

# Chapter 1 *Review of Classical Thermodynamics*

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## 1.1 Introduction

Thermodynamics deals with macroscopic systems containing many particles  $N \approx 10^{23}$ , without attempting to carry out a detailed treatment of the microscopic dynamics. It is found experimentally that for many macroscopic systems in equilibrium, it is possible to measure just a small number of parameters (such as the temperature, volume and particle number for a fluid), and from these, to predict with great accuracy the results of many other measurements, such as the pressure, internal energy etc. We wish to understand how to make such predictions, and to explain why it is that such an endeavour is possible even when the detailed state of the system is almost completely undetermined by the available data. As by-products, we shall find many connections between ideas which might otherwise have seemed unrelated, such as the speed of sound in a solid and its specific heat, the temperature of a piece of rubber and its springiness, etc.

Thermodynamics may be described as the study of energy and its transformations, and the laws of thermodynamics are about describing which transformations are possible, and which are not. Classical thermodynamics starts with these laws, which are generalizations of observations made on macroscopic systems. Historically, the subject was developed in order to understand how to make engines (which are devices that convert heat into work) as efficient as possible, although the generality of the laws mean that they are very widely applicable. It is interesting to note that when the laws of thermodynamics were first formulated, the nature of heat was unknown (it was thought of as a fluid) and the atomic nature of matter had not been established. Nevertheless, by concentrating on the empirical relationships between macroscopic observables rather than on underlying mechanisms, the results have retained their validity and may be applied to exotic systems such as a “gas” of radiation or of the conduction electrons in metals.

Statistical mechanics is about trying to understand how the laws of thermodynamics and the properties of matter arise from a statistical analysis of the collective behaviour of many particles. Macroscopic behaviour arises both from the details of the microscopic behaviour as well as from the process of averaging over all the things that we do not control and hence do not know (or care) about the system. The details of the microscopic behaviour can best be described using quantum mechanics, whereas the process of averaging involves a careful accounting of the possibilities which are consistent with our state of knowledge of the system. We shall find that in many cases, the macroscopic properties are determined more by the effects of statistical averaging than by the details of the microscopic dynamics, and we can get away with using the crudest of physical models (such as ignoring interactions between the particles) and still achieve quite accurate results.

We shall start in this chapter with an overview of classical thermodynamics, mainly using an ideal gas as a specific example of a well-understood thermodynamic system.

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## 1.2 States and functions of state

Given an isolated physical system, we assume that it will ultimately reach an equilibrium state in which all macroscopic variables are constant in time. This is always the case for systems of many particles with weak interactions so that fluctuations of density, pressure etc. will ultimately disappear. In reality, at the microscopic level, an equilibrium state is not static, but the system evolves (often rapidly, think of molecular motions in a gas) between dynamical states which nevertheless look identical from a macroscopic viewpoint. In classical thermodynamics, the word **state** is usually taken to mean **equilibrium state**.

The macroscopic variables which are well determined when a system is in an equilibrium state are known as **state functions** or **state variables**. Examples of state functions are the mass, temperature, pressure, volume, internal energy, enthalpy, free energy, entropy etc. We can think of the state functions as **coordinates** which label the state.

As an analogy, given a point in space, we can find its coordinates  $x, y, z, r, \theta, \phi, \rho$  etc. in different coordinate systems. Notice that not all of these are needed to completely specify the point, although all of them are determined once the point is given. In particular, any of the sets  $(r, \theta, \phi)$ ,  $(x, y, z)$  or  $(\rho, \phi, z)$  may be used to specify points.

In the same way, various **subsets** of the state functions suffice to completely determine an equilibrium state. For example, for a **homogeneous fluid**, we can use the temperature, volume and mass (or various other combinations) as the independent variables and consider all the other state variables as being dependent on these. Note that we do not allow the system to have a “memory” and so we shall assume that the history by which a system reaches an equilibrium state (as defined by the independent variables) does not affect any of the values of the dependent variables.

### 1.2.1 Some properties of ideal gases

An **equation of state** relates the state variables. For an ideal gas, we have the well-known ideal gas law

$$PV = NkT \quad (1.1)$$

where  $P$  is the pressure,  $V$  is the volume,  $N$  is the number of molecules,  $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$  is Boltzmann’s constant and  $T$  is the absolute temperature. If we work in terms of moles of gas,  $\tilde{N} = N/N_A$ , we have

$$PV = \tilde{N}RT \quad (1.2)$$

where  $N_A = 6.023 \times 10^{23}$  is Avogadro’s number and  $R = N_A k = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$  is the gas constant. The result that  $PV$  is constant for a fixed mass of gas at a given temperature is known as **Boyle’s law**.

From elementary kinetic theory, recall that if we model a gas as a large number of non-interacting particles of mass  $m$ , and consider the pressure that it exerts as due to collisions between the particles and the walls of the vessel, we find that

$$PV = \frac{1}{3}Nm \langle v^2 \rangle \quad (1.3)$$

where  $\langle v^2 \rangle$  is the mean square velocity of the particles.

If we now specialize to the case of a **monatomic gas**, the internal energy is given by the translational kinetic energy of the atoms which is  $\frac{1}{2}mv^2$  per atom. Thus

$$E = \frac{1}{2}Nm \langle v^2 \rangle \quad (1.4)$$

and by combining the last two equations and the ideal gas law, we see that

$$E = \frac{3}{2}NkT. \quad (1.5)$$

From this, we see that the internal energy of a fixed mass of ideal gas (so that  $N$  is fixed) depends only on the temperature and not the volume or pressure. The fact that the internal energy of an ideal gas depends only on the temperature is known as **Joule’s law**, and is a consequence of the assumption that the particles do not interact. Joule’s law is true for all ideal gases, but the coefficient  $\frac{3}{2}$  in equation (1.5) holds only for a **monatomic gas**.

If we take an ideal gas at constant volume and heat it, the amount of heat required to raise the temperature of the gas by one Kelvin is called the **heat capacity** of the gas at constant volume, and is denoted by  $C_V$ . For the monatomic ideal gas, we see that  $C_V = \frac{3}{2}Nk$ . We sometimes also work with the heat capacity per molecule  $c_V = C_V/N$ , the molar heat capacity  $\tilde{c}_V = C_V N_A/N$  or the specific heat capacity which is the heat capacity per unit mass. For an ideal gas, Joule’s law may be written as

$$E = C_V T \quad (1.6)$$

which holds whether or not the gas is monatomic.

### 1.3 First law of thermodynamics

The internal energy of a system is usually taken as the energy of the system excluding the kinetic energy or potential energy that the system may have as a macroscopic object. The internal energy of a system can be changed by passing energy through the **boundary** of the system. We distinguish two ways of passing energy through a boundary

1. We may introduce **heat**  $Q$  into the system. Heat is energy flow across the boundary that is caused by a **temperature difference**.
2. We may do **work**  $W$  on the system. This takes care of everything else. Work can be done for example by changing the system volume, introducing a current carrying resistor (electrical work), stirring the substance, introducing new particles into the system (chemical work) etc.

In Physics the usual convention is that work is positive when work is done **on** the system, and heat is positive when it flows **into** the system. (Note however that engineers often think in terms of engines which convert heat into work and so they define work to be positive when it is done **by** the system. We shall not use this convention, but you should be aware of its existence.)

The first law of thermodynamics is simply the statement of the law of conservation of energy, namely that in any process which brings a system with a fixed number of particles from one state to another,

$$\Delta E = Q + W. \quad (1.7)$$

Note that

1. The internal energy  $E$  is a state function, but  $Q$  and  $W$  are not. As an analogy, think of a bank account, in which the amount of money is analogous to the internal energy. This amount can be changed by depositing cheques  $Q$  or cash  $W$ . Given an initial and final state, it is possible to work out the change  $\Delta E$ , but there is no unique way of determining  $Q$  and  $W$  that caused this, as there are many different values of  $Q$  and  $W$  that lead to the same change of state.
2. For a **thermally isolated system**,  $Q = 0$  and we see that in this case

$$\Delta E = W. \quad (1.8)$$

Thus the amount of work required to bring the system between two specified states is independent of the way in which this work is done. This result was established by Joule.

3. For an **infinitesimal change of state**, we write

$$dE = \bar{d}Q + \bar{d}W \quad (1.9)$$

where the symbol  $\bar{d}$  signifies that the infinitesimal heat and work are **not** functions of state. They depend on the path or process that is taken between the initial and final states.

**Example:** Free expansion of an ideal gas

A thermally insulated vessel is separated by a partition into two sections of volumes  $V_1$  and  $V_2$  respectively. An ideal gas is placed in volume  $V_1$  so that at equilibrium, the pressure is  $P_1$  and the temperature is  $T_1$ . The volume  $V_2$  is initially evacuated. The partition is then removed, allowing the gas to expand to fill the entire volume. Calculate the final temperature and pressure of the gas, once equilibrium has been re-established.

