$c_v(T) = \sum_{n=-\infty}^{\infty} b_n T^n, \quad (4.96)$$

where b_n are coefficients independent of T . Note that if $b_n = 0$ for $n < -2$, we recover an expansion similar to Eq. (3.39). When Eq. (4.96) is substituted into the first line of Eq. (4.94) and the integration is performed, there follows the isochoric component of ΔS :

$$(\Delta S)_{isochoric} = \sum_{\substack{n=-\infty \\ (n \neq 0)}}^{\infty} \left[\frac{b_n}{n} T^n + b_0 \ln T \right]_{T_1}^{T_2}.$$

By combining this with the isothermal component of ΔS we obtain the overall entropy change for ideal diatomic or polyatomic gases.

4.8 Free Energies

4.8.1 Helmholtz Free Energy

The fundamental relations introduced earlier such as for dE and dH are differential forms in the space of variables (S, V) and (S, p) , respectively. It is often convenient to use other sets of variables. For example, the variable set (T, V) may be used because it is more convenient than, for example, the variable pair (S, V) . To express the fundamental relation in this set of variables, we introduce the Legendre transformation

$$A = E - TS. \quad (4.97)$$

Taking differential of this relation and using Fundamental Relation (4.43) we find the fundamental relation for Helmholtz free energy A :

$$dA = -S dT - p dV. \quad (4.98)$$

This is clearly a differential form in the space of variables (T, V) . This is a measure of energy available for useful work for the task of interest.

4.8.2 Gibbs Free Energy

It is possible to have a Legendre transformation of H as follows:

$$G = H - TS. \quad (4.99)$$

On substitution of H from this relation into the fundamental relation for H in Eq. (4.88) there follows the fundamental relation for Gibbs free energy, G :

$$dG = -S dT + V dp, \quad (4.100)$$

which is a differential form in the space of variables (T, p) . This variable set is the most convenient of the variable sets considered so far from the thermodynamic viewpoint, since temperature and pressure are easily amenable to measurement. This is also one of the reasons that the Gibbs free energy is one of the most convenient and commonly used among thermodynamic functions. It is also a measure of available energy for a given task.

4.9 Maxwell's Relations

The various forms of energy introduced in the previous section are all state functions and their differential forms are exact. They are combined expressions for the first and the second law in the case of a closed system

undergoing a reversible process. We will collect them in one place:

$$dE = T dS - p dV, \quad (4.101)$$

$$dH = T dS + V dp, \quad (4.102)$$

$$dA = -S dT - p dV, \quad (4.103)$$

$$dG = -S dT + V dp. \quad (4.104)$$

Since these are all exact differentials, they satisfy the exactness conditions discussed in the mathematical notes in Chapter 2.

Equation (4.101) enables us to compute two derivatives of E :

$$\left(\frac{\partial E}{\partial S}\right)_V = T, \quad \left(\frac{\partial E}{\partial V}\right)_S = -p. \quad (4.105)$$

Differentiating the derivatives once again with V and S , respectively, and remembering that

$$\frac{\partial^2 E}{\partial S \partial V} = \frac{\partial^2 E}{\partial V \partial S},$$

we find the relation

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V. \quad (4.106)$$

Performing similar calculations with Eqs. (4.102)–(4.104) we derive the following relations:

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p, \quad (4.107)$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V, \quad (4.108)$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p. \quad (4.109)$$

These derivatives involving T , S , p , and V are called Maxwell's relations. They are equivalent to the integrability conditions for the differential forms (Eqs. (4.101)–(4.104)) and are extremely powerful and useful relations for various calculations in thermodynamics.

Mnemonics: It is very useful for computational purposes to devise a mnemonic scheme to construct the Maxwell relations, particularly, since their similarity creates considerable difficulty to

remember them yet one does not wish to compute them from the fundamental relations whenever encountering them. The following rules for constructing them are found effective.

First, take the quadruplet of S , T , p , and V of variables and group them into conjugate pairs, (S, T) and (p, V) . Then the products of differentials are balanced in the form¹⁴

$$dS dT = (-1)^\alpha dp dV. \quad (4.110)$$

Note that the conjugate variable pairs (S, T) and (p, V) are each made up of an intensive and an extensive variable. The value of exponent α will be determined by the rules stated below — it is the essence of the mnemonics presented here.

