

## CHAPTER FIVE

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# The second law of thermodynamics

The first law of thermodynamics arose from the conservation of energy principle. The first law, even though it implies that we cannot create or destroy energy, places no limits on how energy can be transformed from one form to another. Thus, on the basis of the first law, heat can be transformed into work, work into heat, work can be done at the expense of internal energy, and so on. However, if no other laws existed the first law would allow certain phenomena to happen that never happen in reality. For example, consider a heavy body falling on the ground. We will observe that during the impact the body will warm. The opposite phenomenon according to which a body at rest on the ground begins to rise by itself while it is cooling is impossible. Similarly, no engine has yet been built which, for instance, would receive heat from the sea, transform it to work, and then set a ship in motion. Both the above examples are not in disagreement with the first law since the work would be done at the expense of the internal energy of the soil or the sea. The impossibility of these phenomena is due to the second law of thermodynamics, often hailed as the supreme law of nature. We will start our discussion of this law with the following example.

### 5.1 The Carnot cycle

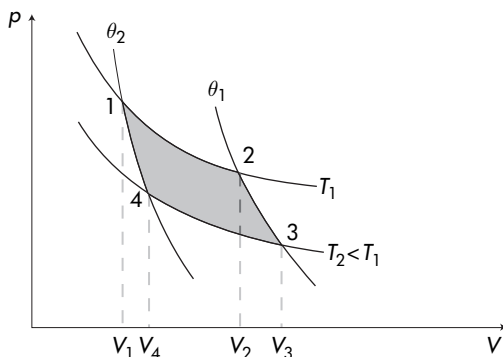
The Carnot cycle is a thermal engine. A thermal engine is one that receives from some source an amount of heat, part of which it transforms into work. In thermodynamical terms the Carnot cycle is a cyclic transformation consisting of the following four steps (Figure 5.1):

Step 1: reversible isothermal expansion ( $1 \rightarrow 2$ ),  $T = T_1 = \text{constant}$

Step 2: reversible adiabatic expansion ( $2 \rightarrow 3$ ),  $\theta = \theta_1 = \text{constant}$

**Figure 5.1**

Steps in a Carnot cycle.



Step 3: reversible isothermal compression ( $3 \rightarrow 4$ ),  $T = T_2 = \text{constant}$

Step 4: reversible adiabatic compression ( $4 \rightarrow 1$ ),  $\theta = \theta_2 = \text{constant}$

with  $T_2 < T_1$ ,  $\theta_2 < \theta_1$ .

Let us now calculate the work done and heat absorbed when an ideal gas is subjected to this cycle. The change in internal energy is zero because the overall transformation is a cyclic one. We will consider each step separately.

#### Step 1

$$\Delta T = 0$$

$$W_{12} = \int_{V_1}^{V_2} p dV = nR^*T_1 \int_{V_1}^{V_2} \frac{dV}{V} = nR^*T_1 \ln \frac{V_2}{V_1}$$

$$\Delta U_{12} = C_V \Delta T = 0$$

$$Q_{12} = W_{12}$$

Since  $V_2 > V_1$  it follows that  $W_{12}, Q_{12} > 0$  indicating that during step 1 work was done by the gas and heat was absorbed by the gas from the heat source at temperature  $T_1$ .

#### Step 2

$$Q_{23} = 0$$

$$\Delta U_{23} = C_V(T_2 - T_1) < 0$$

$$W_{23} = -\Delta U_{23} = -C_V(T_2 - T_1) > 0$$

#### Step 3

$$\Delta T = 0$$

$$W_{34} = \int_{V_3}^{V_4} p dV = nR^*T_2 \ln \frac{V_4}{V_3}$$

$$\Delta U_{34} = 0$$

$$Q_{34} = W_{34}$$

Since  $V_4 < V_3$  it follows that  $W_{34}, Q_{34} < 0$  indicating that now work is done on the gas and heat is given away by the gas to the source at temperature  $T_2$ .

**Step 4**

$$Q_{41} = 0$$

$$\Delta U_{41} = C_V(T_1 - T_2) > 0$$

$$W_{41} = -\Delta U_{41} = -C_V(T_1 - T_2) < 0$$

From the above it follows that the total work done is

$$\begin{aligned} W &= W_{12} + W_{23} + W_{34} + W_{41} \\ &= nR^*T_1 \ln \frac{V_2}{V_1} + nR^*T_2 \ln \frac{V_4}{V_3} \end{aligned} \quad (5.1)$$

Because transformations  $2 \rightarrow 3$  and  $4 \rightarrow 1$  are adiabatic the following relations apply:

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

and

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

By dividing the above two equations we have

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}.$$

Accordingly, equation (5.1) can be written as

$$W = nR^*T_1 \ln \frac{V_2}{V_1} - nR^*T_2 \ln \frac{V_2}{V_1}$$

or

$$W = nR^* \left( \ln \frac{V_2}{V_1} \right) (T_1 - T_2).$$

The total amount of heat absorbed during this cycle is

$$Q = Q_{12} + Q_{34} = W_{12} + W_{34} \quad (5.2)$$

or

$$Q = W = nR^* \left( \ln \frac{V_2}{V_1} \right) (T_1 - T_2) \quad (5.3)$$

For simplicity we will now denote the amount of heat absorbed by the gas from the heat source at  $T_1$  (i.e.  $Q_{12}$ ) as  $Q_1$  and the amount of heat given by the gas to the source at  $T_2$  (i.e.  $Q_{34}$ ) as  $Q_2$ . Since  $W$  is the area enclosed by the cycle it follows that  $W > 0$ . Then

from equation (5.3) it follows that  $Q > 0$ . Since  $W = Q_1 + Q_2$  and  $Q_2$  is negative it follows that only part of the heat absorbed by the gas at the source  $T_1$  (higher temperature) can be transformed into work. The other part is surrendered to the source at  $T_2$  (lower temperature). We define the efficiency of the Carnot cycle,  $\eta$ , as the ratio between the work done and the heat absorbed by the gas at the source  $T_1$ .

