

where  $a$ ,  $b$  are constants; the virial equation of state

$$P - \frac{Nk_B T}{V} \left[ 1 + \frac{NB_2(T)}{V} + \frac{N^2 B_3(T)}{V^2} + \dots \right] = 0 \quad (1.3)$$

where the functions  $B_2(T)$ ,  $B_3(T)$  are called virial coefficients; and in the case of a paramagnet, the Curie law,

$$M - \frac{CH}{T} = 0 \quad (1.4)$$

where  $C$  is a constant called the Curie constant. Equations (1.1), (1.2), and (1.4) are approximations, and we shall use them primarily to illustrate various principles. Equation (1.3) is, in principle, exact, but as we shall see in Chapter 4, calculation of more than a few of the virial coefficients is very difficult.

## 1.2 Laws of Thermodynamics

In this section we explore the consequences of the zeroth, first, and second laws of thermodynamics. The zeroth law can be thought of as the statement that matter in equilibrium can be assigned values for the temperature, pressure and chemical potentials, which in principle can be measured. Formally the law can be stated as:

If system  $A$  is in equilibrium with systems  $B$  and  $C$  then  $B$  is in equilibrium with  $C$ .

The zeroth law allows us to introduce universal scales for temperature, pressure etc.

Another way of looking at the zeroth law is through an analogy with mechanics. In equilibrium the forces are balanced. This implies that the intensive variables are constant throughout the system. In particular:

$$\begin{aligned} T &= \text{const.} \rightarrow \text{Thermal equilibrium} \\ P &= \text{const.} \rightarrow \text{Mechanical equilibrium} \\ \mu &= \text{const.} \rightarrow \text{Chemical equilibrium} \end{aligned}$$

As we shall see in the next chapter, the zeroth law has a fairly straightforward statistical interpretation and this will allow us to make contact between the thermodynamic and statistical description.

### 1.2.1 First law

The first law of thermodynamics restates the law of conservation of energy. However, it also partitions the change in energy of a system into two pieces, heat and work:

$$dE = \delta Q - \delta W . \quad (1.5)$$

In (1.5)  $dE$  is the change in internal energy of the system,  $\delta Q$  the amount of heat *added to* the system, and  $\delta W$  the amount of work *done by* the system during an infinitesimal process. Aside from the partitioning of the energy into two parts, the formula distinguishes between the infinitesimals  $dE$  and  $\delta Q$ ,  $\delta W$ . The difference between the two measurable quantities  $\delta Q$  and  $\delta W$  is found to be the same for any process in which the system evolves between two given states, independently of the path. This indicates that  $dE$  is an exact differential or, equivalently, that the internal energy is a state function. The same is not true of the differentials  $\delta Q$  and  $\delta W$ , hence the difference in notation.

Consider a system whose state can be specified by the values of a set of state variables  $x_j$  (e.g., the volume, the number of moles of the different constituents, the magnetization, the electric polarization, etc.) and the temperature. As mentioned earlier, thermodynamics exploits an analogy with mechanics and we write, for the work done during an infinitesimal process,

$$\delta W = - \sum_j X_j dx_j \quad (1.6)$$

where the  $X_j$ 's can be thought of as generalized forces and the  $x_j$ 's as generalized displacements.

Before going on to discuss the second law, we pause to introduce some terminology. A thermodynamic transformation or process is any change in the state variables of the system. A *spontaneous* process is one that takes place without any change in the external constraints on the system, due simply to the internal dynamics of the system. An *adiabatic* process is one in which no heat is exchanged between the system and its surroundings. A process is *isothermal* if the temperature is held fixed, *isobaric* if the pressure is fixed, *isochoric* if the density is constant, and *quasistatic* if the process is infinitely slow. A *reversible* process is by nature quasistatic and follows a path in thermodynamic space which can be exactly reversed. If this is not possible, the process is irreversible. An example of a reversible process is the slow adiabatic expansion of a gas against a piston on which a force is exerted externally. This force is infinitesimally less than  $PA$ , where  $P$  is the pressure of the gas and  $A$  the

area of the piston. An example of an irreversible process is the free adiabatic expansion of a gas into a vacuum. In this case the initial state of the gas can be recovered if one compresses it and removes excess heat. This is, however, not the same thermodynamic path.

### 1.2.2 Second law

The second law of thermodynamics introduces the *entropy*  $S$  as an extensive state variable and states that for an infinitesimal reversible process at temperature  $T$ , the heat given to the system is

$$dQ|_{rev} = TdS \quad (1.7)$$

while for an irreversible process

$$dQ|_{irrev} \leq TdS .$$

If we only are interested in thermodynamic equilibrium states we can use (1.7) and treat the entropy  $S$  as the generalized displacement which is coupled to the 'force'  $T$ . The above formulation of the second law is due to Gibbs.<sup>1</sup>

We present next two equivalent statements of the second law of thermodynamics. The *Kelvin* version is:

There exists no thermodynamic process whose sole effect is to extract a quantity of heat from a system and to convert it entirely to work.