**Solution:**

Since the vessel is thermally insulated, no heat flows and so  $Q = 0$ . No work is done on or by the system when the partition is removed, and so  $W = 0$ . Thus the internal energy of the gas at the end of the process

is equal to that at the start of the process. By Joule's law, the final temperature of the gas is equal to the initial temperature, namely  $T_1$ . By the ideal gas law, we see that the final pressure is  $P = P_1 V_1 / (V_1 + V_2)$ .

### Exercise:

Repeat the above problem, except that we now assume that volume  $V_2$  is initially filled with the same gas as  $V_1$  but at pressure  $P_2$  and temperature  $T_2$ .

## 1.4 Quasi-static and non quasi-static processes

A process which takes a system from one state to another is said to be **quasi-static** if the system is at all times arbitrarily close to an equilibrium state. This means that the process must be carried out slowly compared to the time that it takes for the system to approach equilibrium. All the state variables are well defined and change smoothly during a quasi-static process and we can draw a smooth path between the initial and final states showing the intermediate states that the system passes through.

Let us first consider work done by changing the **volume** of the system. By the definition of work, the work done  $\Delta W$  on a system by an external pressure  $P_{\text{ext}}$  when the volume of the system changes by  $\Delta V$  is given by

$$\Delta W = -P_{\text{ext}} \Delta V \quad (1.10)$$

This is true for **any** process, whether quasi-static or not. This expression involves  $P_{\text{ext}}$  which is not a state variable of the **system**. In the absence of friction, the work takes place quasi-statically only if the difference between the **external** (applied) pressure  $P_{\text{ext}}$  remains arbitrarily close to the **internal** pressure of the system, which we denote by  $P$ . Unless otherwise stated, we shall assume that there are no frictional effects. Thus for a **quasi-static** process, we can calculate the work done in terms of system state variables only, and we obtain

$$\Delta W = -P \Delta V. \quad (1.11)$$

By integration, the work done during a quasi-static process which takes a system from state  $a$  to state  $b$  is given by

$$W_{ab} = - \int_a^b P \, dV. \quad (1.12)$$

As an example of quasi-static work, consider a gas which is kept in thermal contact with a heat bath at temperature  $T$ . If the pressure on the gas is reduced gradually in such a way so as to keep  $PV$  constant, so that the gas is always in equilibrium with the heat bath, the work done on the gas in changing the volume from  $V_a$  to  $V_b$  is

$$W_{ab} = - \int_a^b P \, dV = - \int_a^b \frac{NkT}{V} \, dV = NkT \log \left( \frac{V_a}{V_b} \right) \quad (1.13)$$

As an example of non quasi-static work, we can consider changing the external pressure suddenly so that it is not equal to the internal pressure. The system goes through non-equilibrium states before coming to a final equilibrium state. During the process, the system pressure will in general be spatially varying and it is not possible to plot a smooth path between the initial and final states. The work done is not given by (1.12) as the pressure may not even be defined along the path. As another example of non quasi-static work, consider the process of stirring a fluid. The system is never in equilibrium while the stirring occurs, and if the stirring process is slowed down, the amount of work done is also reduced correspondingly.

In order to have quasi-static heat transfer, the system must be brought into contact with another body or a heat bath whose temperature is only infinitesimally different from the temperature of the system. As an example of non quasi-static heat flow, we need only consider bringing two bodies initially at different temperatures into thermal contact. During the process of energy transfer, the composite system is not close to an equilibrium state.

A process is said to be **reversible** if its direction can be reversed by making an infinitesimal change in the applied conditions. Reversible processes are necessarily **quasi-static** and exhibit no **hysteresis**.

### 1.4.1 The ratio of heat capacities

We have defined  $C_V$  to be the heat capacity of a material at constant **volume**. i.e.,

$$C_V = \left( \frac{dQ}{dT} \right)_V = \left( \frac{dE}{dT} \right)_V \quad (1.14)$$

since no work is done on the material if it is maintained at constant volume. Similarly, we define  $C_P$  to be the heat capacity of a material at constant **pressure**. i.e.,

$$C_P = \left( \frac{dQ}{dT} \right)_P \quad (1.15)$$

An interesting relationship holds between  $C_V$  and  $C_P$  for the case of an ideal gas. As we change the temperature of the gas and keep the pressure constant, the volume must change. From the ideal gas law,  $PV = NkT$ , we see that

$$V = \frac{NkT}{P}, \quad (1.16)$$

and so changing the temperature by  $dT$  while keeping  $P$  fixed results in a volume change

$$dV = \frac{Nk}{P} dT. \quad (1.17)$$

If we do this change quasi-statically, the work done on the gas is

$$W = -PdV = -Nk dT \quad (1.18)$$

By Joule's law, we know that the effect of changing the temperature by  $dT$  is to change the internal energy by

$$dE = C_V dT \quad (1.19)$$

Using the first law of thermodynamics, we find the heat input to be

$$\begin{aligned} dQ &= dE - dW \\ &= C_V dT + Nk dT = (C_V + Nk) dT \end{aligned} \quad (1.20)$$

Remembering that this process is being carried out at constant pressure, we see that

$$C_P = C_V + Nk \quad (1.21)$$

for an ideal gas.

The **ratio** of heat capacities  $C_P/C_V$  is also an important quantity. It is usually denoted by  $\gamma$  and for an ideal gas, we see that

$$\gamma = \frac{C_P}{C_V} = 1 + \frac{Nk}{C_V} \quad (1.22)$$

For a **monatomic** ideal gas, we found earlier that  $C_V = \frac{3}{2}Nk$  and so for a monatomic ideal gas,  $\gamma = \frac{5}{3}$ .

### 1.4.2 The special role of reversible processes

Suppose that we have a vertical cylinder containing some gas which is thermally insulated from its surroundings. A frictionless piston exerts a pressure  $P_a$  on the gas. If we reduce the pressure exerted by on the gas to  $P_b$ , the gas will expand, and in this process will do some work. We want to try to maximize the amount of work that the gas does by carefully examining the different ways in which can reduce the pressure from  $P_a$  to  $P_b$ . Let us suppose that the initial temperature of the gas is  $T_a$  and that there are  $N$  molecules, so that the initial volume is

$$V_a = \frac{NkT_a}{P_a}. \quad (1.23)$$

First let us suppose that we suddenly reduce the pressure from  $P_a$  to  $P_b$ . For example, suppose that  $P_b$  is the pressure that the piston exerts on the gas due to its own weight, and that initially there is an additional weight sitting on top of the piston which increases the pressure to  $P_a$ . In this first scheme, we consider flicking the additional weight off the piston (horizontally so that it comes to rest onto an adjacent shelf, with no work being done). Clearly the gas is going to expand and the piston is going to rise, possibly oscillating a few times before coming to a new equilibrium position. Where is this new equilibrium position going to be? Since no heat flow occurs (such a process is said to be **adiabatic**),  $\Delta E = W$  where  $W$  is the work done **on** the gas which is negative in this case. By Joule's law, this means that the temperature of the gas is going to fall, and

$$C_V \Delta T = W \quad (1.24)$$

The work done by the gas  $-W$  serves to change the potential energy of the piston. If the piston rises by height  $h$  during the expansion of the gas, the change in the potential energy is equal to the weight of the piston  $w$  multiplied by  $h$ . i.e.,

$$-W = wh = (w/A)(Ah) \quad (1.25)$$

where  $A$  is the area of the cylinder. Identifying  $w/A$  as the pressure exerted by the piston  $P_b$  and  $Ah$  as the change in volume  $\Delta V$ , we see that

$$-W = P_b \Delta V. \quad (1.26)$$

After the expansion, the ideal gas law states that

$$P_b (V_a + \Delta V) = Nk (T_a + \Delta T) \quad (1.27)$$

Solving (1.23) for  $T_a$ , (1.24) for  $\Delta T$  and (1.26) for  $\Delta V$ , and substituting these into (1.27) yields

$$P_b \left( V_a - \frac{W}{P_b} \right) = Nk \left( \frac{P_a V_a}{Nk} + \frac{W}{C_V} \right). \quad (1.28)$$

Hence

$$-W = \left( \frac{C_V}{C_V + Nk} \right) (P_a - P_b) V_a \quad (1.29)$$

and using (1.26),

$$\Delta V = \left( \frac{C_V}{C_V + Nk} \right) \left( \frac{P_a}{P_b} - 1 \right) V_a \quad (1.30)$$

Let us now suppose that instead of reducing the pressure suddenly from  $P_a$  to  $P_b$ , we do the process in two halves. We imagine that the weight on the piston is divided into two, and on the first step, only one of these is flicked (horizontally) off the piston. This reduces the pressure from  $P_0 = P_a$  to  $P_1 = \frac{1}{2}(P_a + P_b)$ . By the above argument the work done by the gas in this step is

$$-W_1 = \left( \frac{C_V}{C_V + Nk} \right) (P_0 - P_1) V_0 \quad (1.31)$$

where  $V_0 = V_a$ , and the volume after this first step is

$$V_1 = V_0 + \left( \frac{C_V}{C_V + Nk} \right) \left( \frac{P_0}{P_1} - 1 \right) V_0. \quad (1.32)$$