$$\eta = \frac{Q_1 + Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1} \quad (Q_1 > 0, Q_2 < 0).$$

By considering the relations derived for  $Q_1$  and  $Q_2$  we can write the above ratio as

$$\eta = 1 + \frac{nR^*T_2 \ln \frac{V_4}{V_3}}{nR^*T_1 \ln \frac{V_2}{V_1}}$$

or

$$\eta = 1 - \frac{T_2}{T_1} \quad (5.4)$$

## 5.2 Lessons learned from the Carnot cycle

- According to equation (5.4) the thermodynamic efficiency of the cycle depends only on the temperatures of the two heat sources and it becomes zero if  $T_2 = T_1$  (i.e. if the two sources collapse into one source). As such we conclude that doing work via a thermal engine operating at only one source of heat is impossible. This is known as Kelvin's postulate and is an expression of the second law of thermodynamics. Another way of stating this postulate is that it is impossible to construct an engine which transforms heat into work without surrendering some heat to a source at a lower temperature. This explains why stones on the ground do not rise in the air or why no machine has been discovered which by taking heat from the sea or the air sets in motion a ship or a car. According to the second law, apart from the warm heat source (sea or air), a second colder heat source would be required which we do not really have. I use the word *really* because some differences in temperature do exist in both the oceans and the atmosphere. For example, the temperature of the surface air is around 35 K warmer than the air at 5 km, and the temperature at the surface of the oceans is about 20 K warmer than at a depth of 1 km. In both cases, however, it turns out that the Carnot efficiency is about 10%. This is a low efficiency given the tremendous expenses that would be required to build such engines. On the other hand if the atmosphere, in the horizontal, is thought of as a Carnot cycle operating at  $T_1$  = equatorial temperatures and  $T_2$  = polar temperatures we can explain why in the winter the

circulation is stronger. Recall from above that

$$\eta = 1 + \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

or

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

If we think of summer as the limiting case where  $T_1 - T_2 \rightarrow 0$ , then during summer  $Q_2 \rightarrow -Q_1$  and  $\eta \rightarrow 0$ . On the other hand if we think of winter as the limiting case where  $T_2 \ll T_1$ , then during winter  $\eta \rightarrow 1$  and  $Q_2 \rightarrow 0$ . It follows that the efficiency of this “machine” is higher in the winter than in the summer. Accordingly, the amount of heat given by the atmosphere to the cold source is smaller in the winter, than in the summer. Since the amount of heat absorbed by the atmosphere from the warm source is more or less constant, this means that there is more heat “remaining” in the atmosphere in the winter than in the summer that can be transformed into kinetic energy.

Apart from the impossibility of transformations whose only final result is to transform into work heat extracted from only one source of heat, there is another type of transformation that is impossible. Such transformations refer to transfer of heat from a cold body to a warm body without work being done. This phenomenon is allowed by the first law (since heat lost by the cold body will be exactly equal to the heat gained by the warm body) but has never been observed. Of course transformations that result in heat flow from a colder body to a warmer body are allowed if work is done (such as in refrigerators). This leads to another expression of the second law of thermodynamics. A transformation whose only final result is to transfer heat from a body at a given temperature to a body at a higher temperature is impossible. This is known as Clausius’s postulate. It is easy to show that both postulates are equivalent and two expressions of the same law. To do that we shall prove that if Clausius was wrong then Kelvin would be wrong and vice versa. If Kelvin was wrong and we could transform into work heat extracted from only one heat source, then we could transform this work (by means of friction) into heat and with this heat raise the temperature of a given body of a higher initial temperature. This would be a violation of Clausius’s postulate. Now if Clausius was wrong and we could transfer a certain amount  $Q_1$  from a source at  $T_2$  to a source at  $T_1$  ( $T_2 < T_1$ ) in such a way that no other change in the state of the system occurred, then with the help of a Carnot cycle we could absorb this amount and produce an amount of work,  $W$ . Since the source  $T_1$  receives and gives up the same amount of heat ( $Q_1$ ) it suffers no final change. But

what we have just described is a process whose only final result is to transform into work the heat extracted from a source at the same temperature  $T_2$  throughout. This is contrary to Kelvin's postulate.

- From the definition of efficiency it follows that

$$\eta = 1 + \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

$$\frac{T_2}{T_1} = -\frac{Q_2}{Q_1} \quad (Q_1 > 0, Q_2 < 0).$$

Based on the above relationship an important application of Carnot cycle is that it offers a definition of the absolute temperature (Kelvin) scale based on pure thermodynamic arguments. For this we only need to have a value for a given temperature. An example for such value could be the melting point of ice. As such if we choose for the melting point of ice the value  $T_1 = 273^\circ\text{C}$  every other temperature  $T_2$  can be defined via a Carnot cycle operating between heat source  $T_1$  (consisting of melting ice) and a heat source  $T_2$ . If we then measure  $Q_1$  and  $Q_2$  we can apply the above relationship to calculate  $T_2$ . This thermodynamic definition of the Kelvin scale allows us to present a thermodynamic definition of absolute zero: the absolute zero is the temperature of a heat source (assumed to be the cold source of a Carnot cycle) which absorbs no heat (i.e.  $Q_2 = 0$ ) even though the cycle produces work.

- In reality natural processes are irreversible processes. However, if some processes happen very slowly and the heat losses are small enough not to affect the temperature (which supposes that friction is also negligible), then the results will not differ from those expected from perfectly reversible processes. Such processes are often called partially reversible. If on the other hand friction and heat flow are important then the degree of reversibility decreases. In nature the degree of reversibility varies between almost perfectly reversible and perfectly irreversible.