The equivalent statement of *Clausius* is:

No process exists in which the sole effect is that heat flows from a reservoir at a given temperature to a reservoir at a higher temperature.

A corollary of these statements is that the most efficient engine operating between two reservoirs at temperatures  $T_1$  and  $T_2$  is the Carnot engine. The Carnot engine is an idealized engine in which all the steps are reversible. We show the Carnot cycle for an ideal gas working substance in Figure 1.1. In step  $AB$  heat  $Q_1$  is absorbed by the gas, which expands isothermally and does work in the process. The next step,  $BC$ , is adiabatic and further work is done.

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<sup>1</sup>Readers who are interested in the history of thermodynamics will enjoy the article by M. J. Klein [134] on J. Willard Gibbs.

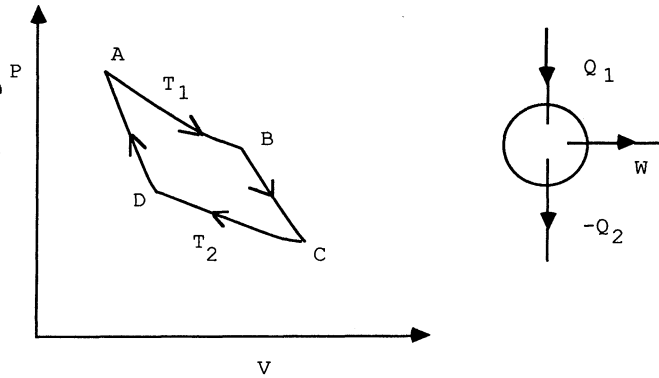


Figure 1.1: Carnot cycle for an ideal gas working substance.

In step  $CD$  heat  $(-Q_2)$  is given off to the low-temperature reservoir and work is done on the gas. Step  $DA$  returns the working substance adiabatically to its original state.

The efficiency,  $\eta$ , of the engine is defined to be the ratio of the total work done in one cycle to the heat absorbed from the high-temperature reservoir:

$$\eta = \frac{W}{Q_1} = \frac{Q_1 + Q_2}{Q_1}. \quad (1.8)$$

In (1.8) we have followed the convention of the first law that heat transfer is positive if added to the working system. Suppose now that a second more efficient engine operates between the same two temperatures. We can use this engine to drive the Carnot engine backwards—since it is reversible,  $Q_1$ ,  $Q_2$ , and  $W$  will simply change sign and  $\eta$  will remain the same.

In Figure 1.2 the Carnot engine is denoted by  $C$ , the other hypothetical engine, with efficiency  $\eta_O > \eta_C$  is denoted by  $O$ . We use all the work done by engine  $O$  to drive engine  $C$ . Let the heat absorbed from the reservoirs be  $Q_{1C}$ ,  $Q_{1O}$ ,  $Q_{2C}$ ,  $Q_{2O}$ . By assumption we have

$$\eta_O = \frac{W}{Q_{1O}} > \frac{-W}{Q_{1C}} = \eta_C. \quad (1.9)$$

The inequality implies that  $|Q_{1C}| > Q_{1O}$  and the net effect of the entire process is to transfer heat from the low-temperature reservoir to the high-temperature reservoir. This violates the Clausius statement of the second law. Similarly, if we take only part of the work output of engine  $O$ , and adjust

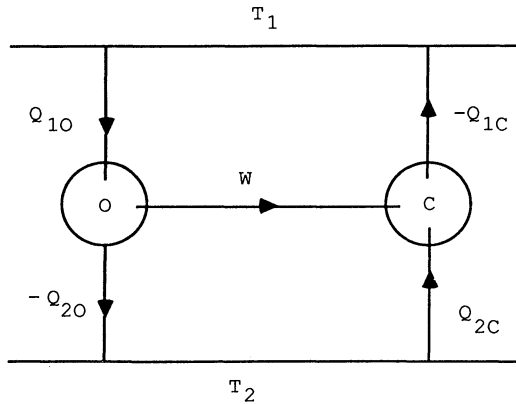


Figure 1.2: Carnot engine (C) driven in reverse by an irreversible engine (O)

it so that there is no net heat transfer to the low-temperature reservoir, a contradiction of the Kelvin statement of the second law results. We conclude that no engine operating between two reservoirs at fixed temperatures is more efficient than a Carnot engine. Equivalently, all reversible engines operating between fixed temperatures have the same efficiency and are Carnot engines. The result that all Carnot engines operating between two temperatures have the same efficiency can be used to define a temperature scale. One possible definition is

$$\frac{T_2}{T_1} = 1 - \eta_C(T_1, T_2) \quad (1.10)$$

where  $\eta_C(T_1, T_2)$  is the Carnot efficiency. Using an ideal gas as a working substance, one can easily show (Problem 1.1) that this temperature scale is identical with the ideal gas (or absolute) temperature scale. Substituting for  $\eta$  in equation (1.8), we have, for a Carnot cycle,