The Maxwell relations are of partial derivatives which are formed with intensive and extensive variables, one each, from the two conjugate variable pairs of the quadruplet. For example, to form Relation (4.109), we divide the equation with $dp dT$ in which p and T are the variables with which we differentiate S on the left and V on the right. Thus we obtain

$$\left(\frac{\partial S}{\partial p}\right)_l = (-1)^\alpha \left(\frac{\partial V}{\partial T}\right)_r.$$

Then the value of l on the left is $l = T$, the conjugate variable of S of the pair (S, T) , whereas the value of r on the right is $r = p$, the conjugate variable of the pair (p, V) . Thus we obtain

$$\left(\frac{\partial S}{\partial p}\right)_T = (-1)^\alpha \left(\frac{\partial V}{\partial T}\right)_p.$$

The value of α is determined by the following rule:

$\alpha = 1$ if both intensive variables (e.g., p and T) occur on both sides of the equation.

¹⁴The mathematical basis is as follows: Under the transformation $(S, T) \rightarrow (p, V)$

$$dS dT = \frac{\partial(S, T)}{\partial(p, V)} dp dV$$

and

$$\frac{\partial(S, T)}{\partial(p, V)} = \pm 1.$$

The Jacobian of transformation is usually taken 1, but here it is relaxed to take -1 as well.

$\alpha = 0$ if both intensive variables occur on one side only, left or right, of the equation.

Since $\alpha = 1$ for the present example, it follows

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p,$$

which is Relation (4.109).

Using these rules, other Maxwell relations can be easily constructed. For example, by dividing Eq. (4.110) with $dV dT$ we find the relation

$$\left(\frac{\partial S}{\partial V}\right)_l = (-1)^\alpha \left(\frac{\partial p}{\partial T}\right)_r$$

where by the rules stated earlier, $l = T$, $r = V$, and $\alpha = 0$. Hence

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

which is Relation (4.108). If we divide Eq. (4.110) with the product $dS dp$ and use the rules stated we find

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

and if we divide with $dV dS$ there follows relation

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

which is Relation (4.106).

We have earlier utilized calorimetric data to compute the internal energy and the enthalpy as well as the entropy. In order to reinforce the method of computation we observe the following relations:

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V, \quad (4.111)$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p. \quad (4.112)$$

Notice in these relations that the entropy has the same dimension as the specific heats.

We illustrate applications of the Maxwell relations with a few examples in the following.

Example 1. $(\partial T/\partial p)_E$ may be expressed in terms of more easily measurable quantities. By the chain relation introduced in the mathematical notes in Chapter 3

$$\left(\frac{\partial T}{\partial p}\right)_E = -\frac{\left(\frac{\partial E}{\partial p}\right)_T}{\left(\frac{\partial E}{\partial T}\right)_p}.$$

Since

$$\begin{aligned}\left(\frac{\partial E}{\partial T}\right)_p &= \left[\frac{\partial}{\partial T}(H - pV)\right]_p \\ &= C_p - p\left(\frac{\partial V}{\partial T}\right)_p,\end{aligned}\quad (4.113)$$

$$\begin{aligned}\left(\frac{\partial E}{\partial p}\right)_T &= \left[\frac{\partial}{\partial p}(G - pV + TS)\right]_T \\ &= -p\left(\frac{\partial V}{\partial p}\right)_T - T\left(\frac{\partial S}{\partial p}\right)_T \\ &= -p\left(\frac{\partial V}{\partial p}\right)_T + T\left(\frac{\partial V}{\partial T}\right)_p,\end{aligned}\quad (4.114)$$

by putting these equations together, we find

$$\left(\frac{\partial T}{\partial p}\right)_E = -\frac{V(p\kappa - T\alpha)}{C_p - pV\alpha},\quad (4.115)$$

where α and κ are respectively the isobaric expansion coefficient and the isothermal compressibility:

$$\begin{aligned}\alpha &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \\ \kappa &= -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T.\end{aligned}\quad (4.116)$$

Example 2. We show that for ideal gases

$$\left(\frac{\partial E}{\partial V}\right)_T = 0, \quad \left(\frac{\partial E}{\partial p}\right)_T = 0.$$

Proof. (a)

$$\begin{aligned}\left(\frac{\partial E}{\partial V}\right)_T &= \left[\frac{\partial}{\partial V}(A + TS)\right]_T \\ &= -p + T\left(\frac{\partial S}{\partial V}\right)_T \\ &= -p + T\left(\frac{\partial p}{\partial T}\right)_V.\end{aligned}$$

Since for ideal gases

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V},$$

it follows

$$\left(\frac{\partial E}{\partial V}\right)_T = 0.$$

(b)

$$\begin{aligned}\left(\frac{\partial E}{\partial p}\right)_T &= \left[\frac{\partial}{\partial p}(G - pV + TS)\right]_T \\ &= -p\left(\frac{\partial V}{\partial p}\right)_T - T\left(\frac{\partial V}{\partial T}\right)_p.\end{aligned}$$