If in a thermal engine we increase the degree of irreversibility (for example, by increasing friction or direct leakages of heat), then the work from a given amount of heat will decrease. If the thermal losses keep on increasing we will end up with a perfectly irreversible engine. It follows that the efficiency of a thermal engine can take on values from zero (corresponding to the worst thermal engine operating at perfectly irreversible conditions) to some maximum value (corresponding to the best engine operating at perfectly reversible conditions). The Carnot cycle is a perfectly reversible cycle and as such it gives the maximum value the efficiency can take. This expresses the Carnot theorem

which states that it is impossible to construct an engine operating between two heat sources which would have an efficiency greater than the efficiency of a Carnot cycle operating between the same heat sources. However, this maximum value will not be equal to one as this would require that  $T_2 = 0\text{ K}$  which is practically impossible. Recall from section 5.1 that

$$Q_1 = nR^*T_1 \ln \frac{V_2}{V_1}$$

and

$$Q_2 = nR^*T_2 \ln \frac{V_4}{V_3}.$$

It follows that

$$\frac{Q_1}{T_1} = nR^* \ln \frac{V_2}{V_1}$$

and

$$\frac{Q_2}{T_2} = -nR^* \ln \frac{V_2}{V_1}$$

or

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \quad (Q_1 > 0, Q_2 < 0). \quad (5.5)$$

Now by considering equation (5.4) we can, for the reversible Carnot cycle, rewrite equation (5.5) as

$$\frac{Q_1\eta_{\text{rev}}}{T_1 - T_2} + \frac{Q_2}{T_2} = 0.$$

Since  $Q_2/T_2$  is less than zero it follows that  $Q_1\eta_{\text{rev}}/(T_1 - T_2)$  must be greater than zero. Since their sum must equal zero and, as we discussed above, the value of  $\eta$  is maximum for perfectly reversible processes, it follows that for irreversible processes where  $\eta$  becomes smaller

$$\frac{Q_1\eta_{\text{irrev}}}{T_1 - T_2} + \frac{Q_2}{T_2} < 0.$$

This proves that

$$\sum_{i=1}^2 \frac{Q_i}{T_i} \leq 0$$

where the equality applies to reversible processes. The above argument can be extended to any cyclic transformation in which the system receives heat from or surrenders heat to a set of temperatures  $T_1, T_2, \dots, T_N$  (Fermi, 1936). If the amounts of heat exchanged are  $Q_1, Q_2, \dots, Q_N$  (positive when heat is given to the system, negative otherwise) it can be shown that

$$\sum_{i=1}^N \frac{Q_i}{T_i} \leq 0$$

where again the equality applies to reversible processes. In the limit where  $N \rightarrow \infty$  the above equation takes the form

$$\oint \frac{\delta Q}{T} \leq 0. \quad (5.6)$$

We may conclude that with the aid of the Carnot cycle we can introduce a quantity, which for reversible processes is an exact differential. This quantity,  $\delta Q/T$ , is defined as  $dS$ , where  $S$  is a new state function called *entropy*. Since  $\delta Q/T$  is, for reversible processes, an exact differential it follows that for any reversible transformation  $i \rightarrow f$

$$\int_i^f \frac{\delta Q}{T} = \Delta S = S_f - S_i. \quad (5.7)$$

In other words the change in entropy depends only on the initial and final states, not on the particular transformation. This result is fundamental in the formulation of the second law.

Since  $S$  is a state function it follows that entropy changes are due to changes in both temperature and volume (or pressure). Using the first law we have that for a *reversible* process

$$dS = \frac{\delta Q}{T} = C_V \frac{dT}{T} + p \frac{dV}{T}$$

or

$$dS = C_V \frac{dT}{T} + nR^* \frac{dV}{V}$$

or

$$\frac{dS}{C_V} = \frac{dT}{T} + \frac{nR^*}{C_V} \frac{dV}{V}$$

or

$$\frac{dS}{C_V} = \frac{dT}{T} + (\gamma - 1) \frac{dV}{V}$$

or

$$S_f = S_i + C_V \ln \left( \frac{T_f V_f^{\gamma-1}}{T_i V_i^{\gamma-1}} \right). \quad (5.8)$$

Equation (5.8) provides the change in entropy of an ideal gas (since the ideal gas law was used) as a function of the initial and final temperature and volume. This relation cannot, therefore, be used for liquids or solids. For liquids or solids  $C_V \equiv C_p = C$  and one can show (but we will not go into this proof here) that in this case the entropy change is dominated by the temperature change. As such for liquids or solids and for *reversible* processes

$$S_f - S_i = C \ln \frac{T_f}{T_i} \quad (5.9)$$



### 5.3 More on entropy

As in the case of energy, we will choose an arbitrary equilibrium state  $O$  as the standard state where by definition  $S_O$  is zero. Then we will define the entropy  $S_A$  of an equilibrium state  $A$  as

$$S_A = \int_O^A \frac{\delta Q}{T}$$

where the integral is taken over a reversible transformation. It can easily be shown that if instead of a standard state  $O$  we had chosen a standard state  $O'$  then the entropy of state  $A$  would differ from the original one by an additive constant: from the above equation we have

$$S'_A = \int_{O'}^A \frac{\delta Q}{T}.$$

From equation (5.7) it follows that

$$S'_A = S_A - S_{O'}$$

or

$$S_A - S'_A = S_{O'}.$$

Since  $O'$  is fixed,  $S_{O'}$  is some constant. The entropy is thus defined except for an additive constant. As in the case of energy this does not present a problem as long as we are dealing with differences, not actual values of entropy. Now let us consider the cyclic transformation shown in Figure 5.2. The path  $i \xrightarrow{R} f$  represents a reversible transformation and the path  $f \xrightarrow{I} i$  represents an irreversible transformation. As we know, for any cycle  $\oint \delta Q/T \leq 0$ . As such