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0. \quad (1.11)$$

With this equation we are in a position to define the entropy. Consider an arbitrary reversible cyclic process such as the one drawn in Figure 1.3. We can cover the region of the  $P - V$  plane, enclosed by the reversible cycle  $R$  in Figure 1.3, with a set of Carnot cycles operating between temperatures arbitrarily close to each other. For each Carnot cycle we have, from (1.11),

$$\sum_i \frac{Q_i}{T_i} = 0. \quad (1.12)$$

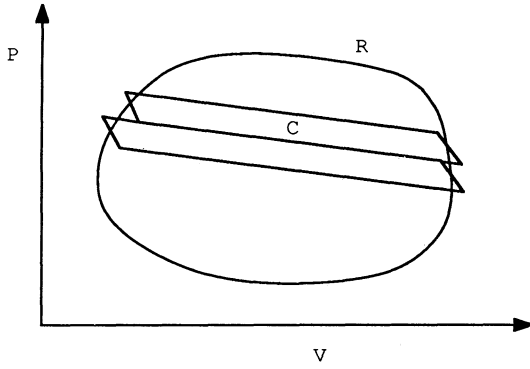


Figure 1.3: Arbitrary reversible process covered by infinitesimal Carnot cycles.

As the number of Carnot cycles goes to infinity, the integral of  $dQ/T$  over the uncompensated segments of these cycles approaches

$$\int_R \frac{dQ}{T} = 0. \quad (1.13)$$

Thus the expression  $dQ/T$  is an exact differential for reversible processes and we define the state function, whose differential it is, to be the entropy  $S$ . For reversible processes the first law can therefore be written in the form

$$dE = TdS - dW = TdS + \sum_j X_j dx_j. \quad (1.14)$$

The fact that the Carnot cycle is the most efficient cycle between two temperatures allows us to obtain an inequality for arbitrary processes. Consider a possibly irreversible cycle between two reservoirs at temperatures  $T_1$  and  $T_2$ .

$$\frac{Q_1 + Q_2}{Q_1} \leq \frac{Q_{1C} + Q_{2C}}{Q_{1C}} = \eta_C. \quad (1.15)$$

This implies that  $Q_2/Q_1 \leq T_2/T_1$  and

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0. \quad (1.16)$$

Generalizing to an arbitrary process, we obtain

$$\oint \frac{dQ}{T} \leq 0 \quad (1.17)$$

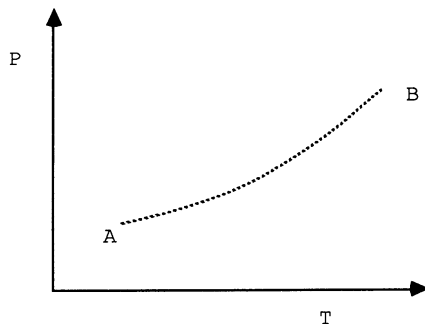


Figure 1.4: Thermodynamic Path

where the equality holds for reversible processes. Since the entropy is a state function,  $\oint dS = 0$  for any reversible closed cycle. We can imagine an arbitrary process combined with a reversible process to form a cycle and we therefore obtain for an arbitrary infinitesimal process  $T\Delta S \geq \Delta Q$ . Combining this with the first law we have, for arbitrary infinitesimal processes,

$$T\Delta S \geq \Delta E + \Delta W \quad (1.18)$$

where, once again, the equality holds for reversible processes.

A further consequence of the foregoing discussion is that the entropy of an isolated system cannot decrease in any spontaneous process. Imagine a spontaneous process in which the system evolves from point  $A$  to point  $B$  (Figure 1.4) in the thermodynamic space. (Note that the irreversible path cannot be represented as a curve in the  $P-T$  plane. The dotted line represents a reversible path connecting the same endpoints.) Since the system is isolated  $\Delta Q = 0$  and

$$\int_A^B dS \geq \int_A^B \frac{\delta Q}{T} = 0 \quad (1.19)$$

or

$$S(B) - S(A) \geq 0. \quad (1.20)$$

Since spontaneous processes tend to drive a system toward equilibrium, we conclude that the equilibrium state of an isolated system is the state of maximum entropy.