On the second step, the remaining weight is flicked off the piston. The pressure falls from  $P_1$  to  $P_2 = P_b$ , and the work done is

$$-W_2 = \left( \frac{C_V}{C_V + Nk} \right) (P_1 - P_2) V_1 \quad (1.33)$$

The total work done is

$$\begin{aligned} -W_1 - W_2 &= \left( \frac{C_V}{C_V + Nk} \right) (P_0 V_0 - P_1 V_0 + P_1 V_1 - P_2 V_1) \\ &= \left( \frac{C_V}{C_V + Nk} \right) [(P_0 - P_2) V_0 + (P_1 - P_2) (V_1 - V_0)] \end{aligned} \quad (1.34)$$

Now, from (1.29) and the definitions  $P_0 = P_a$ ,  $P_2 = P_b$  and  $V_0 = V_a$ , the work done when the pressure is reduced in one step is

$$-W = \left( \frac{C_V}{C_V + Nk} \right) (P_0 - P_2) V_0$$

Since  $P_0 > P_1 > P_2$  and  $V_0 < V_1 < V_2$ , the additional term  $(P_1 - P_2)(V_1 - V_0)$  in (1.34) is positive and so the work done **by** the gas when the pressure is reduced in two steps is **greater** than when the reduction occurs in one step.

We can continue this argument, carrying out the pressure reduction in more and more steps. As we do this, we find that the amount of work done **by** the gas gets greater and greater. The maximum amount of work is done when the pressure reduction is gradual, proceeding in infinitesimal steps.

Let us consider what happens in the limiting situation when the pressure reduction occurs gradually. Instead of considering weights on top of the piston, we imagine there to be a pile of sand which can be flicked off a grain at a time. At each stage, the pressure exerted by the sand and the piston is equal to the pressure inside the gas, and the removal of one grain of sand causes only a very small pressure change, so that the system remains close to equilibrium at all times. This equality of applied and internal pressures makes it possible to write the incremental quasi-static work done **on** the gas by the applied pressure as  $-PdV$ , even though  $P$  is the pressure of the **gas**. We see that the work done **by** the gas  $-W$  is maximized when the work is done quasi-statically. For any other process,

$$-dW_{\text{non q-s}} < -dW_{\text{q-s}}$$

or

$$dW_{\text{non q-s}} > dW_{\text{q-s}} = -P \Delta V. \quad (1.35)$$

If we consider adiabatic **compression** of a gas rather than expansion, we find that the work done **on** the gas is **minimized** when the work is performed quasi-statically. Thus the result (1.35) holds for both expansion and compression.

An easy way to remember this result is to remember that  $dW = -P_{\text{ext}}dV$  is always true whether or not the process is quasi-static. In order to **expand** a gas non quasi-statically,  $dV > 0$  and  $P_{\text{ext}} < P$ . Hence

$$dW_{\text{non q-s}} = -P_{\text{ext}}dV > -PdV = dW_{\text{q-s}} \quad (1.36)$$

On the other hand, to **compress** a gas non quasi-statically,  $dV < 0$  and  $P_{\text{ext}} > P$  so that the **same** inequality applies.

In the above example, it is easy to see that the strategy of removing the weight from the piston in infinitesimal steps is **reversible**, since we can re-compress the gas to its original state by simply replacing the weights gradually, each weight being replaced at the same height as that at which it was removed. On the other hand, when a single finite weight is removed suddenly, this is **irreversible** since we need to lift the weight up by a finite amount in order to replace it on top of the piston, and even after the system comes to equilibrium, the state is different from the initial state.

In the absence of friction and hysteresis, quasi-static processes are **reversible**. Reversibility is a useful theoretical idealization, and all real processes are to some extent irreversible. With friction, even quasi-static processes can be irreversible, as the external and internal pressures are no longer equal, but differ by the frictional force. We shall usually be ignoring frictional effects, and so shall use the terms reversible and quasi-static essentially interchangeably.

### 1.4.3 Reversible adiabatic processes in an ideal gas

Let us suppose that a fixed amount of an ideal gas is placed in a thermally insulated vessel, and the pressure on the gas is changed slowly so that all changes occur reversibly. We wish to find the law which connects pressure  $P$  and volume  $V$  under these circumstances.

Suppose that we change the volume reversibly by  $dV$ . The work done on the gas is  $-PdV$ . Since no heat enters the gas, the change in the internal energy of the gas is also given by  $dE = -PdV$ . By Joule's law, the temperature of the gas will change by

$$dT = \frac{dE}{C_V} = -\frac{PdV}{C_V}. \quad (1.37)$$

How does the pressure change? By the ideal gas law, we have

$$P = \frac{NkT}{V}.$$

In the reversible adiabatic process, **both**  $T$  and  $V$  change, and so we need to consider the dependence of  $P$  on both of these variables. Using Taylor's theorem,

$$\begin{aligned} dP &= \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV \\ &= \frac{Nk}{V} dT - \frac{NkT}{V^2} dV \end{aligned} \quad (1.38)$$

Substituting for  $dT$  from (1.37) we see that the change of volume  $dV$  leads to a change in pressure

$$dP = -\frac{Nk}{V} \frac{P}{C_V} dV - \frac{NkT}{V^2} dV \quad (1.39)$$

Eliminating  $T$  by using the ideal gas law, we see that

$$\frac{dP}{P} = -\left(1 + \frac{Nk}{C_V}\right) \frac{dV}{V} = -\gamma \frac{dV}{V} \quad (1.40)$$

Integrating this equation yields

$$\log P = -\gamma \log V + c \quad (1.41)$$

where  $c$  is the constant of integration. Rearranging this gives

$$PV^\gamma = \text{constant}. \quad (1.42)$$

Using the ideal gas law, this rule for reversible adiabatic processes in a fixed mass of gas may be alternatively written as

$$TV^{\gamma-1} = \text{constant} \quad (1.43)$$

or as

$$T^\gamma P^{1-\gamma} = \text{constant} \quad (1.44)$$

## 1.5 Second Law of Thermodynamics

The first law of thermodynamics is a statement of conservation of energy. A process which violates the first law **cannot** take place. On the other hand, even if a process obeys the first law, it is still not the case that the process must be a possible one. For example, when a hot body and cold body are placed in thermal contact, heat flows from the hot body to the cold body and the temperatures equalize. The reverse process, in which we start with two bodies at equal temperatures and end up with bodies at unequal temperatures due to a heat flow from one body to the other certainly conserves energy, but is never observed to occur **spontaneously**. As another example, a gas which is initially confined to one half of a box will spontaneously expand to fill the whole box, but the reverse process is never observed to occur spontaneously. The second law of thermodynamics tells us about the **direction** that a **spontaneous** process which obeys the first law can take.

We wish to formulate a **quantitative** statement of the second law. For example if someone claimed to have invented a device which would take a stream of compressed air at pressure of 400 kPa and temperature 20° C and spontaneously produce two equal streams at 100 kPa, one with temperature -15° C and the other at 55° C, could we determine whether such a device is possible or not? Such are the types of questions that the second law can help us to answer.

The statement of the second law which we wish to arrive at makes use of the concept of **entropy**, which is also a **state variable** of a system. This means that for any **equilibrium** state, a system has an entropy,

just as it has a pressure, temperature or internal energy. Given two equilibrium states of a system, labelled  $a$  and  $b$ , we know that we can get from  $a$  to  $b$  in many ways. Even if we insist that the process be carried out **reversibly** so that all the intermediate states are known, it is still possible to carry out different combinations of heat and work input in order to achieve the same change of state. According to the first law of thermodynamics, however, we know that if we add together the work done on the system  $W$  and the heat input  $Q$ , for any path between the two states, we always get the **same result**, since  $W + Q = E_b - E_a$ , and the internal energy  $E$  is a **state variable**.

Let us consider a particular reversible path from  $a$  to  $b$  which passes through intermediate (equilibrium) states  $s_0 = a, s_1, s_2, \dots, s_N = b$ . For a truly reversible process,  $N$  is infinite, but we can get arbitrarily close to this by considering take  $N$  to be large but finite. Let us suppose that the temperature when the system is in state  $s_i$  is  $T_i$  and that  $Q_i$  is the heat introduced into the system to bring it from state  $s_{i-1}$  to  $s_i$ . It is found experimentally that if we compute

$$\sum_{i=1}^N \frac{Q_i}{T_i} \rightarrow \int_a^b \frac{dQ}{T} \quad (1.45)$$

this quantity depends only on the initial and final states  $a$  and  $b$  and **not** on the **reversible** process by which we connected them. This path independence means that we can define this integral to be the difference between the values of a state function at the endpoints. This state function is the **entropy**, and we write

$$\Delta S_{ab} = S_b - S_a = \int_a^b \frac{dQ}{T} \quad (1.46)$$

which holds for a **reversible** change of state.