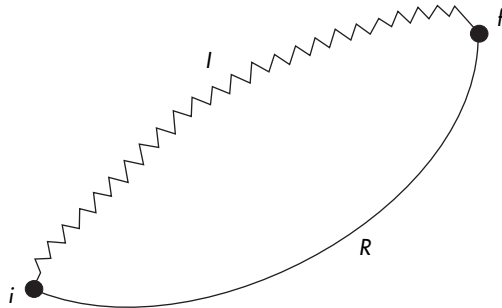
$$\oint_{iRfIi} \frac{\delta Q}{T} \leq 0$$

or

$$\left[ \int_i^f \frac{\delta Q}{T} \right]_R + \left[ \int_f^i \frac{\delta Q}{T} \right]_I \leq 0.$$

**Figure 5.2**

A cyclic transformation consisting of a reversible part from  $i$  to  $f(R)$  and an irreversible part from  $f$  to  $i(I)$ .



Since  $i \xrightarrow{R} f$  is reversible we have that

$$S_f - S_i = \left[ \int_i^f \frac{\delta Q}{T} \right]_R.$$

Combining the last two equations leads to

$$S_f - S_i + \left[ \int_f^i \frac{\delta Q}{T} \right]_I \leq 0$$

or

$$\left[ \int_f^i \frac{\delta Q}{T} \right]_I \leq S_i - S_f.$$

By interchanging  $i$  and  $f$  we conclude that for any process

$$\int_i^f \frac{\delta Q}{T} \leq S_f - S_i \quad (5.10)$$

or

$$\Delta S \geq \int_i^f \frac{\delta Q}{T} \quad (5.11)$$

or

$$dS \geq \frac{\delta Q}{T} \quad (5.12)$$

where the equality applies to reversible processes only. Equation (5.12) is the general expression of the second law of thermodynamics and it indicates that the upper bound to the heat that can be absorbed by the system during a given change is  $\delta Q = TdS$ . For a completely isolated system ( $\delta Q = 0$ ) equation (5.10) translates to

$$S_f \geq S_i. \quad (5.13)$$

This is an important conclusion as it indicates that for any spontaneous irreversible transformation (i.e. one not related to external influences) occurring in an isolated system, the final entropy is greater than the initial entropy. It follows that when an isolated system has attained a state of maximum entropy it cannot undergo any further transformation because any change would decrease its entropy, and this is not allowed by equation (5.13). Thus the state of maximum entropy is a state of stable equilibrium. Note that if the isolated system consists of a number of microscopic subsystems it would be possible for some of the subsystems to reduce their entropy but only at the expense of the rest of the subsystems, whose entropy must increase enough that the overall entropy of the system increases. A perfect isolated system is our universe (assuming that no other universes exist with which our universe can interact). It follows that the entropy of our universe increases in time. Equations (5.10)–(5.12) as well as equation

(5.13) are the basic mathematical expressions of the second law of thermodynamics.

## 5.4 Special forms of the second law

Given the above definitions of the second law we can derive its expression for special cases such as the following.

- **Finite isothermal transformations** ( $\Delta U = 0$ )

From equation (5.11) it follows that in this case

$$\Delta S \geq \frac{1}{T} \int_i^f \delta Q$$

or

$$\Delta S \geq \frac{Q}{T}$$

or

$$\Delta S \geq \frac{W}{T}. \quad (5.14)$$

- **Adiabatic transformations**

Using equation (5.12) we obtain

$$dS \geq 0. \quad (5.15)$$

- **Isentropic transformations**

An isentropic transformation is one during which the entropy does not change. In this case it is clear that (recall equation (5.12))

$$\delta Q \leq 0. \quad (5.16)$$

Note that according to equation (5.15) a reversible adiabatic process is isentropic.

- **Isochoric transformations**

From the first law we have that when  $dV = 0$  then  $\delta Q = C_V dT$ . As such for isochoric transformations

$$dS \geq C_V \frac{dT}{T}$$

or

$$\Delta S \geq C_V \ln \frac{T_f}{T_i}. \quad (5.17)$$

- **Isobaric transformations**

In this case

$$\delta Q = C_p dT$$

and it follows that

$$dS \geq C_p \frac{dT}{T}$$

or

$$\Delta S \geq C_p \ln \frac{T_f}{T_i}. \quad (5.18)$$

From equation (5.14) it follows that irreversible work increases a system's entropy. From equation (5.17) it follows that in the absence of work the change in entropy depends on the relation between  $T_f$  and  $T_i$ .

## 5.5 Combining the first and second laws

Consider the following form of the first law:

$$\delta Q = C_p dT - V dp.$$

Combining the above equation with  $dS \geq \frac{\delta Q}{T}$  yields

$$TdS \geq C_p dT - V dp.$$

Recalling that  $C_p = dH/dT$  we can reduce the above equation to

$$TdS \geq dH - V dp$$

or

$$dH \leq TdS + V dp. \quad (5.19)$$

Similarly, from

$$\delta Q = C_v dT + p dV$$

we arrive at

$$TdS \geq dU + \delta W$$

or

$$dU \leq TdS - p dV. \quad (5.20)$$

It is often convenient to introduce two new functions: the Helmholtz function  $F = U - TS$  and the Gibbs function  $G = H - TS = U + pV - TS$ . Since  $S = S(T, V)$  and  $U = U(T)$  it follows that both  $F$  and  $G$  are state functions (i.e.  $F = F(T, V)$ ,  $G = G(T, V)$ ), and thus are exact differentials. The advantage of these functions is that they can be used to express equations (5.19) and (5.20) in a form where the pairs  $(T, p)$  and  $(T, V)$  appear as the independent variables instead of the pairs  $(S, p)$  and  $(S, V)$ . In this case equations (5.20) and (5.19) can be written as:

$$dF \leq -SdT - p dV \quad (5.21)$$

and

$$dG \leq -SdT + V dp. \quad (5.22)$$

The interpretation of the above functions is that for isothermal processes  $dF \leq -\delta Q$  or  $dF \leq -\delta W$  which makes  $F$  the energy

available for conversion into work. The usefulness of  $G$  becomes clearer for isothermal-isobaric transformations. During such transformations (which apply in phase transitions, for example water to vapor)  $dG = 0$  and therefore  $G$  is conserved. Relations (5.19)–(5.22) are often referred to as the fundamental relations.