For ideal gases the right hand side is equal to zero and consequently

$$\left(\frac{\partial E}{\partial p}\right)_T = 0.$$

Example 3. We show that for any substance

$$C_p = C_v + \frac{TV\alpha^2}{\kappa}.$$

To show it the following calculation is performed:

$$\begin{aligned}C_p - C_v &= T\left[\left(\frac{\partial S}{\partial T}\right)_p - \left(\frac{\partial S}{\partial T}\right)_V\right] = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \\ &= T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p = -\frac{T\left(\frac{\partial V}{\partial T}\right)_p^2}{\left(\frac{\partial V}{\partial p}\right)_T} \\ &= \frac{TV\alpha^2}{\kappa}.\end{aligned}$$

Problems

- (1) Show that the efficiency of the Carnot cycle of a mole of a gas obeying the equation of state

$$p(V - b) = RT$$

is given by

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

Assume that the specific heats of the gas are constants.

- (2) Show that the efficiency of the Carnot cycle of a mole of a van der Waals gas obeying the equation of state

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

is given by

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

Assume that the specific heats of the gas are constants.

- (3) By using Eq. (4.87) show that Eq. (4.86) still holds true.
 (4) Prove the following relations:

$$(a) \left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{C_v} \left(\frac{\partial p}{\partial T}\right)_V,$$

$$(b) \left(\frac{\partial T}{\partial p}\right)_S = \frac{T}{C_p} \left(\frac{\partial V}{\partial T}\right)_p,$$

$$(c) \left(\frac{\partial V}{\partial p}\right)_S = \frac{C_v}{C_p} \left(\frac{\partial V}{\partial p}\right)_T,$$

$$(d) \left(\frac{\partial T}{\partial p}\right)_H = \frac{-V + T \left(\frac{\partial V}{\partial T}\right)_p}{C_p},$$

$$(e) \left(\frac{\partial T}{\partial V}\right)_E = \frac{p - T \left(\frac{\partial p}{\partial T}\right)_V}{C_v},$$

$$(f) \left(\frac{\partial H}{\partial G}\right)_E = \frac{C_p(\kappa p - \alpha T) - (1 - \alpha T)(C_p - \alpha pV)}{-S(\kappa p - \alpha T) - (C_p - \alpha pV)}.$$

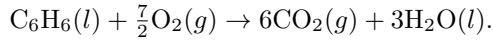
- (5) Show the following:

$$(a) \left(\frac{\partial E}{\partial S}\right)_p = T - p \left(\frac{\partial T}{\partial p}\right)_S = T \left[1 - \frac{p}{C_p} \left(\frac{\partial V}{\partial T}\right)_p \right],$$

$$(b) \left(\frac{\partial G}{\partial T} \right)_V = -S + V \left(\frac{\partial p}{\partial T} \right)_V = -S + \frac{V\alpha}{\kappa},$$

where α and κ are defined in Example 1.

- (6) The following change is maintained isobaric and isothermal:



It is found that $\Delta G = -3174.9 \text{ kJ mol}^{-1}$. Find ΔA at the same condition at $p = 1 \text{ atm}$ and $T = 298.2 \text{ K}$.

- (7) Show that dQ/T is an exact differential by using the fundamental relation for E . Also show that for a Carnot cycle working with an ideal gas its cyclic integral vanishes.
- (8) An extended strip of rubber has a length l when subjected to a tensile force f . If the volume change on extension may be neglected, show that

$$\left(\frac{\partial E}{\partial l} \right)_T = f - T \left(\frac{\partial f}{\partial T} \right)_l.$$

Show that the small temperature rise, ΔT , which takes place in a slow adiabatic stretching, is given by

$$\frac{\Delta T}{T} = \int_{l_0}^l \frac{1}{C_l} \left(\frac{\partial f}{\partial T} \right)_l dl,$$

where l_0 and l refer to the initial and final lengths, respectively, and C_l is the heat capacity of the rubber at constant extension. [Note that the work is equal to $f dl$ so that $dE = T dS + f dl$. For the second part of the problem calculate $(\partial T/\partial l)_S$ in terms of C_l and $(\partial f/\partial T)_l$. New "Maxwell's relations" are necessary for the present situation.]

- (9) Between 0 and 60 K the molar heat capacity of $\text{Ag}(s)$ is given approximately by the following expression:

$$c_p = (0.23 T + 2.5 \times 10^{-3} T^2 - 1.9 \times 10^{-5} T^3) \text{ J mol}^{-1}.$$

Calculate the entropy of $\text{Ag}(s)$ at 60 K. Note $S(T = 0) = 0$.