Let us now check that this integral really is dependent only on the endpoints for the special case of an ideal gas. It is important to note, however that it is an experimental fact that the entropy is a state function in general, **not** only for the case of an ideal gas.

For  $N$  molecules of an ideal gas, we can use the first law of thermodynamics and Joule's law to find the heat flow into the gas

$$dQ = dE - dW = Nc_V dT - dW. \quad (1.47)$$

For a **reversible process**, we can write

$$dW = -PdV = -\frac{NkT}{V} dV \quad (1.48)$$

and so

$$dQ = Nc_V dT + \frac{NkT}{V} dV. \quad (1.49)$$

This tells us how to calculate the amount of heat entering the gas when the volume is changed by  $dV$  and the temperature by  $dT$ . You will often read that  $dQ$  is **not** an **exact differential** because  $Q$  is not a state variable. What does this mean? Well, were  $Q$  to be a state variable, it would be a function of the independent variables  $T$  and  $V$  (since we are considering a fixed mass of gas,  $N$  is constant). If we change  $T$  and  $V$  by incremental amounts  $dT$  and  $dV$ , we would expect that

$$dQ = \left( \frac{\partial Q}{\partial T} \right)_V dT + \left( \frac{\partial Q}{\partial V} \right)_T dV \quad (1.50)$$

Comparing this with (1.49), we try to identify

$$\left( \frac{\partial Q}{\partial T} \right)_V = Nc_V \quad \text{and} \quad \left( \frac{\partial Q}{\partial V} \right)_T = \frac{NkT}{V} \quad (1.51)$$

A moment's thought shows that this cannot be true, since the mixed partial derivatives should be equal, i.e., we should have

$$\frac{\partial^2 Q}{\partial V \partial T} = \frac{\partial^2 Q}{\partial T \partial V} \quad (1.52)$$

but with the identification above,

$$\frac{\partial}{\partial V} \left( \frac{\partial Q}{\partial T} \right) = 0 \neq \frac{Nk}{V} = \frac{\partial}{\partial T} \left( \frac{\partial Q}{\partial V} \right). \quad (1.53)$$

This is how the mathematics tells us that  $Q$  is not well-determined by  $T$  and  $V$ , i.e., that  $Q$  cannot be a state variable.

Let us return to (1.49) and play a trick. We divide throughout by  $T$  to obtain

$$\frac{dQ}{T} = \frac{Nc_V}{T} dT + \frac{Nk}{V} dV \quad (1.54)$$

Is it possible that we have turned the left-hand side into an exact differential? Let us tentatively write  $dS = dQ/T$ , and see if it is all right for us to identify

$$\left( \frac{\partial S}{\partial T} \right)_V = \frac{Nc_V}{T} \quad \text{and} \quad \left( \frac{\partial S}{\partial V} \right)_T = \frac{Nk}{V}. \quad (1.55)$$

This time, when we compute the mixed partials, we find that

$$\frac{\partial^2 S}{\partial V \partial T} = 0 = \frac{\partial^2 S}{\partial T \partial V}, \quad (1.56)$$

and so we are in good shape. This means that  $S$  **can** be regarded as a function of  $V$  and  $T$ , and we can integrate the equations (1.55) directly to obtain

$$S = Nc_V \log T + Nk \log V + \text{constant}, \quad (1.57)$$

where, of course,  $\log$  means the natural logarithm. We need to be careful about the constant of integration, because all we know is that it cannot depend on  $T$  or on  $V$  (as this would affect the partial derivatives). It is still possible that the “constant” depends on  $N$ , as in fact it does.

In order to find the dependence on  $N$ , we make use of the fact that  $S$  is an **extensive quantity**. What this means is that if we double the amount of substance in a system, some quantities remain unchanged (such as the temperature, the pressure or the density), while others (such as the volume, the internal energy or the mass) are doubled. Quantities of the former class are called **intensive** while those of the latter class are called **extensive**. Since  $dS = dQ/T$ , and since doubling the amount of substance doubles  $dQ$  but keeps  $T$  fixed, we see that  $dS$  must be doubled.

Let us express the fact that  $S$  is an extensive variable mathematically. If we believe that  $S(T, V, N)$  is the correct functional form for  $S$ , the effect of replacing  $V$  by  $\lambda V$  and  $N$  by  $\lambda N$  must be to give  $\lambda$  times the original value of  $S$ , i.e.,

$$S(T, \lambda V, \lambda N) = \lambda S(T, V, N) \quad (1.58)$$

Returning to (1.57), let us write the constant as  $c(N)$  to indicate its (possible) dependence on  $N$ . Thus we have

$$S(T, V, N) = Nc_V \log T + Nk \log V + c(N) \quad (1.59)$$

and so the condition (1.58) becomes

$$\lambda Nc_V \log T + \lambda Nk \log \lambda V + c(\lambda N) = \lambda [Nc_V \log T + Nk \log V + c(N)] \quad (1.60)$$

which simplifies to

$$\lambda Nk \log \lambda + c(\lambda N) = \lambda c(N). \quad (1.61)$$

The aim of the exercise is to find out how  $c$  depends on its argument. The above equation is true for all values of  $\lambda$  and  $N$ , and so, in particular, we may substitute  $N = 1$  to obtain

$$c(\lambda) = \lambda c(1) - \lambda k \log \lambda \quad (1.62)$$

We now relabel  $\lambda$  as  $N$  to obtain

$$c(N) = N (\text{constant} - k \log N) \quad (1.63)$$

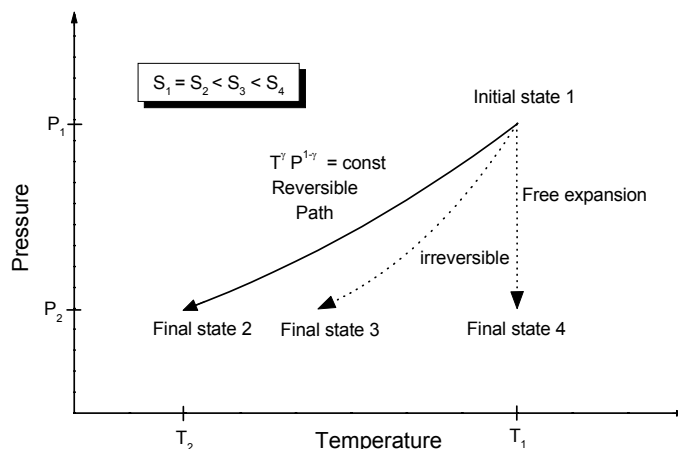


Figure 1.1 Reversible and irreversible expansion of a gas

where the new constant is  $c(1)$ , a quantity which is independent of  $N$  (and also independent of  $T$  and  $V$ ). Substituting into (1.59) gives

$$S(T, V, N) = Nk \left( \frac{c_V}{k} \log T + \log V - \log N + \text{constant} \right) \quad (1.64)$$

which is our expression for the entropy of an ideal gas. Later in the course, we shall rederive this using statistical mechanics and work out the value of the remaining constant, which turns out to depend on Planck's constant, and so requires quantum mechanics for its derivation.

**Exercise:** For a **monatomic** ideal gas, rewrite  $S$  as a function of  $E$ ,  $V$  and  $N$  and verify that

$$S(E, V, N) = Nk \left[ \log \left( \frac{E^{3/2} V}{N^{5/2}} \right) + \text{constant} \right] \quad (1.65)$$

### 1.5.1 Increase of entropy for irreversible processes

Let us first consider **adiabatic processes** for which the heat input is zero. For a **reversible** process,

$$dQ = TdS \quad (1.66)$$

and so we see that  $dS = 0$ . i.e., the entropy of a system which undergoes a reversible, adiabatic process remains **unchanged**.

Suppose that we start with a thermally isolated ideal gas at a given temperature  $T_1$  and pressure  $P_1$  and reduce the pressure to  $P_2$  reversibly so that the gas expands adiabatically. For an ideal gas, equation (1.44) shows us that the path taken during the expansion is given by

$$T^\gamma P^{1-\gamma} = T_1^\gamma P_1^{1-\gamma} \quad (1.67)$$

We may show this path on the  $PT$  plane by the solid line in Figure 1.1. The starting state is labelled 1 and the ending state is labelled 2. As stated above, this line is a line of **constant entropy** and so the process is also said to be **isentropic**.

Now let us consider a **irreversible** adiabatic expansion. Since the process is irreversible, we cannot plot a path in the  $PT$  plane (since the values of  $P$  and  $T$  are not well-defined throughout the path). All we know is that the final state 3 lies somewhere on the line  $P = P_2$ .