## 5.6 Some consequences of the second law

### Thermodynamic definition of temperature

As we know, the integral  $\int_i^f \delta Q$  depends on the path from  $i$  to  $f$ , not just the states  $i$  and  $f$ . In this chapter we showed that the integral  $\int_i^f \delta Q/T$  depends only on the initial and final states, not on the particular path from  $i$  to  $f$ . As such  $1/T$  is the integration factor that makes  $\delta Q$  an exact differential. It follows that in thermodynamical terms *temperature is the inverse of the integration factor of the differential of heat in reversible processes*.

### The statistical nature of thermodynamics

The change in entropy during a reversible cooling at constant pressure of  $m$  grams of dry air from  $T_1$  to  $T_2$  ( $T_1 > T_2$ ) is

$$\Delta S = \int_{T_1}^{T_2} \frac{\delta Q}{T}.$$

Since  $p = \text{constant}$  we have that  $\delta Q = mc_{pd}dT$  where  $c_{pd}$  is the specific heat capacity of dry air. It follows that

$$\Delta S = \int_{T_1}^{T_2} mc_{pd} \frac{dT}{T}$$

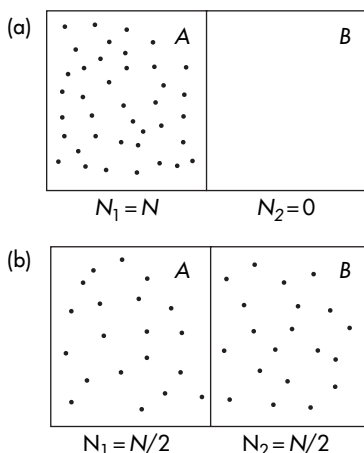
or assuming that  $c_{pd}$  does not vary significantly with temperature

$$\Delta S = S_{T_2} - S_{T_1} = mc_{pd} \ln \frac{T_2}{T_1}.$$

Since  $m$  and  $c_{pd}$  are greater than zero and  $\ln \frac{T_2}{T_1} < 0$  it follows that  $\Delta S < 0$ . Thus, the entropy decreases during the cooling. This decrease does not violate the second law. Even though the dry air decreases its entropy the environment that provided the heat suffers a positive change so that the overall entropy change of the system is positive. We can extend the above arguments to show that as the temperature goes down so does the entropy (or as temperature goes up so does the entropy). The question is why and what is the physical meaning of this. Kinetic theory provides an explanation for the above. According to the theory, at very low temperatures the motion of the molecules is very slow with the molecules being

**Figure 5.3**

The situation in (a) represents greater order and a lower number of complexions than in (b) where the number of complexions and disorder have increased.



more or less uniformly distributed in space. This is a picture of a high order, with complete order (motionless molecules uniformly spaced) presumably achieved at absolute zero. As the temperature increases the motion of the molecules increases and the order is soon destroyed. If we combine this with the above result it follows that we can associate entropy with order or disorder. Accordingly, decreasing entropy implies increasing order and increasing entropy implies increasing disorder. This association justifies the word entropy, which in Greek means the “inner behavior” (*εντροπία*). Now if such an association is correct we should be able to find a measure that defines disorder which should be mathematically related to entropy.

Let us consider a volume  $V$  consisting of two compartments  $A$  and  $B$ , with  $N$  total particles moving around. Let us denote with  $N_1$  the number of particles in compartment  $A$  and with  $N_2$  the number of particles in compartment  $B$ . Statistics tells us that the number of different ways,  $P$ , in which  $N_1$  particles will be found in  $A$  and  $N_2$  particles in  $B$  is

$$P = \frac{N!}{N_1!N_2!}. \quad (5.23)$$

Now consider two cases as shown in Figure 5.3. In the first case all particles are found in  $A$  (Figure 5.3(a)), and in the second case the particles are all over the box (Figure 5.3(b)). The first case ( $N_1 = N, N_2 = 0$ ) obviously represents a state of more order than the second where it can be assumed that  $N_1 = N_2 = N/2$ . Applying equation (5.23) to both cases yields

Case 1:

$$P = \frac{N!}{N!0!} = 1$$

Case 2:

$$P = \frac{N!}{N/2! N/2!} \gg 1.$$

We thus see that we have a measure  $P$  (often called the number of complexions) that increases as disorder increases. If we consider the first case as the initial state and the second case as the final state we can conclude (since  $i \rightarrow f$  is an irreversible process) that as the entropy increases  $P$  increases. So  $P$  is a possible candidate to relate disorder to entropy. But how can we find their functional relationship?