- (10) Find ΔA for $\text{O}_2(g, 300.15 \text{ K}, 2 \text{ atm}) \rightarrow \text{O}_2(g, 300.15 \text{ K}, 1 \text{ atm})$, assuming that the gas is ideal.
- (11) In the temperature range of 298 to 2000 K the molar heat capacity of $\text{NH}_3(g)$ obeys the equation,

$$c_p = (29.75 + 2.51 \times 10^{-2} T - 1.55 \times 10^{-5} T^2) \text{ J K}^{-1} \text{ mol}^{-1}.$$

Find the entropy change at constant pressure arising from the temperature change from $T = 300$ to 1000 K.

- (12) At 0°C , aluminum has the following properties: atomic weight = 2.70×10^{-2} kg mol $^{-1}$, density = 2.70 kg M $^{-3}$, $c_p = 0.930 \times 10^3$ J kg $^{-1}$ K $^{-1}$, $\alpha = 71.4 \times 10^{-6}$ K $^{-1}$, $\kappa = 1.34 \times 10^{-21}$ m 2 N $^{-1}$. Calculate at 0°C the molar heat capacity at constant volume and the ratio of heat capacities γ .
- (13) Find the entropy change for the reversible process of taking n moles of an ideal gas with constant heat capacity from T_1 and p_1 to T_2 and p_2 .
- (14) A gas obeys the following molar heat capacity equation and equation of state:

$$c_p = a + bT + cT^2$$

and

$$pv = RT + B_2(T)p + B_3(T)p^2.$$

Calculate the enthalpy and entropy changes for the reversible process from (T_1, p_1) to (T, p) .

- (15) Show Eq. (4.72).
- (16) Show that for the Carnot cycle using an ideal gas as the working substance

$$\oint dE = 0, \quad \oint dH = 0, \quad \oint dA = 0, \quad \oint dG = 0, \quad \oint dS = 0.$$

Assume constant specific heats.

- (17) Calculate the efficiency of the Rankine cycle and show

$$\oint dS = 0$$

for the cycle.

- (18) Obtain the efficiency of the Otto cycle. Compare the efficiency of this cycle with the efficiency of the Carnot cycle. Also show that for the cycle

$$\oint dS = 0.$$

- (19) Calculate the efficiency of the Diesel cycle and compare it with the efficiency of the Carnot cycle. Show that the efficiency of the Diesel cycle is greater than the efficiency of an Otto cycle at the same peak pressure. Also show that for the cycle

$$\oint dS = 0.$$

- (20) The van der Waals constants for nitrogen are as follows:

$$a = 1.39 \text{ L}^2 \text{ atm mol}^{-2}, \quad b = 3.92 \times 10^{-2} \text{ L mol}^{-1}.$$

Taking the virial form for the van der Waals equation of state

$$\frac{pv}{RT} = 1 + \left(b - \frac{a}{RT}\right) \frac{1}{V} + \dots,$$

calculate the enthalpy change $\Delta h = h(T, p) - h(T, 0)$ arising from compression of the gas from $p = 0$ to 100 atm at constant $T = 300 \text{ K}$.

- (21) By using the van der Waals equation of state for real gas, calculate the reversible work done on the system due to a volume change from V_1 to V_2 at temperature T .
- (22) Mercury vapor at 630.15 K and 1 atm pressure is heated to 823.15 K and its pressure is increased to 5 atm. Calculate the entropy change in the entropy units, the vapor being treated as an ideal monatomic gas.
- (23) Calculate the nonideality corrections for enthalpy, internal energy, and entropy by using the van der Waals equation of state.
- (24) Calculate the molar heat capacity difference $c_p - c_v$ for nitrogen at 298.15 K and 200 atm pressure, to first order in p , using the van der Waals equation of state, the van der Waals constants a and b being $1.39 \text{ L}^2 \text{ atm mol}^{-2}$ and $3.92 \times 10^{-2} \text{ L mol}^{-1}$, respectively.
- (25) Calculate for nitrogen the change of molar heat capacity c_p when the pressure is increased to 100 atm at 298.15 K, using the van der Waals equation of state. The constants are given in Problem 20.
- (26) The molar heat capacity of solid iodine at temperature between 298.15 K to the melting point (386.75 K) at 1 atm pressure is given by the relation

$$c_p = [54.64 + 1.34 \times 10^{-3}(T - 298.15)] \text{ J K}^{-1} \text{ mol}^{-1}.$$

Determine the increase of entropy accompanying the change of 1 mole of iodine from 298.15 to 386.75 K.