We now use the principle that the work done **by** the system is greatest for a reversible process. For the irreversible process, the work done **on** the system satisfies  $dW_{\text{irrev}} > dW_{\text{rev}}$ . Since  $dQ = 0$  in both cases, the change in energy is  $\Delta E = dW$ . Thus

$$E_3 - E_1 = dW_{\text{irrev}} > dW_{\text{rev}} = E_2 - E_1 \quad (1.68)$$

and so

$$E_3 > E_2. \quad (1.69)$$

In order to take the system from state 3 to state 2, we need to **remove** energy at constant pressure. This means that the temperature  $T_3$  must exceed  $T_2$ . If we take the system reversibly from state 3 to state 2, the heat that we have to **introduce** along the path is  $\Delta Q = T\Delta S$ . Since  $\Delta Q < 0$ , this means that the entropy **falls** as we go from 3 to 2, or

$$S_3 > S_2. \quad (1.70)$$

Thus in this example, the entropy of a thermally isolated system **increases** for an irreversible process. This means that for any real process, the state 3 lies to the right of the state 2 in the  $PT$  diagram. In particular, for a free expansion into a vacuum, no work is done, there is no change of temperature and the state 4 is directly below state 1.

Similarly, for adiabatic compression, the reversible process lies on the line of constant entropy, and it can be shown from the principle that the reversible work done on the system is a minimum that all irreversible processes lead to an increase in entropy.

Although we have demonstrated the result only for one specific instance, the second law of thermodynamics asserts that in **any** process the entropy of a **thermally isolated** system satisfies  $\Delta S \geq 0$ , with equality only if the process is reversible. This is not provable, but no exceptions are known. In particular for a completely isolated system in which no heat flow occurs and no work is done, the entropy cannot decrease in a spontaneous process.

### Example

Let us return to the device which supposedly takes a stream of compressed air at room temperature and produces two equal low pressure streams, one hot and the other cold. Since the rise of temperature for one stream is equal to the fall of temperature in the other, it is easy to see that energy is conserved if no heat enters or leaves the system. We now need to check the change of entropy of the air between input and output.

We can check that the change in entropy as the air passes from the input to the output is non-decreasing. Suppose we consider an interval of time in which  $N$  molecules of air have entered the device, producing  $N/2$  molecules in each of the outputs. The expression (1.64) for the entropy is expressed in terms of  $T, V$  and  $N$ , whereas for this problem, it is more convenient to consider  $T, P$  and  $N$ . Substituting  $V = NkT/P$  from the ideal gas law, we obtain

$$S(T, P, N) = Nk \left( \frac{c_P}{k} \log T - \log P + \text{constant} \right) \quad (1.71)$$

where we have used  $c_P = c_V + k$ . and for air,  $c_P \approx 3.5k$ . At the input, we have  $T = 293 \text{ K}$  and  $P = 4 \times 10^5 \text{ Pa}$ , so that

$$S_{\text{in}} = Nk (3.5 \log 293 - \log 4 \times 10^5 + \text{constant}) \quad (1.72)$$

At the low temperature outlet,  $T = 258 \text{ K}$  and  $P = 10^5 \text{ Pa}$ ,

$$S_{\text{cold}} = \frac{N}{2}k (3.5 \log 258 - \log 10^5 + \text{constant}) \quad (1.73)$$

and at the high temperature outlet,  $T = 328 \text{ K}$  and  $P = 10^5 \text{ Pa}$ ,

$$S_{\text{hot}} = \frac{N}{2}k (3.5 \log 328 - \log 10^5 + \text{constant}) \quad (1.74)$$

Thus

$$S_{\text{hot}} + S_{\text{cold}} - S_{\text{in}} = 1.36Nk \quad (1.75)$$

which indicates that the entropy **increases** in this device. This indicates that the device does not violate the laws of thermodynamics, and may in fact be possible. This example was taken from *Understanding Thermodynamics* by H.C. van Ness, Dover, New York (1969), in which a practical implementation of such a device (the Hilsch-Ranque vortex tube, which has no moving parts) is described.

## 1.6 The Fundamental Thermodynamic Relation

The differential form of the first law of thermodynamics  $dE = dQ + dW$  is valid for all processes involving systems with fixed particle number. For **reversible** processes, we know that  $dQ = T dS$  and  $dW = -P dV$ . Hence,

$$dE = T dS - P dV \quad (1.76)$$

Although this was derived for reversible processes, the quantities which are involved are all state variables and so the equation is in fact true for **all infinitesimal** changes between two **equilibrium states**. It is called the **fundamental thermodynamic relation**.

**Example:** As an example of an application of the fundamental relation, consider the situation in which an ideal gas expands adiabatically and freely from volume  $V$  to volume  $V+dV$ . (e.g., by breaking a partition in a vessel) Note carefully that although this expansion may be infinitesimal, it is still **irreversible**, since the gas cannot be restored to its original state by reconstructing the partition. As we have seen, during such free expansion, both the work done  $dW$  on, and the heat input  $dQ$  into the gas are zero. By the first law, the change in the internal energy  $dE = 0$ , and so the temperature remains constant for an ideal gas.

Even though  $dQ = 0$ , we **cannot use**  $TdS = dQ$  to conclude that the entropy does not change. This is because  $TdS = dQ$  only holds for **reversible** processes. Similarly, it is clearly **not the case** that  $dW = -PdV$  in this situation. Nevertheless, the fundamental thermodynamic relation **does allow** us to write

$$0 = dE = T dS - P dV \quad (1.77)$$

and so

$$dS = \frac{P dV}{T} \quad (1.78)$$

We can use the ideal gas law to eliminate the pressure, thus obtaining

$$dS = \frac{Nk dV}{V} \quad (1.79)$$

as the increase in entropy of during this infinitesimal irreversible process. For a finite free expansion from  $V_a$  to  $V_b$ , we may integrate this result to obtain

$$\Delta S = Nk \log \left( \frac{V_b}{V_a} \right). \quad (1.80)$$

The fundamental relation may be used to place a **lower bound** on the entropy change when an amount of heat  $dQ$  enters a system. By the principle that the work done **by** a system is a **maximum** for a reversible process (so that the work done **on** the system is a **minimum**), we see that for any process we must have

$$dW \geq dW_{\text{rev}} = -PdV = dE - T dS \quad (1.81)$$

where equality holds for reversible processes. Since

$$dQ = dE - dW \quad (1.82)$$

we see that in general,

$$dQ \leq T dS \quad (1.83)$$

where once again, equality holds for reversible processes. This shows that when an amount of heat  $dQ$  is added to a system, the entropy of the system rises by **at least**  $dQ/T$ . This minimum increase occurs if the process is reversible. For any real process, the change in entropy is **greater** than this.

The importance of the fundamental thermodynamic relationship is the way it relates together the state variables of a system. From the fundamental relation (1.76) and Taylor's theorem, we see that

$$T = \left( \frac{\partial E}{\partial S} \right)_V \quad \text{and} \quad P = - \left( \frac{\partial E}{\partial V} \right)_S \quad (1.84)$$

If we can write  $E$  for a system consisting of a fixed number of particles as a function of  $S$  and  $V$ , we can derive **all** the state variables of the system in terms of the partial derivatives of  $E$  with respect to  $S$  and  $V$ . For example, we can invert the equation for the entropy of the monatomic ideal gas (1.65) to give

$$E(S, V) = \left(\frac{N^5}{V^2}\right)^{1/3} \exp\left[\frac{2S}{3Nk} - \text{constant}\right] \quad (1.85)$$

Then by calculating the partial derivatives and relating them to  $T$  and  $P$  as above, make sure that you can recover Joule's law and the ideal gas law. Everything we know about the thermodynamics of the monatomic gas is contained in the single function  $E(S, V)$ . This result remains true for more general systems and is the basis of **Gibbs' formulation of thermodynamics**. One of the goals of statistical mechanics is to calculate functions such as  $E(S, V)$  (and its generalizations) for a variety of systems from first principles so that the machinery of classical thermodynamics may then be applied to derive their properties.

From the equality of the mixed partials, we obtain one of Maxwell's relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V. \quad (1.86)$$

### Example

Write the thermal expansion coefficient of a substance

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad (1.87)$$

in terms of  $E(S, V)$  and its derivatives.