The derivation of this relationship (one of the most beautiful yet simplest ones) is due to Boltzmann (Fermi, 1936). From the above we saw that as  $S$  increases,  $P$  increases and vice versa. So let us start with a general relationship of the form

$$S = f(P).$$

Next, consider a system consisting of two subsystems and let  $S_1$  and  $S_2$  be the entropies and  $P_1$  and  $P_2$  the corresponding number of complexions. Then,  $S_1 = f(P_1)$  and  $S_2 = f(P_2)$ . For the whole system we can then write that

$$S = S_1 + S_2$$

and

$$P = P_1 P_2$$

or

$$f(P_1 P_2) = f(P_1) + f(P_2)$$

i.e. the function  $f$  obeys the functional equation

$$f(xy) = f(x) + f(y).$$

Since the above equation is true for all values of  $x$  and  $y$  we may take  $y = 1 + \epsilon$  with  $\epsilon \ll 1$ . Then we can write it as

$$f(x + x\epsilon) = f(x) + f(1 + \epsilon). \quad (5.24)$$

Expanding both sides of the above equation using Taylor's theorem and neglecting terms higher than first order we get

$$f(x) + x\epsilon f'(x) = f(x) + f(1) + \epsilon f'(1) \quad (5.25)$$

where  $f'$  indicates the first derivative. For  $\epsilon = 0$  from equation (5.24) we have that  $f(1) = 0$ . Therefore, equation (5.25) reduces to

$$x\epsilon f'(x) = \epsilon f'(1)$$

or

$$xf'(x) = f'(1).$$

Since  $f'(1)$  is a derivative evaluated at a value of 1 it is a constant. Thus

$$xf'(x) = k$$

or

$$f'(x) = \frac{k}{x}$$

or

$$f(x) = \int \frac{k}{x} dx$$

or

$$f(x) = k \ln x + \text{constant}$$

or by changing  $x \rightarrow P$ ,

$$S = k \ln P + \text{constant}. \quad (5.26)$$

This equation relates order and entropy and constitutes a fundamental relationship connecting statistical mechanics and thermodynamics, thereby giving thermodynamics a statistical character.

### Entropy and potential temperature

Recall that the potential temperature  $\theta$  is given by

$$\theta = T \left( \frac{1000}{p} \right)^{R/c_p}.$$

By taking the logarithms of both sides we obtain

$$\ln \theta = \ln T + \frac{R}{c_p} \ln 1000 - \frac{R}{c_p} \ln p$$

or

$$c_p d \ln \theta = c_p d \ln T - R d \ln p. \quad (5.27)$$

From the first law we have

$$\delta Q = C_p dT - V dp$$

or

$$\frac{\delta Q}{T} = C_p \frac{dT}{T} - V \frac{dp}{T}$$

or

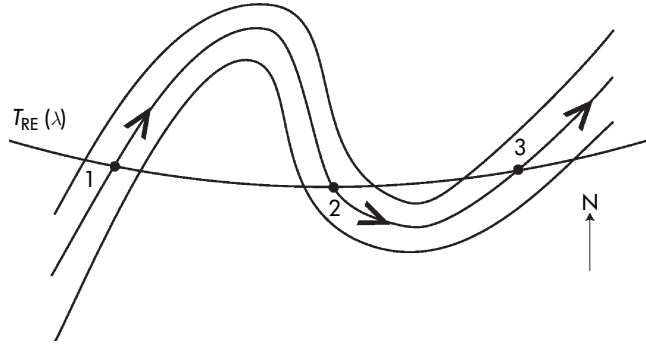
$$\frac{\delta Q}{T} = C_p \frac{dT}{T} - mR \frac{dp}{p}$$

or (for reversible processes)

$$ds = c_p \frac{dT}{T} - R \frac{dp}{p} \quad (5.28)$$



**Figure 5.4**  
A hypothetical upper-level  
flow and the trajectory  
followed by a parcel.



where  $ds$  is the specific entropy. Combining (5.28) and (5.27) leads to

$$ds = c_p d \ln \theta \quad (5.29)$$

or

$$s = c_p \ln \theta + \text{constant}. \quad (5.30)$$

Thus, except for an additive constant, the specific entropy of a system is given by the logarithm of the potential temperature. When  $\theta$  remains constant the entropy remains constant. It follows that a reversible adiabatic process is isentropic. For an irreversible adiabatic process  $ds > 0, d\theta = 0$ . In this case, the increase in entropy comes from irreversible work (for example, dissipation of kinetic energy due to friction). It follows that an isentropic process is adiabatic, but an adiabatic process may not be isentropic.

### Atmospheric motions

Figure 5.4 shows a hypothetical upper-level flow close to some latitude  $\lambda$ . Along this latitude the radiative-equilibrium temperature  $T_{\text{RE}}(\lambda)$  is assumed to be the same. Such thermal structure can be achieved if the motion is completely zonal (i.e. parallel to latitude circles), since air parcels then have infinite time to adjust to local thermal equilibrium. If at position 1 a parcel is allowed to move with the flow two possibilities exist. If the motion is very slow the parcel has time to come into equilibrium with its surroundings, so its temperature differs from  $T_{\text{RE}}$  only infinitesimally. Therefore, we can assume that heat transfer along the trajectory of the parcel is reversible. Then for positions 1 and 2 we have that

$$\int_1^2 c_p d \ln \theta = \int_1^2 ds = \int_1^2 \frac{\delta q}{T}.$$

If we assume that  $\delta q$  depends only on the parcel's temperature (for example,  $\delta q = T f(T)$ ) then we can write the above equation as

$$\int_1^2 c_p d \ln \theta = \int_1^2 df(T) = f(T_2) - f(T_1).$$

Since  $T_2 = T_1 = T_{RE}$  the above relationship reduces to

$$\int_1^2 c_p d \ln \theta = 0$$

or

$$\theta_2 = \theta_1.$$

Thus, the parcel is restored to its initial thermodynamic state when it returns to the original latitude. Since  $\theta$  depends on  $p$  and  $p$  depends on height it follows that under the slow motion conditions, successive crossings of the initial latitude result in zero net vertical motion and zero heat transfer.

On the other hand if the motion is fast enough that reversibility cannot be assumed, then

$$\int_1^2 c_p d \ln \theta < ds \neq 0$$

and therefore  $\theta_2 \neq \theta_1$ . In this case when the parcel returns to the initial latitude it is displaced vertically and the net heat transfer is not zero. Vertical motion resulting from irreversibility in the atmosphere plays an important role in maintaining meridional circulations, heat and moisture transfer, etc.