### Solution

We first consider how  $T$  changes for a small change in the independent variables  $S$  and  $V$ . Since

$$T = \left(\frac{\partial E}{\partial S}\right)_V \quad (1.88)$$

we see that

$$dT = \left(\frac{\partial^2 E}{\partial S^2}\right) dS + \left(\frac{\partial^2 E}{\partial V \partial S}\right) dV. \quad (1.89)$$

Similarly, since we wish to keep the pressure constant, we consider how  $P$  changes for a small change in  $S$  and  $V$ . Since

$$P = -\left(\frac{\partial E}{\partial V}\right)_S \quad (1.90)$$

we see that

$$dP = -\left(\frac{\partial^2 E}{\partial S \partial V}\right) dS - \left(\frac{\partial^2 E}{\partial V^2}\right) dV \quad (1.91)$$

In order to keep the pressure constant, we must adjust  $dS$  and  $dV$  in such a way as to make  $dP$  vanish. Hence

$$dS = -\frac{\left(\frac{\partial^2 E}{\partial V^2}\right)}{\left(\frac{\partial^2 E}{\partial S \partial V}\right)} dV \quad (1.92)$$

So for a change at constant pressure, we can substitute this into (1.89) and see that

$$dT = \left[ -\frac{\left(\frac{\partial^2 E}{\partial S^2}\right) \left(\frac{\partial^2 E}{\partial V^2}\right)}{\left(\frac{\partial^2 E}{\partial S \partial V}\right)} + \left(\frac{\partial^2 E}{\partial V \partial S}\right) \right] dV \quad (1.93)$$

and so

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V} \left[ \frac{\left(\frac{\partial^2 E}{\partial S \partial V}\right)}{\left(\frac{\partial^2 E}{\partial V \partial S}\right)^2 - \left(\frac{\partial^2 E}{\partial S^2}\right) \left(\frac{\partial^2 E}{\partial V^2}\right)} \right] \quad (1.94)$$

You may wish to verify that this evaluates to  $1/T$  for the monatomic ideal gas. Of course the formula given is also applicable for non-ideal gases, liquids and solids. This example illustrates how we can find arbitrary state functions given  $E(S, V)$ .

### 1.6.1 The Entropy Representation

There is nothing particularly special about using  $E$  as the dependent variable. We could, for instance, rewrite the fundamental relation as

$$dS = \frac{1}{T} dE + \frac{P}{T} dV \quad (1.95)$$

We now see that the natural independent variables for writing the entropy  $S$  (for a system consisting of a fixed number of particles) are  $E$  and  $V$ . Once we are given  $S(E, V)$ , we can find out all the thermodynamic quantities in a manner completely analogous to the above. By Taylor's theorem in this case, we see that

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_V \quad \text{and} \quad \frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_E \quad (1.96)$$

For the monatomic ideal gas,  $S(E, V)$  for fixed  $N$  is given by (1.65). Check that you can obtain Joule's law and the ideal gas law from this function by differentiation.

### 1.6.2 Processes in Isolated Systems

Thermodynamics is mainly concerned with **equilibrium** states of systems. Corresponding to each set of values for the state variables (e.g. for a specified energy and volume of an ideal gas), there is a particular equilibrium state which the system will relax towards in the steady-state. The values of state variables for a system are usually determined by the **constraints** which are imposed on the system. For example, a gas has a certain volume because it is constrained to be in a vessel of a particular size, and a certain definite energy because it is constrained so that it cannot exchange heat or work with its surroundings.

In a more complicated situation, a (thermally and mechanically) isolated system at equilibrium may consist of two parts, one with energy  $E_1^{(0)}$  and volume  $V_1^{(0)}$  and the other with energy  $E_2^{(0)}$  and volume  $V_2^{(0)}$ . If these two parts are initially isolated from each other, there are effectively **four** constraints which maintain  $E_1$ ,  $V_1$ ,  $E_2$  and  $V_2$  at their initial values.

If the two subsystems are now brought into thermal contact, energy can flow between them. Instead of there being **two** separate constraints on the energies of the parts, we have the **single** constraint that

$$E_1 + E_2 = E_1^{(0)} + E_2^{(0)}. \quad (1.97)$$

The other two constraints  $V_1 = V_1^{(0)}$  and  $V_2 = V_2^{(0)}$  remain unchanged if we assume that volumes of the two parts are constant.

As a result of removing one or more constraints, a **process** can occur (the flow of energy between the parts, in this case), during which the system is no longer in equilibrium. In order to determine what the final condition of the system will be once equilibrium is re-established, we invoke the **principle of maximum entropy** which applies to **isolated** systems. This states that an isolated system reaches equilibrium when its entropy is maximized subject to all the constraints which are imposed upon it. For an isolated system, these constraints usually mean that the **total** volume and **total** energy remain fixed. The removal of constraints means that states of higher entropy are made accessible to the system, and the system spontaneously tends towards the one with the highest entropy which is accessible.

Let us determine how much energy will flow between the two parts when thermal contact is established. Since entropy is an **additive** variable, the entropy of the system is the sum of the entropies of the two parts, i.e.,

$$S_{\text{total}} = S_1(E_1, V_1^{(0)}) + S_2(E_2, V_2^{(0)}) \quad (1.98)$$

We now wish to **maximize**  $S_{\text{total}}$ , subject to the constraint that  $E_1 + E_2$  is a constant, equal to the original total energy. Since  $E_2$  and  $E_1$  are related to each other, the extremum can be found by setting

$$0 = \frac{dS_{\text{total}}}{dE_1} = \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_2} \frac{dE_2}{dE_1} \quad (1.99)$$

$$= \frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \quad (1.100)$$

since  $dE_2/dE_1 = -1$  in order to satisfy the constraint. Using the definition of the temperature in the entropy representation (1.96), the condition for maximum entropy is

$$0 = \frac{1}{T_1} - \frac{1}{T_2} \quad (1.101)$$

or that  $T_1 = T_2$ .

This shows that thermal equilibrium leads to the equalization of the temperatures of the two parts of the system, and that this is a consequence of the principle of maximum entropy. The fact that temperature is a good state variable which allows us to decide when systems are in thermal equilibrium with each other is the subject of the **zeroth law** of thermodynamics, which is usually stated as: “Two systems which are separately in thermal equilibrium with a third are in thermal equilibrium with each other.”

Besides the principle of maximum entropy which gives the ultimate fate of an isolated system when equilibrium is established, it is also found that on the macroscopic scale, the entropy of a system **increases monotonically with time** as it approaches equilibrium. This may be used to determine the **direction** of heat flow when two bodies are brought into thermal contact. Not surprisingly, the conclusion is that heat flows from the body with higher temperature to that with lower temperature.

If we now consider the situation in which both **thermal** and **mechanical** contact are made between the two parts of the system, this leads to the removal of **two** constraints since the original four are replaced by

$$E_1 + E_2 = E_1^{(0)} + E_2^{(0)} \quad (1.102)$$

$$\text{and } V_1 + V_2 = V_1^{(0)} + V_2^{(0)}. \quad (1.103)$$

It is easy to show that (check!) the principle of maximum entropy now states that at equilibrium,

$$T_1 = T_2 \quad \text{and} \quad P_1 = P_2. \quad (1.104)$$

### 1.6.3 Chemical Work

As another example of an application of the principle of maximum entropy, we consider how chemical reactions proceed in an isolated system. If a system consists of a mixture of several chemicals which can react with each other, and there are  $N_1, N_2, \dots$  molecules of each of the substances, we need to include the effects of “chemical work” due to the changing numbers of molecules. For a system in which both mechanical and chemical work can be performed on a system, the work done on the system in a reversible process is

$$dW = -PdV + \mu_1 dN_1 + \mu_2 dN_2 + \dots \quad (1.105)$$

The fundamental relation in the energy representation (which holds for **all** infinitesimal changes, reversible or irreversible) is thus

$$dE = T dS - P dV + \mu_1 dN_1 + \mu_2 dN_2 + \dots \quad (1.106)$$

where

$$\mu_i = \left( \frac{\partial E}{\partial N_i} \right)_{S, V, N_{j \neq i}} \quad (1.107)$$

is called the **chemical potential** of substance  $i$ . In the entropy representation,

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu_1}{T} dN_1 - \frac{\mu_2}{T} dN_2 - \dots \quad (1.108)$$

So that

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V, N_i}, \quad \frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{E, N_i} \quad \text{and} \quad \frac{\mu_i}{T} = - \left( \frac{\partial S}{\partial N_i} \right)_{E, V, N_{j \neq i}}. \quad (1.109)$$

Now consider a thermally isolated system of constant volume so that  $dE = dV = 0$ . Initially, we start with  $N_1^{(0)}, N_2^{(0)}$  and  $N_3^{(0)}$  molecules of the substances  $X_1, X_2$  and  $X_3$ . Suppose that these chemicals participate in the reaction



As the reaction takes place, if  $n$  is the number of  $X_3$  molecules that are formed, we see that

$$N_1 = N_1^{(0)} - 2n \quad (1.111)$$

$$N_2 = N_2^{(0)} - n \quad (1.112)$$

$$N_3 = N_3^{(0)} + n \quad (1.113)$$

By the principle of maximum entropy, the reaction will proceed until  $n$  is such that  $S$  is maximized. This may be found by considering

$$0 = \frac{dS}{dn} = \frac{\partial S}{\partial N_1} \frac{dN_1}{dn} + \frac{\partial S}{\partial N_2} \frac{dN_2}{dn} + \frac{\partial S}{\partial N_3} \frac{dN_3}{dn} \quad (1.114)$$