## Examples

(5.1) Imagine a volume  $V$  divided into two smaller volumes  $V_1$  and  $V_2$  by a partition. Assume that  $m_1$  grams of an ideal gas at temperature  $T_1$  occupy volume  $V_1$  and  $m_2$  grams of another ideal gas at temperature  $T_2$  occupy volume  $V_2$ . Then the partition is removed. If the specific heat capacities at constant volume of the gases are  $c_{V_1}$  and  $c_{V_2}$ , find (a) the limiting temperature of the mixture, and (b) the change in entropy for each gas and for the system as a whole.

- (a) We assume that while the two gases exchange heat between them and perform work, the system as a whole does not exchange heat with its surroundings and its volume remains constant ( $V = V_1 + V_2$ ). In other words for the whole system the process of mixing is adiabatic, with no work being done. As such,  $\Delta U = 0$ . The total internal energy before mixing is  $C_{V_1} T_1 + C_{V_2} T_2$  and

after the mixing it is  $C_{V_1}T + C_{V_2}T$  (here we have made use of the approximation  $U \approx C_V T + \text{constant}$  and then neglected the constant). Since  $\Delta U = 0$  it follows that

$$C_{V_1}T_1 + C_{V_2}T_2 = C_{V_1}T + C_{V_2}T$$

which yields

$$T = \frac{C_{V_1}}{C_{V_1} + C_{V_2}}T_1 + \frac{C_{V_2}}{C_{V_1} + C_{V_2}}T_2. \quad (5.31)$$

Considering that  $C_{V_1} = c_{V_1}m_1$  and  $C_{V_2} = c_{V_2}m_2$  the above equation becomes

$$T = \frac{c_{V_1}m_1}{c_{V_1}m_1 + c_{V_2}m_2}T_1 + \frac{c_{V_2}m_2}{c_{V_1}m_1 + c_{V_2}m_2}T_2$$

- (b) From equation (5.8) and the additive property of entropy it follows that for each gas the total entropy change is the sum of the entropy change due to the temperature change of the gas alone and the entropy change due to the volume change of the gas alone, i.e.

$$\Delta S_1 = \Delta S_{1T} + \Delta S_{1V}$$

$$\Delta S_2 = \Delta S_{2T} + \Delta S_{2V}$$

where the lower limits for  $\Delta S_{1T}$ ,  $\Delta S_{1V}$ ,  $\Delta S_{2T}$ , and  $\Delta S_{2V}$  are given by (recall equation 5.8)

$$\Delta S_{1T} = C_{V_1} \ln \frac{T}{T_1}$$

$$\Delta S_{2T} = C_{V_2} \ln \frac{T}{T_2}$$

$$\Delta S_{1V} = C_{V_1} \ln \left( \frac{V_1 + V_2}{V_1} \right)^{\gamma_1 - 1} = m_1 R_1 \ln \frac{V_1 + V_2}{V_1}$$

and

$$\Delta S_{2V} = C_{V_2} \ln \left( \frac{V_1 + V_2}{V_2} \right)^{\gamma_2 - 1} = m_2 R_2 \ln \frac{V_1 + V_2}{V_2}$$

where  $R_1$  and  $R_2$  are the specific gas constants of the two gases. For the system as a whole the lower limit for the total entropy change is

$$\Delta S = \Delta S_1 + \Delta S_2$$

or

$$\Delta S = (\Delta S_{1T} + \Delta S_{2T}) + (\Delta S_{1V} + \Delta S_{2V}) = \Delta S_T + \Delta S_V$$

or

$$\begin{aligned}\Delta S = & \left[ c_{V_1} m_1 \ln \frac{T}{T_1} + c_{V_2} m_2 \ln \frac{T}{T_2} \right] \\ & + \left[ m_1 R_1 \ln \frac{V_1 + V_2}{V_1} + m_2 R_2 \ln \frac{V_1 + V_2}{V_2} \right].\end{aligned}\quad (5.32)$$

In equation (5.32) the second term on the right-hand side ( $\Delta S_V$ ) is necessarily greater than zero. The first term ( $\Delta S_T$ ) is either positive or zero when  $T_1 = T_2$  (see problem 5.13). As such for the whole system  $\Delta S > 0$  which according to (5.12) indicates irreversible process. This proves that mixing is irreversible.

- (5.2) Calculate the change in air pressure if the specific entropy decreases by  $0.05 \text{ J g}^{-1} \text{ K}^{-1}$  and the air temperature decreases by 5%.

Assuming that the process is reversible we have

$$\begin{aligned}dS &= C_p \frac{dT}{T} - \frac{V}{T} dp \\ &= C_p \frac{dT}{T} - nR^* \frac{dp}{p}.\end{aligned}$$

Since we do not have any information on the mass of the air involved in the process we will write the above per unit mass:

$$ds = c_p \frac{dT}{T} - R \frac{dp}{p}$$

or

$$\frac{dp}{p} = \frac{c_p}{R} \frac{dT}{T} - \frac{ds}{R}$$

or considering the air as dry

$$\ln \frac{p_f}{p_i} = \frac{1005}{287} \ln \left( \frac{0.95 T_i}{T_i} \right) - \frac{(-50)}{287}$$

or

$$p_f = 0.994 P_i$$

The pressure will decrease by a small amount of about 0.6%.

- (5.3) In example 4.3, what is the change in entropy in each of the three transformations?