For this reaction, it is evident that

$$\frac{dN_1}{dn} = -2, \quad \frac{dN_2}{dn} = -1 \quad \text{and} \quad \frac{dN_3}{dn} = +1 \quad (1.115)$$

and so the condition for maximum entropy becomes

$$0 = -2 \frac{\partial S}{\partial N_1} - \frac{\partial S}{\partial N_2} - \frac{\partial S}{\partial N_3} = -2 \frac{\mu_1}{T} - \frac{\mu_2}{T} + \frac{\mu_3}{T}$$

or

$$-2\mu_1 - \mu_2 + \mu_3 = 0 \quad (1.116)$$

where we have used the relations (1.109), and since all species are at the same temperature

We can proceed further if the chemicals may be treated as ideal gasses, since we then have explicit formulae for the chemical potentials. From the expression for the entropy (1.64), Joule's law  $E = Nc_V T$ , and  $\gamma = 1 + \frac{k}{c_V}$  we see that for an ideal gas,

$$S(E, V, N) = \frac{Nk}{\gamma - 1} (\log E - \gamma \log N + (\gamma - 1) \log V + \text{constant}) \quad (1.117)$$

The chemical potential is then

$$\mu = -T \frac{\partial S}{\partial N} = kT \log \left( \frac{N}{V} \right) + f(T)$$

where  $f(T)$  is some function of  $T$ . We may identify  $N/V$  as the **concentration** of the substance, which is usually denoted in chemistry by square brackets around the symbol for the substance. Thus for  $i = 1, 2$  and  $3$ , we have

$$\mu_i = kT \log [X_i] + f_i(T) \quad (1.118)$$

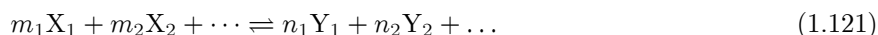
The condition (1.116) thus becomes

$$-2 \log [X_1] - \log [X_2] + \log [X_3] = \frac{2f_1(T) + f_2(T) - f_3(T)}{kT} \quad (1.119)$$

or, on taking exponentials

$$\frac{[X_3]}{[X_1]^2 [X_2]} = K_{\text{eq}}(T) \quad (1.120)$$

where  $K_{\text{eq}} = \exp[(2f_1(T) + f_2(T) - f_3(T)) / (kT)]$  is usually called the **equilibrium constant**. The result that for a reaction at equilibrium,



the concentrations satisfy

$$\frac{[Y_1]^{n_1} [Y_2]^{n_2} \dots}{[X_1]^{m_1} [X_2]^{m_2} \dots} = K_{\text{eq}}(T) \quad (1.122)$$

is called the **law of mass-action** in chemistry, although in practice it is more usual for reactions to take place at constant temperature and pressure rather than in thermal isolation at constant volume.

## 1.7 Clausius' Inequality

We have seen that processes occur when constraints are removed, so that a system moves from an initial state to a final equilibrium states, usually via non-equilibrium states. What do we mean by a **spontaneous** process? For a system isolated from the rest of the universe, this is obvious. A spontaneous process is one which occurs without external influences. A spontaneous process moves a system **towards** equilibrium through non-equilibrium states and is thus **irreversible**. Often however, we do not deal with isolated systems, but ones placed in an environment of constant temperature and/or pressure. We do not wish to regard the heat exchanged with the environment or the work done against the pressure exerted by the environment as being "external influences" when talking about spontaneous changes in these cases. Thus for systems in contact with a specified environment, spontaneous changes actually involve the **environment** as well as the **system**.

There are actually two main questions that we can ask. If we are told that a system moves spontaneously from one state to another, we may wish to work out which state comes first in time. The second question is to determine which equilibrium state a system will ultimately reach from an initial state if it is left alone. Because of our definition of a spontaneous process, the answers to both of these questions depend on the **environment** as well as on the system itself.

From the previous section, we know that if a system is thermally isolated, the direction of any spontaneous process is the direction of **increasing entropy**. If we also insist that the system is maintained at constant volume, no work is done on it. As such a system approaches equilibrium, the **internal energy** is constant and the equilibrium state is that of **maximum entropy**.

We want to consider what happens for systems which are not isolated in this way. In experimental situations, we often consider our systems in contact with a **reservoir** which maintains a constant temperature no matter how much heat is added to or taken from it or with systems which are kept at constant **pressure**.

The trick is to consider a larger composite system consisting of the original system together with the reservoir. The system is placed in contact the reservoir via a diathermal (i.e., heat conducting) and moveable piston. Initially, system and reservoir need not be in equilibrium. The reservoir is chosen to be so large (or have such a large heat capacity) that heat flow does not change its temperature  $T_0$ . Similarly, the volume of the reservoir is taken to be so large that the pressure of the reservoir  $P_0$  is unchanged as the system changes in volume. The system and reservoir together may now be regarded as being an isolated composite system with constant volume and energy.

Applying the entropy principle to the composite system, it is apparent that in any natural process, the **total entropy** must not decrease. Since entropy is **additive**,

$$S_{\text{tot}} = S_{\text{sys}} + S_{\text{res}} \quad (1.123)$$

and so during any process,

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{res}}. \quad (1.124)$$

Let us suppose that during this process, heat  $Q$  **enters** the system and the volume of the system changes by  $\Delta V$ . Since the temperature of the reservoir remains fixed at  $T_0$ ,  $Q$  **leaves** the reservoir, and its change in entropy is

$$\Delta S_{\text{res}} = -\frac{Q}{T_0} \quad (1.125)$$

Note that the reservoir is so large that the change is **reversible** as far as the reservoir is concerned, although it may be irreversible for the system. Since  $\Delta S_{\text{tot}} \geq 0$ ,

$$\Delta S_{\text{sys}} - \frac{Q}{T_0} \geq 0. \quad (1.126)$$

Now by the first law,  $Q = \Delta E - W$  where  $W$  is the work done **on** the system. Since as far as the system is concerned, the **external** pressure is  $P_0$ , the work done is

$$W = -P_0 \Delta V \quad (1.127)$$

and so

$$\Delta S_{\text{sys}} - \frac{\Delta E + P_0 \Delta V}{T_0} \geq 0 \quad (1.128)$$

This is the general form of Clausius' inequality which hold for non-isolated systems. Of course, we may specialize to the case where the system is thermally coupled but is of fixed volume by setting  $\Delta V = 0$  in the above.

We define the **availability** of a **system in its surroundings** by

$$A = E + P_0 V - T_0 S \quad (1.129)$$

Notice that this is a function of **both** the system and surroundings. In terms of  $A$ , Clausius inequality becomes

$$\Delta A \leq 0 \quad (1.130)$$

Note that

- The availability of a system in a given surrounding tends to **decrease during a natural process**, and remains constant for a **reversible process**. Given the initial and final state of the system, we can tell whether the process is possible or not, when the system is in contact with the specified environment. We see that a process is **reversible** provided that the **total** entropy of system and the environment does not change.
- The availability has a **minimum** value when the composite system comes to equilibrium (i.e., when the system and reservoir come into equilibrium). This tells us the final state that the system is tending towards.
- Note that  $T_0$  and  $P_0$  in the formula are the temperature and pressure of the **reservoir**. **During** the process, the temperature and pressure of the system may be undefined and will not in general be equal to those of the reservoir.
- The **change** in  $A$ , namely  $\Delta A$  depends **only** on the initial and final **states**, and **not** on the path taken (which will in general be undefined for irreversible changes).

From the definition of the availability, we see that it is an **extensive, additive** quantity (since each of the energy, volume and entropy have these properties). Although we have emphasized that they are functions of state and so are well-defined for **equilibrium** states of a system, the additivity property means that we can still define the availability, energy, volume and entropy for **composite systems** which consist of several parts each of which is **locally** in equilibrium but which need not be in equilibrium **with each other**. This observation means that it is possible to use the availability to deal with spontaneous processes taking a system from a non-equilibrium state to an equilibrium state, even though at first sight it might appear that the availability is not well defined for a non-equilibrium state. So long that the system in the non-equilibrium state can be split into subsystems for which the availability can be calculated, the **additivity** property allows us to determine the total availability of the non-equilibrium state. (Strictly, this is only possible if the interactions between the subsystems are weak, so that we can add their energies to find the total.)

### Exercise

If two states 1 and 2 of a system in contact with an environment are such that  $A_1 > A_2$ , the system can spontaneously and irreversibly pass from state 1 to state 2. Show that if we attach a device to the system so that it goes **reversibly** from state 1 to state 2 instead, it is possible to extract useful work  $W_u$  from the system (this is in addition to the work done against the environment) where

$$W_u = A_1 - A_2 \quad (1.131)$$

Note that by our usual sign convention, this means that the work done on our system is  $-W_u - P_0 \Delta V$ .  $W_u$  is the **maximum** useful work that can be done **by** the system during this change of state.

## 1.8 Equilibrium and the Thermodynamic Potentials

In order to identify the final state to which a system spontaneously tends towards, it is only necessary to look at **small changes** around the candidate equilibrium state to see if the availability at the equilibrium state is smaller than at all neighbouring states. It is thus useful to look at **differential** relationships involving neighbouring states when trying to identify equilibrium points. By analogy with mechanics, in which equilibrium of a system is found by determining the configuration which minimizes or maximizes the potential energy, the thermodynamic potentials are quantities which are minimized or maximized when a system comes into equilibrium with different types of environment. The thermodynamic potentials are all extensive, additive quantities, so they may be readily computed for some non-equilibrium states of composite systems as well as for the usual equilibrium states.