- (a) The first transformation is an isothermal reversible compression. Thus,

$$\Delta S = \int_i^f \frac{\delta Q}{T} = \frac{1}{T} \int_i^f \delta Q = \frac{Q}{T} = nR^* \ln \frac{V_f}{V_i} = nR^* \ln \frac{p_i}{p_f}.$$

- (b) The second transformation consists of two branches. The first one is a reversible adiabatic transformation. Thus, the entropy change in the first branch is zero. The second branch is an isobaric reversible compression. As such the entropy change of the second transformation is (recall that since  $T_i$  and  $T_f$  lie on the same isothermal  $T_i = T_f = T$ )

$$\begin{aligned} \Delta S &= \int_m^f \frac{\delta Q}{T} = C_p \int_m^f \frac{dT}{T} = C_p \ln \frac{T_f}{T_m} = C_p \ln \frac{T_i}{T_m} \\ &= C_p \ln \left( \frac{p_f}{p_i} \right)^{\frac{1-\gamma}{\gamma}} \\ &= -nR^* \ln \frac{p_f}{p_i} \\ &= nR^* \ln \frac{p_i}{p_f} \end{aligned}$$

- (c) The third transformation also consists of two branches: one reversible isochoric and one reversible isobaric. The total change in entropy is the sum of the changes in entropy in the two branches

$$\begin{aligned} \Delta S &= \Delta S_1 + \Delta S_2 = \int_i^{m'} \frac{\delta Q}{T} + \int_{m'}^f \frac{\delta Q}{T} \\ &= \int_i^{m'} C_V \frac{dT}{T} + \int_{m'}^f C_p \frac{dT}{T} \\ &= C_V \ln \frac{T_{m'}}{T_i} + C_p \ln \frac{T_f}{T_{m'}} \end{aligned}$$

During this transformation  $p_i V_i = nR^* T_i$  and  $p_f V_i = nR^* T_{m'}$ . Thus

$$T_{m'} = \frac{p_f}{p_i} T_i.$$

If we substitute the above value of  $T_{m'}$  in the previous equation we obtain

$$\Delta S = C_V \ln \frac{p_f}{p_i} + C_p \ln \frac{T_f}{T_i} \frac{p_i}{p_f}.$$

Since  $T_f = T_i = T$  it follows that

$$\Delta S = C_V \ln \frac{p_f}{p_i} + C_p \ln \frac{p_i}{p_f}$$

or

$$\Delta S = nR^* \ln \frac{p_i}{p_f}.$$

Thus, in all transformations the change in entropy is the same.

### Problems

- (5.1) Starting from the first law show that  $\delta Q/T$  is an exact differential.
- (5.2) Derive the so-called Maxwell relations for reversible processes

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

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

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

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

- (5.3) Find the lower limit for the change in specific entropy of dry air at a given temperature and pressure which is allowed to expand freely into an insulated chamber to assume twice its original volume. ( $200 \text{ J K}^{-1} \text{ kg}^{-1}$ )
- (5.4) What is the form of isenthalpic lines in a  $(p, V)$  diagram?
- (5.5) Dry air at  $T = 0^\circ \text{C}$  and  $p = 1$  atmosphere is compressed isentropically until its pressure becomes 10 atmospheres. Find the final temperature. ( $527.5 \text{ K}$ )
- (5.6) In a Carnot cycle the *area* for each transformation corresponds to the following work – (a) isothermal expansion:  $31\,165 \text{ J}$ , (b) adiabatic expansion:  $21\,517 \text{ J}$ , (c) isothermal compression:  $24\,282 \text{ J}$ , (d) adiabatic compression:  $21\,517 \text{ J}$ . Calculate (1) the heat provided, per cycle, to the gas by the warm source, and (2) the efficiency of the cycle. ( $6883 \text{ J}$ ,  $0.22$ )
- (5.7) One mole of ideal gas occupies 5 liters at  $273 \text{ K}$ . If it expands into a vacuum until its volume becomes 20 liters, what is the lower limit for the change in entropy and the upper limit for the change in Gibbs's function? ( $11.5 \text{ J K}^{-1}$ ,  $-3146 \text{ J}$ )
- (5.8) A fixed volume  $2V$  is divided into two equal volumes  $V$  separated by a diaphragm. Each volume contains the same amount of the same gas at the same temperature  $T$ . Using

Boltzmann's expression for entropy, show that after the diaphragm is removed the entropy change is zero. How will you approach this problem if the temperature in the two volumes is different? Use the approximation  $\ln N! = N \ln N - N$ .

- (5.9) In a thermodynamic process a parcel of dry air is lifted in the atmosphere such that its pressure decreases from 1000 to 800 mb while its temperature remains constant. Calculate the change in the specific entropy of the parcel. ( $64 \text{ J kg}^{-1} \text{ K}^{-1}$ )
- (5.10) During a process a parcel of dry air descends from 900 to 950 mb and its specific entropy decreases by  $30 \text{ J kg}^{-1} \text{ K}^{-1}$ . If its initial temperature is 273 K what is (a) its final temperature and (b) its final potential temperature. (269 K, 273 K)
- (5.11) Show that for flows on a constant pressure level the relative change (i.e. percent change of original value) in temperature is equal to the relative change in potential temperature.
- (5.12) Cooler air moves over a warmer surface. What will happen to the surface pressure? (Hint: the condition of problem 5.11 does not apply here.)
- (5.13) Show that the first term on the right-hand side of equation (5.32) is greater than zero except when  $T_1 = T_2$  when it is zero. (Hint: define  $b = C_{V_1}/C_{V_2}$  and  $x = T_2/T_1$  and find the first and second derivatives of  $f(x) = \Delta S_T/C_{V_1}$ .)
- (5.14) Try to explain to your friends why the second law of thermodynamics implies a positive arrow of time (i.e. time goes only forwards).
- (5.15) Consider two isolated systems existing very far from each other. The same irreversible transformation occurs in both of them. Will the change in entropy be the same in both of them?
- (5.16) In an isentropic process the specific volume of a sample of dry air increases from  $300 \text{ cm}^3 \text{ g}^{-1}$  to  $500 \text{ cm}^3 \text{ g}^{-1}$ . If the initial temperature was 300 K, what are the final values of  $T$  and  $p$ ? (244.5 K, 1404 mb)
- (5.17) Prove geometrically (in a  $p, V$  diagram) equation (5.2).