### 1.8.1 The (Helmholtz) Free Energy

If we consider a system of **fixed volume** in thermal contact with a heat bath at fixed temperature  $T_0$ , the change in availability between a pair of states is given by

$$\Delta A = \Delta E - T_0 \Delta S \quad (1.132)$$

Remember that  $A$  helps us find out the **direction** of a spontaneous (irreversible) process and the state of **equilibrium** when the system is placed in this environment. If we consider the situation when the initial and final states of the system are at the same **temperature** as the environment (the system temperature is allowed to change in between), we may replace  $T_0$  by the temperature of the **system** and consider instead the quantity

$$F = E - TS \quad (1.133)$$

which depends only on the system variables. This is called the (**Helmholtz**) **free energy** of the system. When considering systems in thermal contact with a bath, **minimizing** the free energy (evaluated at the bath temperature) gives us the condition for **equilibrium**. (Naturally,  $T = T_0$  at equilibrium). Like the energy and entropy, the free energy  $F$  is an example of a thermodynamic potential.

What are the natural coordinates for the free energy? Starting with the definition and using the fundamental relation for the energy for a system of fixed particle number,

$$dF = dE - T dS - S dT = -S dT - P dV \quad (1.134)$$

which shows that the natural variables are  $T$  and  $V$ .

More generally, for systems with many components so that chemical work is important, the fundamental relation for the energy is  $dE = TdS - PdV + \mu_1 dN_1 + \mu_2 dN_2 + \dots$ . This leads to the fundamental relation for the free energy in the form

$$dF = -S dT - P dV + \mu_1 dN_1 + \mu_2 dN_2 + \dots \quad (1.135)$$

and we would normally write  $F(T, V, N_1, N_2, \dots)$ .

By Taylor's theorem, we see that for fixed particle number,

$$S = - \left( \frac{\partial F}{\partial T} \right)_V \quad \text{and} \quad P = - \left( \frac{\partial F}{\partial V} \right)_T \quad (1.136)$$

and from the equality of the mixed partial derivatives,

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad (1.137)$$

which is another of Maxwell's relations.

If we find the dependence of  $F$  on  $T$  and  $V$  and  $N_i$ , it is possible to derive **all** the thermodynamic properties of the system, just as if we had the dependence of  $E$  on  $S$  and  $V$  and  $N_i$ . In particular, we can find the energy as a function of  $T$ ,  $V$  and  $N_i$  using

$$\begin{aligned} E &= F + TS = F - T \left( \frac{\partial F}{\partial T} \right)_V \\ &= -T^2 \left[ \frac{\partial}{\partial T} \left( \frac{F}{T} \right) \right]_V. \end{aligned} \quad (1.138)$$

We shall return to this relationship later in connection with statistical mechanics. From the energy, we can find the heat capacity at constant volume using

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = -\frac{\partial}{\partial T} \left\{ T^2 \left[ \frac{\partial}{\partial T} \left( \frac{F}{T} \right) \right] \right\}_V \quad (1.139)$$

### 1.8.2 The Gibbs' Free Energy

We now consider a system in thermal contact with a heat bath at fixed temperature  $T_0$  and at fixed pressure  $P_0$ . These are the conditions under which chemical reactions tend to be conducted. The change in availability between a pair of states is then given by

$$\Delta A = \Delta E - T_0 \Delta S + P_0 \Delta V \quad (1.140)$$

If we consider the situation when the initial and final states of the system are at the same **temperature** and **pressure** as the environment (they may change in between), we may replace  $T_0$  and  $P_0$  by the **system** variables and consider the quantity

$$G = E - TS + PV \quad (1.141)$$

which depends only on the system variables. This is called the **Gibbs' free energy** of the system. When considering systems in thermal and mechanical contact with a bath, **minimizing** the Gibbs' free energy gives us the condition for **equilibrium**. The Gibbs' free energy  $G$  is also a thermodynamic potential. The fundamental relation for the Gibbs' free energy is

$$dG = -S dT + V dP + \mu_1 dN_1 + \mu_2 dN_2 + \dots \quad (1.142)$$

and so the natural variables for  $G$  are  $T$ ,  $P$  and  $N_i$ .

By Taylor's theorem, we see that for fixed particle number

$$S = - \left( \frac{\partial G}{\partial T} \right)_P \quad \text{and} \quad V = \left( \frac{\partial G}{\partial P} \right)_T \quad (1.143)$$

and from the equality of the mixed partial derivatives,

$$\left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P \quad (1.144)$$

which is another of Maxwell's relations.

**Exercise:** For a homogeneous system consisting of one component, use the fact that  $G$  is an extensive quantity, i.e., that for any  $\lambda$ ,

$$G(T, P, \lambda N) = \lambda G(T, P, N) \quad (1.145)$$

to show that  $\mu = G(T, P, 1)$ . We denote the Gibbs' free energy for a single particle by  $g(T, P) \equiv G(T, P, 1)$ .

**Exercise:** Suppose that we have a composite system consisting of two phases of the same material in contact, such as ice and water, maintained at a given temperature  $T_0$  and pressure  $P_0$ . If there are  $N_1$  particles in the first phase and  $N_2$  particles in the second phase, the Gibbs' free energy of the composite system is

$$G(T_0, P_0, N_1, N_2) = G_1(T_0, P_0, N_1) + G_2(T_0, P_0, N_2) \quad (1.146)$$

where  $G_1$  and  $G_2$  are the Gibbs' free energies of each of the two phases taken individually. Using the facts that  $G$  is a minimum at equilibrium, and that  $N_1 + N_2$  is fixed, show that the condition for the phases to be in equilibrium with each other is that

$$g_1(T_0, P_0) = g_2(T_0, P_0) \quad \text{or equivalently, that} \quad \mu_1 = \mu_2. \quad (1.147)$$

### 1.8.3 The Enthalpy

This potential is useful when considering a system which is thermally isolated and maintained at constant pressure. It is defined by

$$H = E + PV \quad (1.148)$$

and so the fundamental thermodynamic relation in terms of  $H$  is

$$\begin{aligned} dH &= dE + PdV + VdP \\ &= T dS + V dP \end{aligned} \quad (1.149)$$

For a **reversible** adiabatic process at constant pressure, the enthalpy is constant. The enthalpy plays much the same role for processes at constant pressure as the internal energy does for processes at constant volume. As a system approaches equilibrium at constant pressure, the **enthalpy** is constant and the equilibrium state is again that of **maximum entropy**.

The natural variables for the enthalpy are the entropy and pressure. We see that for fixed particle number

$$T = \left( \frac{\partial H}{\partial S} \right)_P \quad \text{and} \quad V = \left( \frac{\partial H}{\partial P} \right)_S \quad (1.150)$$

and from the equality of the mixed partial derivatives, we obtain the Maxwell relation

$$\left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P. \quad (1.151)$$

If we consider the heat capacity of a substance at **constant pressure** rather than constant volume, we see that for a reversible process,  $dQ = dE - dW = dE + PdV$ , and so

$$C_P = \left( \frac{dQ}{dT} \right)_P = \left( \frac{dE + PdV}{dT} \right)_P = \left( \frac{\partial H}{\partial T} \right)_P \quad (1.152)$$

Note that the right hand side only involves state functions. This should be compared with the expression  $C_V = (\partial E / \partial T)_V$ . In practice, it is relatively easy to measure  $C_P$  as a function of temperature, and so one can find the enthalpy of a substance (up to an additive constant) by integrating  $C_P(T)$ .

The enthalpy is also useful in the analysis of problems of **steady fluid flow** such as those involving throttles and turbines. Consider a black box which is thermally isolated and within which no work is done. If fluid enters the box at constant pressure  $P_1$  and leaves at constant pressure  $P_2$ , the enthalpy per unit mass of the fluid on each side of the box is the same. If heat is introduced and/or rotating shaft work is done within the black box (i.e., work done without change of volume, such as with a stirrer or a turbine), the change in enthalpy per unit mass is

$$\Delta h = q + w_{rs} \quad (1.153)$$

where  $q$  is the heat input and  $w_{rs}$  is the rotating shaft work per unit mass.

Another application of the enthalpy is to the analysis of heat flow in chemical reactions where the reactants are maintained at constant pressure,  $P$ . If we consider the system to be the reacting chemicals, and if during a reaction the volume of the system changes by  $\Delta V$ , the work done **by** the system is  $P\Delta V$ . The heat input into the system during the reaction is

$$Q = \Delta E + P\Delta V = \Delta H \quad (1.154)$$

since the pressure is constant. Thus the change of **enthalpy** gives the heat of reaction at constant pressure.